THE STRUCTURAL AND ELECTROCHEMICAL DYNAMICS OF THE
ELECTRODE-ELECTROLYTE INTERPHASE OF METAL FLUORIDE
NANOCOMPOSITE POSITIVE ELECTRODES FOR Li BATTERIES

by

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ABSTRACT OF THE DISSERTATION

The Structural and Electrochemical Dynamics of the Electrode-Electrolyte Interphase of Metal Fluoride Nanocomposite Positive Electrodes for Li Batteries

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Metal fluorides are attractive for use as positive electrodes in Li and Li-ion batteries because of their high gravimetric and volumetric energy densities. When synthesized into nanocomposites, these materials undergo conversion reactions and exhibit near theoretical specific capacity and good rate capability. Despite these positive attributes, metal fluorides nanocomposites generally exhibit unacceptable rates of capacity loss during cycling. This stands as a significant barrier to their realization as a viable battery technology. This thesis explored a candidate material, BiF$_3$, and for the first time, the mechanisms by which metal fluoride nanocomposite positive electrode materials fail during cycling have been investigated. The chemistry of the electrode / electrolyte interface and its influence on the BiF$_3$ material were of greatest interest.

Early in the course of study, it was discovered that the Bi$^0$ metal produced through the discharge reaction of BiF$_3$ was a catalytically active site for the electrochemical reduction of ethylene carbonate (EC) at potentials exceeding 2 V vs. Li/Li$^+$. This potential range is well above the values typically observed on carbonaceous negative electrodes on which preferential reduction of electrolyte species yields insoluble phases. These ionically conducting layers are deemed solid-electrolyte interphases (SEI),
and in the case of carbonaceous materials, they are necessary for enabling functionality of the electrode and preventing deleterious interactions with the electrolyte. Thorough electrochemical and spectroscopic examinations identified Li$_2$CO$_3$ as the predominant SEI species formed on Bi$^0$ from EC. In stark contrast to carbonaceous materials, the presence of SEI on Bi$^0$ was detrimental to the cycling performance of BiF$_3$. Elaboration of this topic identified instability of the SEI during the charging process of the BiF$_3$ and the formation of BiO$_x$F$_{3-2x}$ in the fully charged state.

Electrolytes composed of linear organic carbonates, as opposed to cyclic organic carbonates, did not exhibit SEI formation, and a distinct improvement in the cycling performance of BiF$_3$ nanocomposites was observed. Extending this concept, other straight-chained solvents including dinitriles and 3-alkoxypropionitriles were formulated into novel electrolytes with low additive concentrations. After proving their stability and functionality in a 4 V Li-ion configuration, these nitrile electrolytes were investigated with BiF$_3$ nanocomposites. To date, the best long-term cycling performance of a BiF$_3$ nanocomposite has been achieved using a dinitrile electrolyte.

The findings of this dissertation merit consideration of SEI formation in other metal fluoride conversion systems. The experimental designs serve as a platform for the exploration of the potentially complex and dynamic interactions of the electrolyte with metal fluoride nanocomposite electrodes during cycling.
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Badway contributed early electrochemical results and the optimized mass ratio of the bismuth (III) fluoride nanocomposite material. Rangan and Bartynski provided the XPS analysis performed on the Kratos instrument. Halajko deposited Bi films as well as performed FESEM/EDS measurements. Pereira contributed iron (II) fluoride nanocomposite materials.

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Dedication

I am forever grateful to my parents, Tom and Jeannette, for providing a loving, supportive environment and for surrendering their immediate desires and happiness such that my brother and I could have opportunities to flourish in our schooling and careers. I am indebted to them, now and always, for their care and love. I am thankful to my extended family, who, with my parents, has nurtured my inquisitive mind. They have instilled the importance of challenging oneself to become better, whether through education or labor. And, they have given me confidence when I feared failure or uncertainty. As much as I may have fulfilled the course requirements and toiled away countless hours in the lab to prepare this thesis, my entire family and all those who have prepared me to become a scholar should celebrate in its completion. Without them, my successes would not have been possible.

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Figure 5.4. Potentiodynamic scans of MCMB half cells in 1 M LiTFSI + 0.25 M LiBF₄ 3MPN with (a) no additive, (b) 5 vol% VC, and (c) 5 vol% FEC. Insets have been included to show effective SEI formation on the first reduction sweep.

Figure 5.5. Galvanostatic cycling results of LiCoO₂ vs. MCMB Li-ion cells in (a) 1 M LiPF₆ EMC electrolytes, (b) 1 M LiTFSI + 0.25 M LiBF₄ EMC electrolytes, (c) 1 M LiTFSI + 0.25 M LiBF₄ ADN electrolytes, and (d) 1 M LiTFSI + 0.25 M LiBF₄ 3MPN electrolytes.

Figure 5.6. Impedance data for LiCoO₂ vs. MCMB Li-ion cell cycled in 1 M LiTFSI + 0.25 M LiBF₄ ADN + 5% FEC.

Figure 5.7. XPS spectra for MCMB negative electrode tapes cycled 100 times vs. LiCoO₂. Curve A (· · ·): plain MCMB electrode tape, no electrochemical treatment. Curve B (- - -): MCMB tape, cycled, non-rinsed. Curve C (—): MCMB tape, cycled, rinsed with DMC. Upper row: ADN + 5% VC. Lower row: ADN + 5% FEC.

Figure 5.8. XPS spectra for spectroscopically pure carbon planchet working electrodes. Curve A (—, hairline): raw carbon planchet. Curve B (· · ·): 1 M LiClO₄ EMC + 5% FEC at OCV for 24 h. Curve C (—, bold): 1 M LiClO₄ EMC + 5% FEC swept to 1 V. Curve D (· · ·): 1 M LiClO₄ EMC without FEC swept to 1 V. Care was taken to have approximately the same signal intensity over the survey spectrum for each of the four samples.

Figure 5.9. Potentiodynamic scans of MCMB half cells in 1 M LiTFSI + 0.25 M LiBF₄ ADN + 5% EC. The inset has been included to more clearly show the current associated with EC solvent reduction.

Figure 5.10. Galvanostatic cycling performance of LiCoO₂ vs. MCMB Li-ion cells in 1 M LiTFSI + 0.25 M LiBF₄ ADN comparing EC and FEC as additives.

Figure 6.1. Specific capacity of BiF₃ nanocomposites cycled galvanostatically between 4.50 V and 2.00 V vs. Li. (a) 1 M LiPF₆ carbonates. (b) 1 M LiTFSI + 0.25 M LiBF₄ electrolytes. Best cycling overall with 1 M LiPF₆ EMC and 1 M LiTFSI + 0.25 M LiBF₄ ADN + 10 vol% VC when using Li as negative electrode.

Figure 6.2. Similarities observed in the voltage profiles of BiF₃ in three-electrode cells in which the counter electrode was Li (a) or LCO (b). WE: BiF₃ nanocomposite. RE: SS. Electrolyte: 1 M LiTFSI + 0.25 M LiBF₄ ADN. The electrolyte in (a) contained a small amount of additive (VC) to stabilize the interface with the Li.
Figure 6.3. Specific capacity of BiF$_3$ nanocomposites cycled galvanostatically between 0.55 V and -1.95 V vs. LCO. Best cycling overall with 1 M LiTFSI + 0.25 M LiBF$_4$ ADN. 1 M LiPF$_6$ EC:DMC included as a comparison to highlight the rapid capacity fade when using 50 vol% EC.

Figure 6.4. Specific capacity of BiF$_3$ nanocomposites cycled galvanostatically between 4.50 V and 2.00 V vs. Li in 1 M LiTFSI + 0.25 M LiBF$_4$ ADN:VC electrolytes. 10 vol% was selected as the additive concentration to be used in subsequent cycling trials.

Figure 6.5. Specific capacity of BiF$_3$ nanocomposites cycled galvanostatically between 4.50 V and 2.00 V vs. Li in 1 M LiTFSI + 0.25 M LiBF$_4$ ADN electrolytes.

Figure 6.6. Voltage profiles of BiF$_3$ nanocomposites plotted as a function of capacity. First two cycles shown for samples cycled galvanostatically between 4.50 V and 2.00 V vs. Li in 1 M LiTFSI + 0.25 M LiBF$_4$ ADN electrolytes. The theoretical capacity is 266 mAh g$^{-1}$ nanocomposite. Note the different x-axes for panels (e), (h), and (i). (a) no additive, (b) 10 vol% EC, (c) 10 vol% FEC, (d) 10 vol% PC, (e) 10 vol% VEC, (f) 10 vol% EMC, (g) 10 vol% VC, (h) 10 vol% DMDO, (i) 10 vol% ES, (j) 10 vol% DTD, (k) 10 vol% PDCS, (l) 10 vol% PS, (m) 10 vol% BS, and (n) 10 vol% EtNCO.

Figure 7.1. Schematic of a proposed vessel combining electrochemical and spectrophotometric techniques.

Figure 7.2. Conductivity data for EC:DMC, ADN, and 3MPN electrolytes. Data collected with Solartron SI 1260 and 1287, Metrohm conductivity cell, and Haake programmable temperature circulating bath. At temperatures ≤ -10°C, both EC:DMC 1:1 electrolytes partially solidified. 3MPN is the solvent best suited for low temperature operation.
1. Introduction

1.1. Motivation

The lithium-ion battery has become ubiquitous, especially with the rise in popularity of personal electronics. The vast majority of rechargeable (aka secondary) lithium-ion cells are comprised of a carbonaceous negative electrode, nonaqueous electrolyte containing a dissolved lithium salt, and a positive electrode with a cubic close-packed arrangement of oxygen. Examples of positive electrodes include LiCoO$_2$, a transition metal oxide with the $\alpha$-NaFeO$_2$ structure, LiMn$_2$O$_4$, a spinel closely related to the $\alpha$-NaFeO$_2$ layered structure, differing in the distribution of the cations among the available octahedral and tetrahedral sites, and LiFePO$_4$, typically an olivine with low electronic conductivity.[1] While these positive electrode materials offer good cycling life, good rate capability, and high discharge voltages, among other desirable properties, LiCoO$_2$ is limited by the amount of lithium that can be reversibly intercalated / extracted (~0.5 Li per Co) and LiFePO$_4$ contains a phosphate polyatomic ion.[1] A significant percentage of these materials is either inaccessible to intercalation or electrochemically inactive and is thus deadweight.

As demand grows for portable electronics of higher performance and functionality simultaneously with the desire to miniaturize devices, significant enhancements must be realized in battery technologies. In order to develop a smaller battery while maintaining the same availability of stored charge, the negative and positive electrodes must store more energy per unit volume while continuing to have a high nominal cell potential. Conversely, if the geometry of the battery is fixed, the amount of stored energy can be increased for longer periods of use and/or higher rates of energy consumption. The positive electrode has long been the focus of battery research, but only incremental gains in energy density have resulted because studies have been restricted to lithium intercalation compounds. A cell in which
multiple lithium ions can be reacted with the active material of the positive electrode would greatly improve capacity. Many transition and p-block metal fluorides are reduced by lithium with large free energies of reaction ($\Delta G_{\text{rxn}}$ between -550 kJ/mol and -1050 kJ/mol) which correspond to cell potentials between roughly 2 and 4 V vs. Li/Li$^+$. Table 1.1 lists several materials applicable for positive electrodes.

In a typical intercalation compound, the predominant crystal structure of the host material is maintained and the addition / removal of Li$^+$ expands / contracts the lattice. In sharp contrast, reduction of a conversion material results in its destruction into domains of metal and lithium salt, and oxidation of these should return the material to its initial state. Figure 1.1 illustrates this distinction. The discharge reaction for a metal fluoride conversion material can be represented as $\text{MeF}_x + x\text{Li}^+ + xe^- \rightarrow \text{Me}^0 + x\text{LiF}$. There is a clear correlation with the oxidation state of the metal and the amount of lithium that can be reacted per mole of metal. Unlike a lithium intercalation compound in which usually only one oxidation step is available (e.g. $\text{Co}^{4+}/\text{Co}^{3+}$ in LiCoO$_2$ or $\text{Fe}^{3+}/\text{Fe}^{2+}$ in LiFePO$_4$), the metal in MeF$_x$ is reduced from Me$^{+x}$ to Me$^0$. A major drawback to the operation of a metal fluoride conversion material is that the reaction is not kinetically feasible when considering large particles; the conductivity of the metal fluorides is typically poor owing to their wide band gaps, and highly insulating LiF salt envelops the metal fluoride during discharge. The realization of the metal fluoride positive electrode was not until the early 2000s, largely by the efforts of the Energy Storage Research Group (ESRG) who continue to be pioneers with regard to this technology. Metal fluoride positive electrodes have been demonstrated in nanocomposites blended with carbon, metal sulfides, and metal oxides.[2, 3, 4, 5, 6, 7]
Table 1.1. Positive electrode compounds and their reduction potential vs. Li metal, gravimetric charge capacity (mAhg\(^{-1}\)), gravimetric energy density (Wh·kg\(^{-1}\)), volumetric charge capacity (Ah·L\(^{-1}\)), and volumetric energy density (Wh·L\(^{-1}\)). The potentials listed do not account for multi-step reduction of the metal fluoride or partial intercalation of Li\(^+\) into the metal fluoride. o-BiF\(_3\) is orthorhombic, T-BiF\(_3\) is hexagonal Tysonite phase.

<table>
<thead>
<tr>
<th>Compound</th>
<th>Class</th>
<th>(E^\circ_{\text{cell}}/\text{V})</th>
<th>mAhg(^{-1})</th>
<th>Wh·kg(^{-1})</th>
<th>Ah·L(^{-1})</th>
<th>Wh·L(^{-1})</th>
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<tr>
<td>VF(_3)</td>
<td>Conversion</td>
<td>1.87</td>
<td>745</td>
<td>1389</td>
<td>2505</td>
<td>4673</td>
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<tr>
<td>CrF(_2)</td>
<td>Conversion</td>
<td>2.28</td>
<td>596</td>
<td>1360</td>
<td>2287</td>
<td>5224</td>
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<tr>
<td>CrF(_3)</td>
<td>Conversion</td>
<td>2.29</td>
<td>738</td>
<td>1689</td>
<td>2789</td>
<td>6383</td>
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<td>577</td>
<td>1107</td>
<td>2296</td>
<td>4405</td>
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<tr>
<td>MnF(_3)</td>
<td>Conversion</td>
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<td>1902</td>
<td>2543</td>
<td>6732</td>
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<tr>
<td>FeF(_2)</td>
<td>Conversion</td>
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<td>1522</td>
<td>2336</td>
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<td>FeF(_3)</td>
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<td>SnF(_2)</td>
<td>Conversion</td>
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<td>4665</td>
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<td>SnF(_3)</td>
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<td>619</td>
<td>1852</td>
<td>5243</td>
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<tr>
<td>α-PbF(_2)</td>
<td>Conversion</td>
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<td>302</td>
<td>946</td>
<td>2391</td>
<td>7484</td>
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<tr>
<td>o-BiF(_3)</td>
<td>Conversion</td>
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<td>302</td>
<td>946</td>
<td>2539</td>
<td>7960</td>
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<tr>
<td>LiCoO(_2)</td>
<td>Intercalation</td>
<td>3.95</td>
<td>135-165</td>
<td>530-640</td>
<td>690-840</td>
<td>2700-3250</td>
</tr>
<tr>
<td>LiMn(_2)O(_4)</td>
<td>Intercalation</td>
<td>~4.0</td>
<td>148</td>
<td>590</td>
<td>630</td>
<td>2520</td>
</tr>
<tr>
<td>LiFePO(_4)</td>
<td>Intercalation</td>
<td>3.45</td>
<td>170</td>
<td>586</td>
<td>608</td>
<td>2097</td>
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</table>
Figure 1.1. Illustration of the structural reconfigurations occurring during lithiation / delithiation via intercalation of a layered host material and lithiation / delithiation of a conversion material.
BiF$_3$ nanocomposite positive electrodes have been investigated at ESRG, notably by Bervas et al.[4, 8, 9]. Their work provided the first accounts of cycling in this system and rich crystallographic characterization of the positive electrodes at many levels of charge and discharge. Some distinct contributions included high energy milling synthesis of BiF$_3$ + C nanocomposites[4], identification of Tysonite as opposed to orthorhombic BiF$_3$ as the predominant crystalline phase after reconversion[4], synthesis of bismuth oxyfluoride phases through soft chemistry[8], and a proposed model for the conversion reaction of BiF$_3$.[9] Additional work was undertaken within ESRG to synthesize BiF$_3$ nanocomposites with enhanced cycling performance. Despite these later efforts (unpublished) which were concerned with optimization of the nanocomposite through milling and annealing operations, adjusting the mass fraction of BiF$_3$ in the nanocomposite, and exploring alternative phases to include in the nanocomposite (e.g. MoS$_2$), this positive electrode was limited to roughly 30 cycles before the discharge capacity faded to less than 50% of its initial value.

The development of the BiF$_3$ nanocomposite positive electrode beyond a lab-scale novelty rests on identifying the mechanisms which lead to its rapid loss of capacity. Identification of failure mechanisms can already be a challenging endeavor when considering intercalation compounds. For example, in LiMn$_2$O$_4$, several processes involving the Mn$^{3+}$ ion have been implicated in capacity loss.[1] The cooperative Jahn-Teller distortion of the Mn$^{3+}$O$_6$ octahedra causes expansion of the unit cell in the c-direction, leading to electrochemical grinding. The active material fractures and becomes electronically isolated from the positive electrode, causing capacity loss.[10] In the same system, Mn$^{3+}$ can also undergo disproportionation to Mn$^{4+}$ and Mn$^{2+}$. The Mn$^{2+}$ is soluble in acidic electrolytes and is reduced at the negative electrode, also contributing to capacity loss.[1]
The intricacies of the structural evolution of the conversion metal fluorides further complicate identifying the mechanism(s) most significant for capacity loss.

- Large volumetric changes (e.g., as deduced from unit cell volume calculations, 55.7 Å³ for orthorhombic BiF₃ vs. 84.4 Å³ for Bi⁰ + 3LiF) occur during the discharge and charge processes. Thus, electrochemical grinding, dislodging, and electronic disconnection of the active materials from the bulk material of the positive electrode may occur and result in capacity loss.

- During discharge, the conversion process yields nanodomains of metal and lithium fluoride. If it were more energetically favorable to minimize surface energy, it may be possible for the metal to agglomerate, thus increasing the separation distance between adjacent metal and lithium fluoride nanodomains. Coarsening of the metal would hinder the reconversion process.

- During discharge, the conversion process yields nanodomains of metal and lithium fluoride, and the high surface area associated with these nanodomains would likely lead to a large interaction area with a liquid electrolyte. Issues such as dissolution of the active material into the electrolyte solvent or etching caused by acidic species within the electrolyte would be exacerbated.

- If the nanodomains were catalytic toward the reduction of electrolyte solvents, polymeric and inorganic lithium salt species could form at the interface with the electrolyte. In an ideal scenario, these decomposition products would be self-limited in
growth, stable to oxidation, and nonreactive during the reconversion process. However, complications involving penetration of the electrolyte into areas between nanodomains could prevent the conversion reaction from occurring due to the presence of the decomposition byproducts isolating the metal and lithium fluoride. Electrolyte penetration into areas between nanodomains and the electronically conductive phase of the nanocomposite followed by electrolyte decomposition could lead to a more pronounced separation of the active material from the bulk positive electrode than electrochemical grinding alone. During reconversion, there is certainly the possibility of the metal reacting not exclusively with the lithium fluoride, but also with the phases formed as a result of electrolyte decomposition. It may be that the decomposition products are nonreactive with respect to the active components of the positive electrode, but they are subjected to oxidative decomposition at high potentials. If this oxidative process involving the decomposition products does not yield a quantity of Li\(^+\) equal to the quantity consumed during the electrochemical reduction of the electrolyte solvent(s), over time, the finite amount of Li\(^+\) within the Li-ion cell would be depleted gradually during repeated cycling due to growth of the decomposition layer. The large volumetric changes associated with the conversion reaction may also influence the mechanical stability of the electrolyte decomposition products. If detachment of the decomposition layer from the electrode were to occur, then additional electrolyte decomposition could proceed.

- Lastly, during reconversion of the metal and lithium fluoride back to metal fluoride, the oxidation potential of the metal is often exceeded due to either the reaction proceeding through metastable intermediate phases, or, more likely, kinetic effects leading to
nonequilibrium potentials greater than those for the idealized reaction, \( \text{Me}^0 + x\text{LiF} \rightarrow \text{MeF}_x + x\text{Li}^+ + xe^- \). Thus, electrostripping of the metal out of the positive electrode is certainly a possibility.

It may very well be that all these mechanisms are functioning simultaneously. Addressing interactions of the nanocomposite with the electrolyte was an intriguing area to study owing to the nano-sized features of the nanocomposite electrode and the anticipation of a very large interfacial area, particularly for the nanocomposite in the discharged state, with the electrolyte. This was also an area that was greatly lacking in the literature. Thus, we were concerned with the possibility of interactions occurring between the components of the electrolyte and the nanocomposite electrode. If detrimental reactions were responsible for the capacity losses during cycling, what phases would be formed and would they remain as stable entities or become included into the reconversion chemistry of the BiF\(_3\) nanocomposite? If detrimental reactions were occurring, could these be mitigated or even eliminated with the appropriate selection of electrolyte? It was our intention to engineer a viable device capable of cycling many times with minimal capacity loss. We sought to continue to expand upon the fundamental mechanisms by which BiF\(_3\) cycles and attempt to extend trends witnessed for this compound to other metal fluoride nanocomposites. Before delving into the content of the thesis pertaining to the examination of metal fluorides and electrolyte interactions, a primer on batteries and an overview of Li-ion battery chemistries emphasizing electrolyte decomposition and interfacial properties has been provided.
1.2. Battery basics

A battery is comprised of one or more electrochemical cells, electrically connected in an appropriate series / parallel arrangement to provide the required operating voltage, current levels, and charge capacity for a device.[11] Electrochemical cells in which faradaic currents flow (i.e., the amount of chemical reaction caused by the flow of current is proportional to the amount of electricity passed), can be classified as either galvanic cells or electrolytic cells. A galvanic cell is one in which chemical reactions spontaneously proceed at the electrodes when they are connected externally through a conductive load. Chemical energy is converted into electrical energy during discharge of the cell. At the anode or negative electrode, an oxidation reaction takes place, thus making it a source of electrons. At the cathode or positive electrode, a reduction reaction occurs, thus making it a sink for electrons. The potential of the cathode is positive with respect to the anode in a galvanic cell. An electrolytic cell is one in which an external voltage is applied exceeding the open circuit potential (the potential in the absence of current flow) to cause chemical reactions. Electrical energy is expended to drive otherwise non-spontaneous chemical reactions. As in a galvanic cell, at the cathode, a reduction reaction occurs. But, unlike a galvanic cell, the potential of the cathode is negative with respect to the anode in an electrolytic cell. The potentials determine the positive or negative convention of the electrode, but in either type of electrochemical cell, reduction occurs at the cathode and oxidation occurs at the anode. This distinction is illustrated in Figure 1.2.[12]
Figure 1.2. Illustration of galvanic and electrolytic cells with corresponding reactions occurring at electrodes. Adapted from Ref 12.

Separating the positive and negative electrodes is absolutely necessary to prevent a short circuit condition. After all, in a galvanic cell, it is desired that when the spontaneous reactions proceed, useful work can be extracted from the cell through the external circuit rather than yield heat and reaction products within the cell. Furthermore, if the electrons are conducted through an external circuit, another mechanism must be employed to maintain charge transfer and current flow. The electrolyte provides the medium for transfer of charge, as ions, inside the cell between the positive and negative electrodes. The electrolyte can exist in many forms including liquids, which are typically contained within a porous separator to maintain mechanical separation of the electrodes, gels, polymers, and solid ionic conductors. The electrolyte must have negligible electronic conductivity; otherwise, reactions would proceed without providing work through the external circuit during discharge.
A cell limited by its chemistry to a single discharge sequence is a primary cell. They are typically inexpensive, convenient sources of packaged power exhibiting good shelf life and high energy density at low to moderate discharge rates. They are discarded after use, necessitating replacement in devices and adding to waste streams. Secondary, also known as rechargeable, cells can be restored to the charged condition by forcing current in the direction opposite that of discharge. A rechargeable cell acts as a galvanic cell during discharge and, in a sense, an electrolytic cell during charge. Secondary batteries have favorable properties including high power density, high discharge rates, flat discharge curves, and good low-temperature performance; however, their energy densities are typically lower than primary cells. Their charge retention is poorer than that of most primary batteries, but recharging can restore capacity lost on standing.[11]

When considering materials to integrate into a functional galvanic cell, it would be advantageous to pair negative and positive electrode materials that could provide a high cell potential and high capacity while being lightweight, cost effective, safe, relatively non-toxic, and possibly recoverable. Identifying materials that can satisfy all these attributes is challenging, and there may be no other chemistry more suited for developing cells than lithium. Lithium is the most electropositive metal (-3.04 V vs. standard hydrogen electrode in aqueous media) as well as the lightest, thus making possible the development of cells with high energy density.[13] Lithium metal has an exceptionally high capacity (3860 mAhg⁻¹) and became an attractive candidate for the negative electrode. Concurrently with the adoption of lithium as a negative electrode material, a variety of inorganic compounds were shown to reversibly react with alkali metals, often via intercalation. Identifying compounds that reversibly reacted with Li⁺ with the
possibility of a large cell potential was crucial in the development of high-energy, rechargeable lithium cells.[13]

The early secondary cells developed at Exxon (ca. 1972) utilized lithium metal as the negative electrode, titanium disulfide as the positive electrode, and lithium perchlorate dissolved in dioxolane as the electrolyte. Despite the excellent performance of the positive electrode, this system was not viable. Uneven plating of the lithium metal during each charge sequence led to the growth of lithium dendrites across the electrolyte, causing shorts, and in severe instances, explosion hazards. An alternative design was pursued in which the negative electrode was modified. A second intercalation compound was substituted for the metallic lithium. In this design, the lithium was maintained in its ionic state, and the growth of dendrites was greatly minimized. Drawbacks to this approach were the increase in the potential and decrease of the capacity of the negative electrode, thus dropping both the output voltage and normalized capacity of the cell.[13]

In a functional cell, the output potential is governed foremost by the thermodynamics of the chemical reactions taking place at the positive and negative electrodes. The convention from thermodynamics is that a spontaneous reaction is one in which $\Delta G < 0$. Mapping the energy from the Gibb's coordinate system to emf for the cell reaction can be done by accounting for the charge passed during a fully thermodynamically reversible transformation. In the standard state, the equilibrium condition of the electrochemical cell can be expressed as

$$-\Delta G^o = nFE^o = RT\ln K_{rxn}$$  \hspace{1cm} (1.1)[Ref 12]

$\Delta G^o$ is the free energy of reaction under standard conditions, $n$ is the number of moles of electrons exchanged, $F$ is the Faraday constant which is 96,485 C per mole of electrons, $E^o$ is the
emf under equilibrium conditions with no current flowing, $R$ is the gas constant, $T$ is the absolute temperature, and $K_{\text{eq}}$ is the reaction quotient at equilibrium. In a lithium or lithium-ion configuration, if the chemical potentials for the active ion are considered, it can be shown that

$$E^o = \frac{-\left(\mu_{\text{Li}}^{\text{pos}} - \mu_{\text{Li}}^{\text{neg}}\right)}{nF}$$

(1.2)

The chemical potentials of the lithium in the positive and negative electrodes are denoted by $\mu$.

Rather than consider thermodynamic tables, it is convenient to consider half-cell reactions and potentials. In aqueous electrochemistry, standard electrode potentials are often reported against the normal hydrogen electrode (NHE). The NHE uses platinum metal as the substrate for the exchange of $H_2$ and $H^+$, both at unit activity in water.[12] As an example of the utility of this formalism, consider two metal electrodes immersed in an aqueous electrolyte solution containing corresponding soluble metal salts of each electrode. The negative electrode is zinc and the positive electrode is copper. The half-cell reactions for the electrodes are as follows:

<table>
<thead>
<tr>
<th></th>
<th>Equation</th>
<th>Potential vs. NHE</th>
</tr>
</thead>
<tbody>
<tr>
<td>Negative</td>
<td>$Zn^{2+} + 2e^- \rightleftharpoons Zn^0$</td>
<td>-0.7626 V</td>
</tr>
<tr>
<td>Positive</td>
<td>$Cu^{2+} + 2e^- \rightleftharpoons Cu^0$</td>
<td>0.340 V</td>
</tr>
<tr>
<td>Overall</td>
<td>$Zn^0 + Cu^{2+} \rightarrow Cu^0 + Zn^{2+}$</td>
<td>1.1026 V (positive vs. negative)</td>
</tr>
</tbody>
</table>

The overall potential is calculated by subtracting the half-cell potential of the negative electrode from the half-cell potential of the positive electrode. This also avoids the issues associated with knowing $\Delta G$ for the overall reaction as the free energy of formation for ions is not well-defined.

In an analogous fashion, many potentials for positive and negative electrodes for lithium and lithium-ion cells are reported against lithium metal. The utility is apparent when no longer using lithium metal as the negative electrode. While it would be impractical due to the greatly
diminished output voltage, one could consider assembling a lithium-ion cell using LiFePO$_4$ (3.45 V vs. Li/Li$^+$) as the positive electrode and Li$_4$Ti$_5$O$_{12}$ (1.55 V vs. Li/Li$^+$) as the negative electrode. The open circuit potential, calculated by subtracting the potential of the negative electrode from that of the positive electrode, would be anticipated to be approximately 1.9 V.

During discharge, the cell potential under conditions in which current is flowing is less than the theoretical value (Eqns. (1.1), (1.2)). The processes occurring at the electrode / electrolyte interface are partially at fault. If one considers the scenario of easy diffusion of ionic components to / from the electrode but transfer of electric charge is hindered, then the Butler-Volmer equation is valid.$^{14}$ The Butler-Volmer equation relates the magnitude and direction of current at an electrode with the deviation in potential from the equilibrium potential. This equation can be expressed as

$$i = i_o \left[ e^{\frac{-\alpha F \eta}{RT}} - e^{\frac{(1-\alpha)F \eta}{RT}} \right]$$

The overpotential, $\eta$, is equal to $E - E^\circ$. The other terms in the Butler-Volmer equation are the exchange current density, $i_o$, transfer coefficient, $\alpha$, Faraday constant, $F$, gas constant, $R$, and absolute temperature, $T$. The overpotential associated with sluggish charge transfer kinetics is referred to as the activation overpotential, $\eta_a$. In this case, $\eta_a$ is used solely to overcome the activation energy required to drive the process occurring at the electrode at the rate reflected by the current, $i$. At small values of $\eta_a$, approximately 50mV at room temperature, the Butler-Volmer equation can be reduced to

$$i = -i_o \frac{F \eta_a}{RT}$$

(1.4)
The ratio of $-\eta_a / i$ has units of resistance. Since it has been assumed that the electron-transfer is slow, this yields the charge transfer resistance ($R_{ct}$) for the electrode

$$R_{ct} = \frac{RT}{Fi_o} \tag{1.5}$$

If $\eta_a$ is sufficiently large, one of the terms in the Butler-Volmer equation becomes negligible. The reaction is driven far from equilibrium and is effectively operating in only one direction. $\eta_a$ can then be expressed as

$$\eta_a = \frac{RT}{aF} \ln i_o - \frac{RT}{aF} \ln i \tag{1.6}$$

This leads to Tafel behavior, experimentally observed prior to derivation of and corroborated by the Butler-Volmer treatment. Tafel behavior is an indicator for totally irreversible kinetics.[12, 14]

Another form of overpotential exists in circumstances in which the charge transfer process is rapid (otherwise stated as having a high exchange current or charge transfer virtually at equilibrium) but the interfacial concentration of the electroactive species in solution is non-uniform. Mass transport is slower relative to the charge transfer process, and a potential difference is produced by a concentration change at the interface relative to the bulk solution. The concentration overpotential, $\eta_c$, can be expressed through the Nernst equation to be

$$\eta_c = \frac{RT}{nF} \ln \frac{c_{x=0}}{c^o} \tag{1.7},[Ref 14]$$

$R$, $T$, $n$, and $F$ have the same definitions as above (Eqn. (1.1)), $c_{x=0}$ is the concentration of the active ion at the interface, and $c^o$ is the concentration of the active ion within the bulk of the electrolyte.[14]
The output of a functional cell is also dependent on the conductivity of the electrolyte. A voltage loss equal to current x electrolyte resistance \( E = iR_{\text{elyte}} \) will decrease the output potential. This is a simple result of the complicated mass transport mechanisms occurring within the electrolyte. If the resistivity is high (i.e. the mobility of ions is low) and the electrolyte is sufficiently thick, and/or, a very large current is drawn from the galvanic cell, this term can become significant.

Within the electrolyte, the flux of ions of species \( j \), \( J_j \), can be generalized to the following differential equation:

\[
J_j = -D_j \nabla C_j - \frac{z_j F}{RT} D_j C_j \nabla \phi + C_j \nu
\]  

(1.8)

\( D_j \) is the diffusion coefficient of ion species \( j \), \( C_j \) is the concentration, \( z_j \) is the charge of the ionic species, \( \phi \) is the electric potential, and \( \nu \) is the velocity of the solution. The last term, \( C_j \nu \), can be neglected because the electrolyte is assumed to be stagnant with no density gradients. This leaves a flux of ions comprised of a diffusion term, \( -D_j \nabla C_j \), and a migration term, \( -\frac{z_j F}{RT} D_j C_j \nabla \phi \). The diffusion term is largely unimportant in the bulk electrolyte because the concentration gradients are generally small. Thus, in the bulk electrolyte, the migration term is most important as the current is carried by it. In a one-dimensional system having a cross-sectional area, \( A \), the current for species \( j \) is presented as

\[
i_j = \frac{z^2 F^2 A D_j C_j}{RT} \frac{\partial \phi}{\partial x}
\]  

(1.9)

The mobility is linked to the diffusion coefficient as

\[
u_j = \frac{|z_j| F D_j}{RT}
\]  

(1.10)
The electric field across the electrolyte is linear; thus,

\[ \frac{\partial \phi}{\partial x} = \frac{\Delta E}{l} \]  

(1.11)

Combining the terms for \( i_j \), \( u_j \), and \( \partial \phi/\partial x \) leads to a new expression for \( i_j \).

\[ i_j = \frac{|z_j|FAu_jC_j\Delta E}{l} \]  

(1.12)

The total current throughout the bulk solution is comprised of the sum of the currents carried by the individual species, \( j \).

\[ i = \sum_j i_j = \frac{FA\Delta E}{l} \sum_j |z_j|u_jC_j \]  

(1.13)

From Ohm’s Law, \( i = \Delta E/R \) and \( R = \rho l/A \) in which \( \rho \) is the resistivity. Thus, it can be shown that the conductivity, \( \sigma \), which is the reciprocal of resistivity, is given by

\[ \sigma = F \sum_j |z_j|u_jC_j \]  

(1.14)

Electrolytes tend to become more resistive at low temperatures because the mobility, \( \mu \), decreases. For liquids, the mobility of the solvated ionic species is linked with the viscosity due to frictional drag forces counteracting the migration induced by the electric field. The transference number is the contribution of a given ionic species, \( j \), to the electrolyte conductivity and is given by

\[ t_j = \frac{i_j}{i} = \frac{|z_j|u_jC_j}{\sum_k|z_k|u_kC_k} \]  

(1.15),[Ref 12]

Thus, it can be summarized that the overall output potential of a functional galvanic cell is governed largely by the thermodynamics of the electrode reactions, overpotential effects due to either charge transfer (activation overpotential) or mass transport local to the interfacial region.
of the electrode with the electrolyte (concentration overpotential), and the resistance of the electrolyte. The following equation is applicable during discharge:

\[
E_{output} = E^o - \sum_j \eta_j - iR_{\text{electrolyte}}
\]  

(1.16)

Ohmic losses owing to poorly conducting films on the surface of the electrode or the resistances of the electrodes themselves have not been included in the above discussion, but could be included as additional \(iR\) terms to be subtracted from \(E_{output}\). Figure 1.3 illustrates these losses schematically as a function of the operating current.

Figure 1.3. Polarization within a galvanic cell as a function of the operating current. Adapted from Ref 11.
There are several important performance metrics useful for making comparisons of cells. As explained above (Eqn. (1.16)), the cell potential is governed by thermodynamics, overpotential effects, and iR losses. Lowering of the concentration overpotential is often achieved by designing porous electrodes into which the electrolyte can penetrate, thus minimizing the diffusion distance and maximizing the interfacial area. Selection of appropriate electrolytes with high conductivity or constructing the cell to have a minimal inter-electrode separation helps to minimize the iR drop across the electrolyte.

The capacity is determined by the amount of active materials within the cell. It is expressed as the quantity of electricity involved in the electrochemical reactions. The capacity can be reported for the electrochemical cell or battery itself and often has units of coulombs or ampere-hours. It is instructive to consider the specific capacity (also known as gravimetric capacity) of the active material. The units are typically mAhg\(^{-1}\). The specific capacity, \(C\), is calculated by the following equation:

\[
C \, [\text{mAhg}^{-1}] = \frac{nF}{3.6 \cdot M}
\]

in which \(n\) is the number of electrons transferred per ion of the active material (1 e\(^-\) per 1 Li\(^+\)), \(F\) is the Faraday constant, 3.6 is a constant resulting from unit conversion, and \(M\) is the molar mass in g·mol\(^{-1}\). \(C\) is often reported for the active material of the positive electrode. The volumetric capacity, \(C_v\), for the active material is determined by multiplying its specific capacity by its density and applying the corresponding unit conversion. If \(C\) is reported in mAhg\(^{-1}\), multiplying by g·cm\(^3\) results in \(C_v\) in Ah·L\(^{-1}\). In the scientific literature, \(C\) (and \(C_v\)) are often reported for the active material but caution should be used when identifying materials suitable for deployment in industrially manufactured cells. One must be certain to identify the mass
fraction (and volume fraction) of active material relative to the total electrode mass (volume). If, for instance, the active material is embedded within a voluminous non-active phase, it may be possible for the active material to demonstrate near-theoretical capacity values while the actual cell exhibits low capacity.

The specific energy of a cell can be calculated by considering the voltage. It is determined by multiplying the capacity, $C$, by the operating potential, $E_{\text{output}}$. If $C$ is in units of mAh$^{-1}$, $C \times E_{\text{output}}$ is in units of Wh·kg$^{-1}$. Similarly, the volumetric energy density is reported in units of Wh·L$^{-1}$ when multiplying $C_v \times E_{\text{output}}$.

The power is a measure of how rapidly energy can be extracted from the cell. Power, $P$, is given as either the operating potential $\times$ current extracted from the cell or the total energy delivered divided by time. Designing a cell in which both the energy density and power density (power/mass or power/volume) are both high is very difficult owing to the losses associated with overpotential and iR drop. As the current extracted from the cell is increased, the polarization is increased, and the ability to deliver the theoretical energy is hindered. Figure 1.3 illustrates this point.

Lastly, the cycling efficiency for secondary cells is a very important parameter. The cycling efficiency is a comparison of the capacity during charge and discharge. A value as close to unity as possible is aimed for, but never achieved due to failures such as contact loss of the active materials within the bulk electrode, loss of Li$^+$ due to electrolyte decomposition, and partial dissolution of the active material. Table 1.2 illustrates the importance of cycling efficiency. The
values for cycle number were calculated for a material fading to half its initial capacity. A constant value for the cycling efficiency throughout the service life of the cell has been assumed.

Table 1.2. Cycling efficiency and number of cycles to reach 50% initial capacity.

<table>
<thead>
<tr>
<th>Efficiency [%]</th>
<th>Number of cycles</th>
</tr>
</thead>
<tbody>
<tr>
<td>99.9999</td>
<td>693,146</td>
</tr>
<tr>
<td>99.999</td>
<td>69,314</td>
</tr>
<tr>
<td>99.99</td>
<td>6,931</td>
</tr>
<tr>
<td>99.9</td>
<td>692</td>
</tr>
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<td>99</td>
<td>68</td>
</tr>
<tr>
<td>98</td>
<td>34</td>
</tr>
<tr>
<td>95</td>
<td>13</td>
</tr>
</tbody>
</table>
1.3. Li-ion battery chemistry and the Solid-Electrolyte Interphase (SEI)

The generalized description for a galvanic cell containing a positive electrode, a negative electrode, and an electrolyte is lacking. The interfacial regions of each of the electrodes with the electrolyte must also be described. The phases that are developed at the electrode / electrolyte interface are crucial in establishing the stability of the electrolyte at highly reducing or highly oxidizing conditions, the safety of the electrochemical device, the power capability, the morphology of metals redeposited from the electrolyte, the shelf life under conditions of extended non-use and variations in temperature, and the cycle life.[15] In this section, the properties and formation mechanisms of these passivating films will be described for negative electrodes including lithium metal, carbonaceous materials, and lithium alloys and positive electrodes such as LiCoO$_2$ and LiMn$_2$O$_4$. The majority of the published scientific literature has reported interactions with intercalation materials; thus it would be appropriate to highlight those concerning conversion compounds. Apparatus useful for characterizing these passivating films are provided as well.

1.4.1 Passivation and ion migration

Most of the solid materials encountered are covered, at least in part, by surface films due to reactions in the atmosphere with oxygen, water vapor, carbon dioxide, and nitrogen and by surface groups such as OH and C=O. The chemical stability of metals when exposed to atmosphere or when submerged in water is highly dependent on the properties of these films and surface functionalities. Consider the corrosion of iron which has a film formed on its surface that is permeable to water molecules and ions vs. aluminum, which possesses a thin, impermeable surface film. Due to defects in the crystal structure of these electronically
insulating surface films, conduction of ions can occur, facilitating exposure of the metal to reactive species. The interfacial region is rightly called a solid-electrolyte interphase (SEI).[16]

The simplest SEI should include three steps in describing the kinetics of the ionic and electronic processes. In an electrochemical cell, moving from the electrolyte to the electrode, these steps are as follows: (1) ion transfer at the solution-film interface, (2) ion migration through the surface film, and (3) charge transfer at the film-electrode interface. The ion migration has been identified as the rate-limiting step; thus, the following equation is applicable in describing the potential-current relationship:

\[
i = 4zFav e^{-\frac{W}{RT}} \sinh(azFE/RT)\tag{1.18},[\text{Ref 16}]
\]

i is the current, z is the charge of an ion, F is the Faraday constant, a is the half distance of the jump of an ion, v is the vibrational frequency in the lattice, W is the energy barrier for the ion jump, R is the gas constant, T is the absolute temperature, and E is the electric field. When all the potential falls on the SEI, the overpotential exists there. A similar treatment to the Butler-Volmer equation can be applied. At low overpotential, the surface film acts an ohmic resistor, and at high overpotential, Tafel-like behavior is obtained. The average resistivity of the surface film formed on lithium in nonaqueous solutions used as electrolytes in Li-ion cells is on the order of 10^8 Ω·cm. Even a film thickness of only several nm can impact the output potential. Since the electrochemical response of electrodes is so highly dependent on the nature of these surface films, intensive study and control of their properties is of key importance to enabling high energy density cells.[16]
1.4.2 Spontaneous SEI formation on lithium

In electrochemistry terms, lithium is the most electropositive metal. It reacts spontaneously with gases in the atmosphere to form surface phases including lithium oxide, lithium hydroxide, and lithium carbonate species. The same holds true for the nonaqueous aprotic solvents and polyatomic anions commonly utilized in Li-ion electrolytes which are spontaneously reduced when lithium is the negative electrode in a galvanic cell. When lithium foil is incorporated into a functional cell, a variety of processes occur in parallel at the lithium / electrolyte interface. Dissolution of the initial surface species may occur due to the presence of trace amounts of water in the nonaqueous electrolyte or by solubility into the aprotic solvents comprising the electrolyte. Nucleophilic reactions between lithium oxide and hydroxide with electrophilic solvents such as alkyl carbonates may occur. As the native passivating layer of the lithium is decomposed, solvent molecules can diffuse toward the lithium and be reduced. During these reactions, electrons are injected into the electrolyte local to the electrolyte, thus forming radical anions, which subsequently act to form polyanions or polymeric species. Additionally, the anions of the lithium salt (such as PF$_6^-$ and ClO$_4^-$), may be precipitated as inorganic salts (e.g. LiF, LiCl) due to reactions with lithium cations.[16]

Depending on the point in time during which these reactions are taking place, the components formed at the outermost portion of the growing SEI layer begin to transition. In the initial stages, the lithium metal is passivated by a thin layer of oxide, hydroxide, and carbonate, and nearly any species within the electrolyte is free to be reduced. Typically, these species are the solvents existing at the highest concentration. However, as the SEI grows, electron transport required for reduction to occur is hindered through the insulating film, and the reduction reaction becomes slower and more selective. This results in a multilayered film. The lithium
metal is covered by a compact film including lithium oxide, lithium fluoride, lithium sulfide, and lithium nitride. The exact lithium compounds are determined by the components of the electrolyte. Beyond the inner, compact layer, a more diffuse, porous, outer layer consists largely of lithium carbonate, lithium alkyl carbonate, lithium alkoxides, and polymeric species. Eventually, the SEI becomes sufficiently thick such that electron transfer is blocked, achieving a steady-state condition. There are dynamic processes occurring including dissolution of the precipitated phases into the electrolyte and acid-base reactions of basic lithium salts with acidic species within the electrolyte. Furthermore, electron tunneling may occur locally, continuing the reduction of phases.[16, 17] One of the most widely distributed models for the phase distribution of SEI is provided in Figure 1.4. Note the abundance of lithium oxide and lithium fluoride adjacent to the electrode, and the greater extent of lithium carbonate and organic species away from the lithium surface.
Figure 1.4. Peled model for the polyhetero microphase SEI spontaneously formed on lithium metal when immersed into nonaqueous electrolyte (or driven by electrochemical reduction on a carbon negative electrode). The letters represent different phases. (A) lithium oxide, (B) lithium fluoride, (C) lithium carbonate, (D) polyolefins, and (E) semi-carbonates.[17]
1.4.3 SEI formation on non-reactive metal and carbon negative electrodes

For materials for which a continuous thermodynamic driving force for electrode – electrolyte reactions is not present, passivating films are formed by cathodic polarization. These electrodes would include noble metals such as platinum and gold, nickel, silver, copper, and carbonaceous materials. Their relative inertness is predominantly thermodynamic in nature, but the metals may be partially covered by a native oxide or hydroxide and the carbon materials have surface groups such as OH, C=O, and COOH which may play a small role in preventing reactions at the open circuit potential, typically around 3 V vs. Li/Li\textsuperscript{+}. Surface films resembling the SEI formed spontaneously on lithium metal are formed by electrochemically driving the metal or carbon electrode potential toward negative values. If the potential of the electrode is rapidly moved to approximately 0 V vs. Li/Li\textsuperscript{+}, then this effectively makes the electrode behave as though it were lithium because it is also highly reducing toward electrolyte species at this potential. If the potential of the electrode is gradually decreased from the open circuit condition toward negative potentials, a much different reaction sequence exists. The chemical entities within the electrolyte are selectively reduced at varying potentials owing to their reactivity. Despite the more step-wise reaction sequence, as the potential becomes approximately 0 V vs. Li/Li\textsuperscript{+}, reduction of lithium species to lithium oxide and lithium fluoride occurs adjacent to the metal or carbon electrode, and a multilayered SEI exists with a more porous layer nearer to the electrolyte (Figure 1.4).[16]

Whether the metal or carbon electrode is driven rapidly or gradually to low potentials vs. Li/Li\textsuperscript{+}, a key distinction must be made relative to lithium metal. The principle difference is that for a lithium negative electrode, lithium ions are available from both the metallic lithium and the electrolyte, while in other metals or carbon, lithium ions are only available from the electrolyte.
The electrolyte contains lithium salts dissolved in aprotic, nonaqueous solvents. If a lithium ion is removed from the electrolyte solution in the SEI formation process, there are two pathways to maintaining charge neutrality. Either a corresponding anion must be removed from the electrolyte, or a lithium ion must be provided to replace the one consumed in the SEI. The latter occurs, and the lithium ions are provided by the positive electrode. The lithium ions from the positive electrode which replenish those consumed from the electrolyte are no longer available to partake in electrochemical reactions with the positive electrode. This is the origin of irreversible capacity loss which occurs during the first cycle in a rechargeable lithium-ion cell. In a lithium cell in which there is an excess of lithium metal, there is no irreversible capacity loss of the positive electrode during SEI formation.

In the case of carbonaceous materials such as graphite and petroleum coke, the irreversible capacity loss was first identified by Fong, von Sacken, and Dahn[18] to be proportional to the specific surface area of the carbon electrode. Assuming the SEI was composed of lithium carbonate, an SEI thickness of 4 to 5 nm was calculated, consistent with the barrier thickness necessary to prevent electron tunneling. When all the available surface area was coated with a film of the decomposition products, decomposition of the electrolyte ceased. The carbon electrodes exhibited good cycling performance and essentially no irreversible losses after the first cycle.[18]

### 1.4.4 SEI formation on positive electrodes

The positive electrodes typically used in Li-ion cells are layered LiMO$_2$ compounds in which M is a transition metal including Co, Ni, Mn, or a mixture thereof. The redox potentials of these compounds is between 4 and 5 V vs. Li/Li$^+$. Interestingly, the nonaqueous solvents utilized in electrolytes are stable in this potential range on noble metal electrodes, but they undergo
oxidation type reactions at potentials as low as 4 V vs. Li/Li⁺ on the layered oxide compounds. In addition to products formed through withdrawal of electrons from nonaqueous solvents (e.g., oxidative cleavage of organic carbonate solvents with ring structures), positive electrode SEI may originate from reactions involving the formation of radical species from the electrolyte solvents or nucleophilic reactions between the positive electrode materials and the electrolyte. Thus, surface films are formed at the positive electrode / electrolyte interface which can also be an important factor in determining the cycling performance and thermal stability of the cell. As at the negative electrode, lithium ions must diffuse through a conductive layer between the electrolyte and positive electrode, a process which could become rate-limiting if the surface film were poorly conducting.[16, 19]

The phases encountered in positive electrode SEI include lithium fluoride, lithium alkyl carbonates, and polymeric phases. The lithium fluoride is likely due to HF which is unavoidable in many electrolytes due to side reactions involving fluorinated polyatomic anions (e.g. LiPF₆) with trace amounts of water. The HF can etch the lithiated transition metal oxide phase. The origin of the lithium alkyl carbonate may be derived not from chemical processes inherent to the positive electrode, but instead from growth of lithium alkyl carbonate at the negative electrode followed by dissolution. If this sequence continues to an extent that the electrolyte becomes saturated by lithium alkyl carbonate, then it could precipitate at the positive electrode. The lithiated transition metal compounds of the positive electrode may react nucleophilically with the electrophilic molecules of the nonaqueous electrolyte to yield alkyl carbonate-like phases (e.g. LiMO₂ + EC → MOOCH₂CH₂OCO₂Li).[16] EC is ethylene carbonate, a common cyclic organic carbonate solvent in electrolytes noted for its ability to passivate carbonaceous materials for negative electrodes. Polycarbonate species may be formed by nucleophilic reactions of alkyl
carbonate anions on solvent molecules. Any time radicals are formed, polymerization through ring opening of solvent molecules is possible. Delithiated transition metal oxide (i.e. MO$_2$) may be chemically oxidizing toward the electrolyte solvent through the loss of oxygen from the metal oxide.[16]

A distinct difference should be noted between the SEI formed at the negative and positive electrodes. The significance of the first cycle irreversible capacity loss is more greatly realized in the formation of the SEI at the negative electrode (when using a negative electrode other than lithium metal).[19] More subtle influences on the capacity fade may involve the different phases formed in the SEI and the rate of lithium ion diffusion through a polyhetero microphase SEI (Figure 1.4) vs. one in which polymeric species dominate. Also, upon prolonged storage, particularly at elevated temperatures, the surface film formation mechanisms on the positive electrode intensify, leading to greater resistance of the SEI. Hence, they contribute to capacity fade.[16]

1.4.5 Qualities of the ideal SEI

The interfacial chemistry at the negative and positive electrodes greatly impacts the performance and safety of Li-ion cells. The properties of the SEI influence the following within a rechargeable Li-ion cell:

- Irreversible capacity loss
- Capacity retention during cycling and/or storage
- Power capability
  - Ohmic losses at low currents / low values of overpotential
  - Tafel behavior at high current / high values of overpotential
• Safety
  o Prevention of lithium dendrite growth when charging the cell
  o Prevention of rapid electrolyte decomposition (exothermic).

In order to achieve good performance and safety during operation, SEI films should possess the following attributes[15, 16, 20]:

• Excellent adhesion to the active material over its entire area
  o Prevent continued decomposition of electrolyte and minimize irreversible losses
  o Prevent self-discharge reactions when sitting at rest

• Minimal solubility into the electrolyte

• Minimal swelling of organic components to avoid exposing active sites to the electrolyte

• Resistance to chemical attack (e.g. etching from acidic species from the electrolyte)

• Optimal thickness
  o Minimize diffusion distance of lithium ions to limit polarization effects
  o Eliminate any electronic conductivity

• Good stability at elevated temperatures

• Good electrochemical stability over the potential range of the electrode

• Elasticity to accommodate expansion / contraction of the active electrode materials

• Uniform morphology and chemical composition to ensure homogenous current distribution

• In the special case of graphitic carbons (Section 1.4.6), SEI formation should occur before lithium ion intercalation.
It is evident why stable SEI must be established within functional cells. The next sections consider specific examples of negative electrodes (1.4.6) and positive electrodes (1.4.7) and means of tailoring the SEI to have desirable properties.

**1.4.6 SEI engineering: negative electrodes**

Combining lithium or negative electrodes which operate at very low potentials vs. Li/Li⁺ with the majority of nonaqueous solvents results in decomposition of the solvent. As described in Section 1.4.3, SEI formation at the negative electrode is the contributor to irreversible capacity loss. If a surface film were able to be formed by a process in which a minimal amount of lithium ions were required, the irreversible capacity loss would thereby be minimized. An ideal scenario would be to identify an electrolyte that did not undergo any sort of decomposition on the negative electrode, but the likelihood of withstanding the extremely reducing interfacial environment is highly unlikely. A near-ideal scenario would be to form an SEI through polymerization without the need for lithium ions. If such a method existed, the transport of lithium ions across the organic film could still be problematic, and it would not benefit the cell much beyond eliminating the irreversible capacity loss. Thus, the most pragmatic solution for the negative electrode is to identify compounds that form tight surface films of minimal thickness to minimize the irreversible capacity loss and that form films with sufficiently high rates of lithium ion diffusion to minimize polarization losses.

Lithium, either as a metal foil or as an electrodeposited film on an inert metal substrate, has not been able to be implemented in most commercial cells due to safety concerns regarding dendrite growth. In the laboratory, however, it is still highly instructive to investigate electrolytes using lithium. Solvents ranging from γ-butyrolactone (GBL), tetrahydrofuran (THF), 2-methyl-tetrahydrofuran (2Me-THF), methyl formate (MF), and organic carbonates including
ethylene carbonate (EC), propylene carbonate (PC), diethyl carbonate (DEC), dimethyl carbonate (DMC), and vinylene carbonate (VC), have been explored with particular emphasis on the phases formed within and the resistance of the SEI. Generally, GBL forms SEI exhibiting a greater carbon content than THF, and this is likely due to the higher reactivity (i.e. exchange current) of the GBL at 0 V vs. Li/Li⁺ and propensity to form polymeric species. The organic carbonates are decomposed at potentials much more positive than those for THF and 2Me-THF. Of the organic carbonates, VC was found to have the most positive reduction potential which is of great importance when considering it as an additive to promote SEI formation. MF leads to lithium formate as the predominant lithium species whereas PC favors lithium alkylcarbonates. It is very important to also consider the lithium salt used in the electrolyte. A comparison of the SEI properties on bare lithium revealed that the resistance of LiAsF₆-based electrolytes was nearly twice as high as corresponding LiClO₄-based ones. When comparing LiPF₆ in GBL with LiAsF₆, LiBF₄, and LiClO₄, the thickness of the SEI with LiPF₆ was merely several nanometers whereas the other salts lead to thickness values exceeding 20 nm. Despite the lower thickness of the SEI, LiPF₆ lead to greater interfacial resistance due to the replacement of lithium oxide and lithium carbonate species with lithium fluoride.[15]

Dendrite formation on lithium metal negative electrodes has been minimized but not eliminated. Dendrites are formed during charging of the cell when lithium deposition is nonuniform. Instead, the metal preferentially forms deposits at specific sites and the morphology appears as needle-like dendrites or porous sponge-like lithium. Efforts to minimize dendrites and mossy lithium were undertaken to smooth the interface and minimize the surface area to remove any preferential sites of deposition. At the lithium / electrolyte interface, an SEI with favorable lithium ion diffusion and smoothness was formed form a range of additives.
including carbon dioxide, sulfur dioxide, water, and hydrofluoric acid. SEI promoting additives including nitromethane and 2Me-THF were added to PC solutions because these compounds were preferentially reduced prior to lithium plating. Surfactants such as nitrile cellulose, long chain tetraalkylammonium chlorides, and perfluoropolyethers were added to electrolytes to favor the deposition of less porous lithium. This was due to enhanced and more uniform nucleation. The presence of these additives decreased the interfacial resistance as well. In addition to promoting an ionic conductive SEI layer, other researchers explored lithium-metal alloys that would be deposited at the lithium / electrolyte interface. Aluminum iodide and tin (II) iodide were added in the hundreds of ppm to the electrolyte to limit the growth of dendrites. Not only was the cycling efficiency increased, but the increased efficiency could be retained even when the lithium was transferred to an electrolyte free of the iodide salt additive after the first cycle. The residual aluminum or tin permanently remained as a thin skin of lithium-metal alloy, yielding a durable interface with good cycling.[21]

As candidates for the negative electrode evolved from lithium to carbonaceous materials, engineering of the SEI became more involved. The physicochemical properties of carbon such as wettability, catalysis, and chemical bonding to other materials are affected by its structure and chemical composition. The particle size and shape, pore-size distribution, surface area, and presence of surface species are important parameters to consider when selecting a particular carbonaceous material. Most carbonaceous materials are partially crystalline and are composed of planar sheets of carbon atoms arranged in a honeycomb structure. Basal plane carbon is made up of these graphene sheets. These sheets are stacked in an ordered or disordered manner to form crystallites. The crystallites contain edge sites which, along with impurities and lattice defects, are areas of much greater reactivity toward the electrolyte than the basal planes.
In the extreme case of edge atoms contained within closed pores, the edge atoms are considered to be radicals possessing a dangling bond.[15]

Interestingly, in highly oriented pyrolytic graphite (HOPG), the basal plane carbon showed distinctly different SEI than edge carbon. Regardless of whether LiPF$_6$, LiAsF$_6$, or LiClO$_4$ was used as the lithium salt dissolved in an EC : DEC electrolyte, the basal SEI was thinner than the edge SEI (7 nm vs. 35 nm when using LiPF$_6$). The basal SEI was distinct in that it displayed the presence of 10 to 30 atomic percent lithium carbonate. Depth profiling of the basal SEI revealed lithium carbonates, lithium semi-carbonates, and polymeric species nearer to the electrolyte and lithium oxide adjacent to the HOPG electrode. It was expected for the SEI formed on carbon at low potentials to resemble that found on lithium metal. However, essentially no carbonates and dramatically less polymeric species were observed for the edge SEI. Instead, the edge SEI was comprised predominantly of lithium halide from decomposition of the anions of the lithium salts. The edge SEI is believed to be thicker due to co-intercalation of ion aggregates (e.g. Li$_5$PF$_6$) at the beginning of SEI formation.[15]

The polymeric species, identified more clearly for the SEI occurring on the basal planes of HOPG, have been identified as polyolefins. The atomic mass units for many of the species differ by 14, corresponding to the (CH$_2$)$_n$ repeat units of the polymers. The presence of polymeric species as beneficial to the SEI is debatable. On one hand, they generally do not conduct lithium ions and they tend to dissolve at elevated temperatures, leading to uneven current distribution and safety issues. On the other hand, they impart flexibility to the SEI to effectively cover the active material during small to moderate volume changes.[15]
Another intriguing process may be active when utilizing highly ordered carbonaceous materials as negative electrodes. Lithium ions exist in the nonaqueous electrolyte as solvated entities. Ideally, when these lithium ions diffuse through the SEI layer at the negative electrode/electrolyte interface, they lose their solvation shells and are incorporated into the carbon structure in a solvent-free form. However, in some instances, notably involving PC, lithium intercalates together with its solvation shell. This leads to exfoliation by either distortion of the carbon lattice between graphene sheets or the release of gaseous byproducts. Reduction of the solvated molecules can form propylene which acts to crack the carbon, exposing fresh surfaces which host further reactions.[20]

The implementation of carbonaceous materials requires approaches to minimize deleterious reactions and irreversible capacity loss. The first approach will consider additives to the electrolyte that will promote favorable SEI growth. Within this approach, the additives can be generalized as either reduction-type or reaction-type additives.[21] Reduction-type additives function via electrochemical reduction at low potentials. Thermodynamic instability and kinetic reactivity of the electrolyte culminate in SEI formation.[20] Reduction-type additives are selected such that they are preferably reduced to form insoluble solid products to deactivate the catalytic surface of the carbonaceous electrode material prior to electrochemical reduction of the bulk solvents of the electrolyte. The use of these additives reduces gas generation (from both solvent decomposition and exfoliation processes) and increases the stability of the SEI due to the participation of additive molecular moieties into the SEI.[21]

Many of the reduction-type additives share a common feature, namely, a double-bonded carbon functionality. This unsaturated bond is a reactive site for electrochemical reduction and
subsequent polymerization. Examples of these types of additives include vinylene carbonate, vinyl ethylene carbonate, vinyl acetate, divinyl adipate, acrylic acid nitrile, maleic anhydride, phosphonates, and vinyl-containing silane-based compounds. Furan derivatives that contain two double bonds in each molecule have also been reported as effective SEI forming agents.

The polymerizable reduction-type additives may be propagated by radicals formed at the C=C bond, and they may also be relatively efficient since electron transfer is only required for the first step of SEI formation until the polymeric species is terminated. A drawback of using a polymerizable reduction-type additive is the possibility of promoting a thick SEI layer on the positive electrode via oxidative decomposition and polymerization. Thus, they are used sparingly, less than several percent of the electrolyte.[21]

Another subset of reduction-type additives is the reductive agent which assists SEI formation through adsorption of its reduced products onto the catalytically active sites of the carbonaceous negative electrode. Many of the reductive agents are sulfur-based compounds including SO₂(soln), polysulfides (Sₓ²⁻), and cyclic alkyl sulfites (e.g. ethylene sulfite). As the sulfur content of the molecule increases, so too does the effectiveness of the additive which is consistent with the idea of poisoning the catalytic sites with sulfur. Compared to SEI composed of carbonates, the formation of polysulfides leads to a more conductive SEI. However, the use of sulfur-based reductive agents is problematic because many of them are unstable at high positive potentials vs. Li/Li⁺, and internal redox shuttles result leading to high rates of self-discharge. Other reductive-type additives include nitrogen chemistries based on N₂O(soln), nitrites, and nitrates, halogenated ethylene carbonates, and halogenated lactones. These latter compounds are carbon / oxygen rings and contain carbonyl groups. Hence, they are expected to react similarly to EC but preferably at more positive potentials.[21]
Reaction-type additives have the ability to scavenge either radical anions generated during the decomposition of the bulk electrolyte solvent or reduction-type additives, intermediate compounds of the solvent reduction, and/or combine with phases such as lithium alkyl dicarbonate to form more stable SEI layers. The earliest documented reports involving this type of additive was for carbon dioxide gas dissolved within the electrolyte solvent and a reduced irreversible capacity loss. Lithium oxalate compounds were present with EC and PC-based electrolytes. The solubility of CO$_2$ gas was found to be low; thus dialkyl pyrocarbonate was used to generate CO$_2$ in-situ by its decomposition. Surprisingly, these CO$_2$-reacted SEI displayed low resistances at low temperatures, attributed to the formation of a more compact, thin SEI. Similar results were achieved by saturating the electrolyte with lithium carbonate which was found to reduce gas generation and improve the cycle life of the Li-ion cell.[21]

Generally, reaction-type additives based on phenols, aromatic esters, and succinimides are believed to be capable of stabilizing intermediate radical anions through delocalization of the radical. Since the additives themselves do not partake in reduction and instead capture less stable radical anions, these reaction-type additives typically do not shift the onset potential for SEI formation from the lithium intercalation potential when used in electrolytes containing organic carbonate solvents. Additionally, even if the irreversible capacity loss is not improved, the presence of these reaction-type additives may significantly improve the cycle life of the cell.[21]

Reaction-type additives derived from boron-based compounds have been studied extensively. Enhanced stability of the SEI improved the low temperature performance, rate capability, and capacity fade. The compounds included inorganic B$_2$O$_3$, organic borates, boroxine compounds,
and most notably, soluble lithium salts, including lithium bis(oxalato) borate (LiBOB) and lithium oxalyl difluoroborate (LiODFB). By virtue of the presence of B-O moieties within the SEI when using LiBOB as a lithium salt in the electrolyte, it is expected that LiBOB reacts with lithium alkyl dicarbonate and alkoxides to form more stable oligomers. LiBOB and salts based on its chemistry may not involve any electronic transference but may instead react through a series of complicated exchanges of B-O and R-O bonds.[21]

The second approach to minimize deleterious reactions and irreversible capacity loss considers treatments to modify the surface groups and morphology of the carbonaceous materials prior to cell assembly. Thermal treatments of graphites in air have lead to the formation of carboxylic and oxide groups at the expense of aromatic carbon and CH groups, particularly at the edge sites. The SEI can bond more strongly to the carboxylic groups. Additionally, this treatment yielded nanochannels which enhanced the gravimetric capacity of the carbon and decreased the degradation rate of the electrode during cycling. If the heat treatment is performed in an inert atmosphere of argon, surface groups can be removed, leaving reactive surface sites available. Reactants including oxygen, carbon dioxide, ammonia, sulfur dioxide, hydrogen sulfide, or alkenes can be introduced at lower temperatures. Not only are catalytic sites tuned through this process, but the nano-sized morphological features offered favorable nucleation sites and anchoring points for the SEI.[15] Chemical oxidation of carbonaceous materials can also be performed by strong oxidizing agents including hot nitric acid or ammonium peroxysulfate. As with thermal treatment in air, this also resulted in an increase of the carboxylic groups.[15, 20] Instead of altering the surface groups native to the carbon, aryl (aromatic) functional groups could be immobilized onto the carbon to promote SEI formation.[20] The SEI formation must still be promoted through the use of reduction-type and/or reaction-type additives, but the
intent of the surface modification of the carbon is to decrease the reactivity of the carbon and lower the irreversible capacity loss.

A third and relatively new approach to minimizing irreversible capacity loss is the idea of creating an artificial SEI prior to cell assembly. The artificial SEI must possess the attributes of the SEI formed as a result interaction of reduction-type and reaction-type additives. The artificial SEI can also act as an intermediate phase that promotes in-situ SEI growth but with a much lower extent of lithium ions consumed, thereby greatly lowering the irreversible capacity loss. Either by electropainting or vacuum-insertion of a polyelectrolyte solution into the structural voids of a negative electrode, poly(ethylene-co-acrylic acid) (PEAA) and carboxymethylcellulose (CMC) have been coated. Of these two materials, CMC was more stable thermally and gave a lower interfacial resistance. The films were continuous, homogenous, and conformal, important qualities for the interfacial chemistry.[22]

Despite SEI formation on lithium that minimized the growth of dendrites, negative electrodes for commercial lithium-ion cells were predominantly carbonaceous materials. While carbonaceous materials have been enabled by promoting SEI formation and functionalizing the surface groups, they still exhibit relatively low specific capacity values (< 400 mAhg⁻¹). Much interest has been renewed in lithium alloys for high energy density cells. Lithium alloys would ideally have two to three times greater capacity than carbonaceous materials. Since they react with lithium at slightly more positive potentials than Li/Li⁺, dendrite formation may also be avoided.[13, 23] Despite the anticipated performance gains, lithium alloys, based largely on tin and aluminum, suffered due to very large volume swings (up to 200%) during cycling. The disintegration of the particles led to losses in electrical contact. Attempts to reduce the particle
size of the active material and incorporate the active material into a matrix to minimize the impact of stresses were beneficial, yet insufficient. [13] Thus, in practice, the realization of lithium alloy negative electrodes was hindered.

It is important to note the degradation mechanism of the active lithium alloy material also involves thickening and cracking of the SEI as a result of cycling. [15] The decomposition products within the SEI consume lithium ions each time fresh metal is exposed to the electrolyte, contributing to capacity loss. A variety of metals and alloys have been examined including Si[24, 25], Sn[24, 26, 27, 28, 29], Sb[24, 30], Pb[24], and Bi[24]. Overall, many displayed potentials for solvent reduction more positive than carbonaceous materials, and the phases formed in the SEI were similar to those observed for lithium and carbonaceous materials. While this is important for the development of negative electrodes, it should not be overlooked in the development of positive electrodes composed of conversion compounds that may be discharged to potentials as low as 1.5 V (FeF$_3$ [31], FeOF [7]) or 2.0 V (BiF$_3$ [4]) vs. Li/Li$^+$. When lithiated, the conversion compounds are reduced to lithium salts and metal clusters with nano-sized dimensions which may become active sites for reduction of electrolyte solvents and SEI additives.

### 1.4.7 SEI engineering: positive electrodes

In Section 1.4.4, evidence for SEI appearing on the positive electrode was presented. Growth of a surface film at the positive electrode / electrolyte interface can be beneficial if deleterious reactions are mitigated. However, it can also lead to a more resistive interfacial layer and worse cell performance. Several cases are presented below for commonly encountered positive electrode materials.
The manganese in LiMn$_2$O$_4$ is susceptible to dissolution through disproportionation of trivalent Mn$^{3+}$ through the Hunter reaction: $2\text{Mn}^{3+}(s) \rightarrow \text{Mn}^{2+}(\text{soln}) + \text{Mn}^{4+}(s)$. The acidity of the electrolyte influences the reaction, and the amount of spinel dissolved decreases in the order: LiCF$_3$SO$_3$ (lithium triflate) > LiPF$_6$ > LiClO$_4$ > LiAsF$_6$ > LiBF$_4$. The loss of manganese reduces the amount of active material from the positive electrode.[19] Thus, a surface film that could act as a physical barrier to prevent attack of the manganese or act as an acid neutralizer would seem to benefit the spinel phase.

Interestingly, the LiMn$_2$O$_4$ exhibited the same relative amounts of elements whether the surface film was formed as a result of electrochemical cycling or storage at open circuit. If the studies were conducted for longer durations, the amount of phases at the interface increased, suggesting that the layer formed on the spinel was not sufficiently dense to act as a passivating barrier. The oxidation process could continue because fresh electrolyte could be transported through this diffuse layer. This contrasts with what is typically observed at the negative electrode in which its SEI grows as thick as permitted by electron tunneling and is dense. The layer formed on the positive electrode might be more appropriately deemed a solid permeable interface (SPI). The SPI can continually consume electrolyte, and the lack of fully passivating behavior seems related to the abundance of organic rather than inorganic compounds.[19]

Edström, Gustafsson, and Thomas[19] have provided an extensive review of the many parallel mechanisms occurring at the interface of LiMn$_2$O$_4$ with the electrolyte. They have presented evidence of how the interface is influenced by storage and cycling, storage at various states of charge, salt composition (mainly LiPF$_6$ and LiBF$_4$), and temperature. In short, the following generalizations were made:
• During cycling or at 0% state of charge, a polymeric layer forms adjacent to the active particle surface; this is more likely due to a nucleophilic mechanism of polycarbonate formation as opposed to direct electronic withdrawal from electrolyte solvent molecules as the potential is 3.4 V vs. Li/Li$^+$ at 0% state of charge

• Dissolution of manganese occurs when the spinel is in the lithiated state

• P-O (or B-O) type compounds at the interface are formed as a result of solvating Mn$^{2+}$

• At 100% state of charge, there is a stronger driving force for polymerizing the electrolyte solvent via electrolyte oxidation through the withdrawal of an electron from an electrolyte solvent species

• The formation of lithium-rich spinel phase at the surface can be coupled to manganese disproportionation.

The formation of an SPI (and not a true SEI) on the LiMn$_2$O$_4$ is thus detrimental to the long term stability and performance of cells in which the spinel is used as the positive electrode. A barrier, impenetrable to solvent species, in which lithium ion diffusion were permitted has not yet been achieved. However, the introduction of small amounts of inorganic material into the electrolyte has improved capacity retention, likely by neutralization of the acidic species within the electrolyte. Coatings of Li$_2$CO$_3$ and Al$_2$O$_3$ may have not only lowered the acidity local to the surface of the positive electrode but may have also provided locations to nucleate or anchor decomposition products to more closely resemble an SEI.[19] Lithium borate glass and diamond-like carbon have also been considered as inorganic barrier coatings.[32]

Other common positive electrode materials include layered transition metal oxides such as Li(Ni,Co)O$_2$. As a result of the synthesis conditions and/or exposure to atmospheric carbon
dioxide, Li(Ni,Co)O$_2$ tends to be coated with lithium carbonate which can react with HF in the electrolyte to form lithium fluoride. Li(Ni,Co)O$_2$ promotes electrolyte oxidation more strongly than LiMn$_2$O$_4$. Thus, the interfacial resistance increases considerably during both cycling and storage at elevated temperatures, resulting in capacity fade. When utilizing LiPF$_6$ as the electrolyte salt with these layered compounds, the amounts of LiF, Li$_x$PF$_y$, and Li$_x$PF$_y$O$_z$ systematically decrease when stored at higher temperatures in favor of organic phases. Polycarbonates are formed from electrolyte oxidation, but it is unclear if their origin is driven by electron removal from organic alkyl carbonates such as EC or if salt decomposition resulting in strong Lewis acids such as PF$_5$ and BF$_3$ initiates solvent polymerization.[19]

Methods to restrict growth of thick SEI or SPI layers on Li(Ni,Co)O$_2$ have been investigated. Nanoparticles of magnesium oxide were incorporated into the positive electrode to coat LiCoO$_2$. The nanoparticles of magnesium oxide were observed to prevent interactions with alkyl carbonate solvents. Notably, lithium carbonate species were not observed on coated electrodes charged to as high as 4.4 V vs. Li/Li$^+$. Compared with uncoated LiCoO$_2$ in which a chemical process for the formation of carbonate surface groups on the positive electrode took place before any electrochemical cycling, the magnesium oxide suppressed electrolyte decomposition. The coating aided the positive electrode by suppressing the dissolution of Co$^{4+}$. Also, the coated material was more stable in the charged state and permitted better operation at high potentials.[32] Additives have also been considered to promote the inclusion of different phases at the LiCoO$_2$ / electrolyte interface. Vinylene carbonate and ethylene sulfite, typically investigated for SEI at the negative electrode, were examined and were found to modify the interface at the positive electrode. Vinylene carbonate led to a lower interfacial resistance
whereas ethylene sulfite led to a greater one. Interestingly, the ethylene sulfite was oxidized to form lithium sulfate on the positive electrode.[33]

LiFePO$_4$ is interesting as a positive electrode material because it inherently has a lower oxidizing power than LiMn$_2$O$_4$ or Li(Ni,Co)O$_2$ due to the lower redox potential of iron. Furthermore, some processing methods leave residual carbon on the surface of the particles by design to promote electronic conductivity. Upon immersion into the electrolyte, lithium carbonate is not generated on the surface of LiFePO$_4$ via nucleophilic reactions as demonstrated on the surfaces of the transition metal oxides. The growth of a surface layer on LiFePO$_4$ due to electrolyte interactions is relatively insensitive to storage at elevated temperatures or electrochemical cycling. The phases encountered in the surface film are dominated by decomposition products of the electrolyte salt and are no more than 5 nm in thickness. Thus, the interfacial properties when using LiFePO$_4$ as the positive electrode do not seem to impact performance as negatively as with LiMn$_2$O$_4$ and Li(Ni,Co)O$_2$.[32]

1.4.8 SEI and conversion materials

A generalized reaction scheme for a conversion material can be written as

$$M^{x^+}X_y + zLi^+ + ze^- \xrightarrow{\text{charge}} M^0 + yLi_{(z/y)}X$$  \hspace{1cm} (1.19),[Ref 4]

Compared with intercalation materials described in Sections 1.4.6 (carbon) and 1.4.7 (transition metal oxides), conversion systems have the ability to make use of the full range of oxidation states of the metal, M. Thus, the capacities of these materials are outstanding, many times greater than those of carbonaceous materials for negative electrodes and transition metal oxides for positive electrodes.[34] (See Table 1.1 for a comparison of metal fluorides with transition metal intercalation materials). The full reduction of the MX$_y$ compound leads to a
composite of nano-domains of metal (2-8 nm) dispersed in a matrix of Li(\text{\textsubscript{z/y}})X salt. Many conversion systems across a variety of compounds including metal sulfides, phosphides, nitrides, oxides, and fluorides, have been demonstrated with good reversibility.[34] Compounds with polyatomic anion groups have also been demonstrated including oxalates[35, 36], carbonates[35, 37, 38], and formates[39]. Of these compounds, only those involving metal fluorides are suitable for positive electrodes, owing to the very high ionicity of the M-F bond. The discharge potentials (Table 1.1), for metal fluorides can exceed 2 V vs. Li/Li\textsuperscript{+}, in stark contrast with the potentials observed with metal oxides, sulfides, nitrides, phosphides, and oxysalts, which are typically less than 1.5 V vs. Li/Li\textsuperscript{+}.[40] Hence, these other materials have been considered as negative electrodes in Li-ion cells.

Electrodes based on conversion systems offer the opportunity to achieve high capacities while using low-cost materials. The nature of the reaction to yield an internal nanostructure during the first discharge sequence is advantageous for maintaining an enhanced volumetric capacity and energy density. The structure avoids combining individual nanoparticles with low packing fractions into the active material. The redox potential of the conversion reaction can also be controlled by tuning the ionicity of the anion.[34]

A significant drawback of conversion materials lies in their poor kinetics. Assuming the reconversion sequence is simply the reverse electrochemical process of the discharge sequence (i.e., no intermediate phases are formed during charge that do not appear during discharge), the limitations in the diffusion of lithium ions result in a large hysteresis. The potential difference between discharge and charge can exceed 1 V for metal fluorides, and the difference systematically decreases as the metal-anion bond becomes less ionic.[34] Thus, the voltage
efficiency can be quite low despite good coulombic efficiency. Comparatively, intercalation compounds exhibit much lower voltage hysteresis unless cycled at very rapid rates.

When a conversion-type negative electrode is used in conjunction with an intercalation-type positive electrode, the initial discharge of the Li-ion cell yields a lithiated negative electrode. A foreseeable disadvantage of designing a functional cell with a conversion-type positive electrode (i.e. MFₙ) would be that it does not contain any lithium. At present, Li-ion cells are fabricated with the positive electrode in the fully lithiated state. Two methods have been proposed to work around this limitation of the metal fluoride. Either metal and lithium fluoride can be milled into a nanocomposite prior to cell assembly, or the metal fluoride can be reacted with lithium. The latter has been demonstrated in which lithium nitride (Li₃N), a highly reducing compound, was reacted in the solid state with bismuth (III) fluoride or iron (III) fluoride to yield bismuth or iron metal, lithium fluoride, and nitrogen, a fugitive gas.[41] Nanostructured composites were formed which exhibited reversible cycling with a carbon negative electrode.

With the exception of metal fluorides, systems that undergo conversion reactions have been considered for negative electrodes in Li-ion cells. As described extensively in Sections 1.4.3 and 1.4.6, when the negative electrode is driven below a potential at which an electrolyte component is thermodynamically unstable, and there is a sufficient exchange current for its electrochemical reduction (i.e., a kinetic parameter), solvents, additives, and/or salts can decompose at the negative electrode / electrolyte interface to form an SEI. This phenomenon has been witnessed on a variety of 3d transition metal oxides[42, 43, 44, 45, 46, 47, 48, 49, 50, 51, 52, 53, 54] and metal sulfides[47, 55, 56]. Very interestingly, observations made on conversion systems indicate that the SEI seems to evolve drastically with its state of lithiation.
This is quite different than the behavior observed on carbonaceous materials or lithium-alloys. Whereas the SEI formed on carbon and lithium-alloys has been proven to change as a function of potential, the modifications were subtle and the SEI remained largely intact.\cite{57} The potential of the carbon or lithium-alloy negative electrode was almost always at a value less than that necessary to maintain the electrochemical reduction of electrolyte species. However, owing to the large voltage hysteresis of the conversion materials and the redistribution of bonds during each cycle, the SEI was observed to decompose reversibly during the delithiation (reconversion) process.\cite{44, 45, 46, 51, 54}

The first reported indication of a decomposition layer occurring on a metal oxide conversion material was by Poizot et al\cite{42} who showed a coating on CoO that developed in the fully discharged state. Electrochemical evidence consistent with electro-catalytic decomposition of electrolyte was shown below 0.8 V vs. Li/Li$^+$ for CoO, NiO, FeO, and CuO.\cite{43} This decomposition led to additional electrochemical capacity beyond the theoretical value for the full discharge of the metal oxide conversion material.\cite{44} The decomposition layer behaved in a markedly different manner than the SEI on carbon or lithium-alloys. A thick gel-like film enveloped the negative electrode at low potentials, yet above 2 V vs. Li/Li$^+$, this layer was no longer observed on the electrode. Furthermore, the cycling of the electrode was improved as the electrode was charged to increasingly higher potentials.\cite{44} In contrast, Obravac and Dahn\cite{47} dismissed these claims of reversible SEI formation/dissolution.

As more resources were dedicated to understanding the interfacial chemistry, the phases developed at the interface, particularly on the active metal of the lithiated conversion material, were shown to include lithium carbonate\cite{45, 48, 50}, lithium alkyl carbonate\cite{45, 50}, and
polymeric species[50, 52, 53]. In the fully discharged state, lithium oxide and lithium carbonates were found adjacent to the metal, and the polymeric species, most often described as ethylene oxide oligomers, existed nearer to the electrolyte.[50, 52, 53] The polymeric layer of the gel-like film was found to dissociate through a dissolution process that seemed to be electrochemically driven while the lithium carbonate type phases remained intact.[54] It was noteworthy that these thick gel-like layers of the SEI (20-50 nm) could be decomposed, and even more so, that these layers could be reversibly formed/decomposed after the initial cycle. Also, it was surprising that they were able to grow so thick and still permit diffusion of lithium ions. In general, as long as the negative electrode was able to reach potentials greater than 2 V vs. Li/Li⁺, it exhibited good reversibility and good capacity retention during cycling.

The catalytic nature of the 3d transition metal toward the decomposition of the organic carbonate electrolytes provided additional capacity at low potentials (< 0.8 V vs. Li/Li⁺), but SEI formation did not seem to impact cell performance beyond a large first cycle irreversible capacity loss. In the cases above, the rates of discharge were slow because of the inherent difficulty of converting the metal oxide; thus, interfacial processes did not become rate-limiting. But, moving away from the negative electrode, it became very interesting to consider what types of electrode / electrolyte interactions, if any, were active on metal fluoride conversion materials suitable for positive electrodes.

Many of the metal fluorides contain 3d transition metal clusters in the lithiated state. The 3d metal was proven to be the active site for the catalytic decomposition of the electrolyte[49]; however, the discharge potential for 3d metal fluorides was rarely ever driven below 1.5 V vs. Li/Li⁺. This value is significantly more positive than the < 1 V potential required to induce
electroreduction of electrolyte species on 3d metals. Thus, it would be greatly unexpected for any type of reduction reaction to occur on the 3d metals of the fluorides unless lithiation were permitted to occur at potentials below 1 V vs. Li/Li$^+$. This same rationale was adopted for p-block metal fluorides including SnF$_2$, PbF$_2$, and BiF$_3$. But, was it correct? One of the aims of this thesis will be to prove whether or not such electrolyte interactions occur with BiF$_3$ positive electrodes as have been observed on 3d metal oxides and sulfide negative electrodes. Although not a topic of thesis research, the metal fluoride conversion systems are often recharged at potentials exceeding 4 V vs. Li/Li$^+$, and electro-oxidation of salts and solvents to form inorganic and polymeric species like those observed on LiMn$_2$O$_4$, Li(Ni,Co)O$_2$, and LiFePO$_4$ should also be considered.

1.4.9 Characterization techniques for the SEI

Section 1.3 has thus far provided a primer on the mechanisms of SEI formation and phases formed at the electrode / electrolyte interfaces. It is worth including a brief description of the array of characterization techniques available to probe the SEI (Table 1.3). The advantages and disadvantages of the techniques useful for characterizing the SEI are presented in Table 1.4 through Table 1.7. In general, any of the techniques which require disassembly of an electrochemical cell are subject to complications of sample transfer to the analytical tool. These ex-situ methods require specialized gloveboxes to enable sample transfer directly to the characterization instrument while under inert conditions or mechanisms to encapsulate samples from atmospheric contaminants including oxygen, water vapor, carbon dioxide, and nitrogen. Otherwise, the SEI may be altered or damaged.[20] The “disadvantage” column in Table 1.4 through Table 1.7 does not include this item because it would be redundant to state this across all the techniques.
More thorough descriptions for the techniques used toward the completion of this thesis are presented in Chapter 2: Experimental techniques. Reviews concerning characterization methods of SEI have been composed by Aurbach and Cohen[16], Aurbach and Zaban[58], and Verma, Maire, and Novák[20].
Table 1.3. Analytical techniques for characterizing SEI.

<table>
<thead>
<tr>
<th>Technique</th>
<th>Abbreviation</th>
</tr>
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<tbody>
<tr>
<td>Fourier Transform Infrared Spectroscopy</td>
<td>FTIR</td>
</tr>
<tr>
<td>Raman Spectroscopy</td>
<td>usu. Raman</td>
</tr>
<tr>
<td>Ultraviolet/Visible Light Spectroscopy</td>
<td>UV/Vis</td>
</tr>
<tr>
<td>X-ray Absorption Spectroscopy</td>
<td>XAS</td>
</tr>
<tr>
<td>Extended X-Ray Absorption Fine Structure</td>
<td>EXAFS</td>
</tr>
<tr>
<td>X-ray Absorption Near Edge Structure</td>
<td>XANES</td>
</tr>
<tr>
<td>X-ray Photoelectron Spectroscopy</td>
<td>XPS</td>
</tr>
<tr>
<td>Auger Electron Spectroscopy for Chemical Analysis</td>
<td>ESCA</td>
</tr>
<tr>
<td>Auger Electron Spectroscopy</td>
<td>AES</td>
</tr>
<tr>
<td>Energy Dispersive X-ray Analysis</td>
<td>EDX</td>
</tr>
<tr>
<td>Secondary Ion Mass Spectroscopy</td>
<td>SIMS</td>
</tr>
<tr>
<td>Electron Energy Loss Spectroscopy</td>
<td>EELS</td>
</tr>
<tr>
<td>Electrochemical Quartz Crystal Microbalance</td>
<td>EQCM</td>
</tr>
<tr>
<td>Electrochemical Impedance Spectroscopy</td>
<td>EIS</td>
</tr>
<tr>
<td>Atomic Force Microscopy</td>
<td>AFM</td>
</tr>
<tr>
<td>Scanning Tunneling Microscopy</td>
<td>STM</td>
</tr>
<tr>
<td>Scanning Electron Microscopy</td>
<td>SEM</td>
</tr>
<tr>
<td>Transmission Electron Microscopy</td>
<td>TEM</td>
</tr>
<tr>
<td>X-ray Diffraction</td>
<td>XRD</td>
</tr>
<tr>
<td>X-ray Fluorescence</td>
<td>XRF</td>
</tr>
<tr>
<td>Nuclear Magnetic Resonance</td>
<td>NMR</td>
</tr>
<tr>
<td>Electron Paramagnetic Resonance (EPR)</td>
<td>EPR</td>
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<tr>
<td>aka Electron Spin Resonance (ESR)</td>
<td>ESR</td>
</tr>
<tr>
<td>Mössbauer Spectroscopy</td>
<td>usu. Mössbauer</td>
</tr>
<tr>
<td>Ellipsometry</td>
<td>n/a</td>
</tr>
<tr>
<td>Differential Scanning Calorimetry</td>
<td>DSC</td>
</tr>
<tr>
<td>Accelerated Rate Calorimetry</td>
<td>ARC</td>
</tr>
<tr>
<td>Differential Electrochemical Mass Spectrometry</td>
<td>DEMS</td>
</tr>
</tbody>
</table>
Table 1.4. Spectroscopic, surface specific, analytical techniques for characterizing SEI.

<table>
<thead>
<tr>
<th>Technique</th>
<th>Advantages</th>
<th>Disadvantages/Limitations</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>FTIR</strong></td>
<td>Does not require ultra high vacuum (UHV) conditions(^{20})</td>
<td>Very thin SEI may not impart strong enough vibration signals(^{20})</td>
</tr>
<tr>
<td></td>
<td>Variety of modes including attenuated total reflectance (ATR), photoacoustic, diffused reflectance, subtractively normalized interfacial (SNIFTIR), transmission, and grazing incidence(^{20})</td>
<td>Differentiation of functional groups is challenging due to similar vibration frequencies(^{20})</td>
</tr>
<tr>
<td></td>
<td>Very high signal to noise ratio(^{16,58})</td>
<td>\textit{In-situ} techniques may suffer from high absorption of the electrolyte(^{20})</td>
</tr>
<tr>
<td></td>
<td>Handle liquids, powders, films(^{16})</td>
<td>Quantitative analysis is difficult(^{20})</td>
</tr>
<tr>
<td><strong>Raman</strong></td>
<td>Complementary to FTIR to show presence of species which vibrate in symmetric modes</td>
<td>Species such as lithium fluoride are not visible(^{16})</td>
</tr>
<tr>
<td></td>
<td>Well-suited for examining intercalation of Li(^+) into graphite</td>
<td>Low signal to noise except for Surface Enhanced Raman Spectroscopy (SERS)(^{16,58})</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Incident laser beam can damage sample due to localized heating(^{16,58})</td>
</tr>
<tr>
<td><strong>UV/Vis</strong></td>
<td>Can indicate electroadsorption processes \textit{in-situ}</td>
<td>Sensitivity of species adsorbed onto thin layers is difficult(^{16,58})</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Lack of appropriate chromophores(^{16,58})</td>
</tr>
<tr>
<td><strong>XAS</strong></td>
<td>High intensity x-rays can penetrate cell casing, facilitating \textit{in-situ} measurements(^{16,58})</td>
<td>Requires synchrotron radiation(^{16,58})</td>
</tr>
<tr>
<td></td>
<td>EXAFS provides method for determining structure of amorphous phases(^{59})</td>
<td></td>
</tr>
<tr>
<td><strong>XPS</strong></td>
<td>Allows analysis of all elements excluding H and He(^{20})</td>
<td>\textit{Ex-situ} technique</td>
</tr>
<tr>
<td></td>
<td>Semi-quantitative with 10% error(^{20})</td>
<td>Due to highly energetic incident photons, risk of beam damage(^{20})</td>
</tr>
<tr>
<td>Technique</td>
<td>Advantages</td>
<td>Disadvantages/Limitations</td>
</tr>
<tr>
<td>-----------</td>
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</tr>
</tbody>
</table>
| **XPS (cont.)** | Highly surface sensitive, typically only the outermost 10 nm are probed\(^{20}\)  
Highly chemistry specific when used in conjunction with good standards and accurate calibration\(^{20}\)  
Option of depth profiling with ion etching\(^{20}\)  
Option of charge compensation with flood gun attachment | Requires UHV conditions\(^{16,58}\)  
Differential etch rates for inorganic and organic SEI components\(^{20}\)  
Surface charging occurs on non-conductive samples, shifting spectra\(^{20}\)  
Requires precise knowledge of system and good reference values\(^{20}\)  
Deconvolution of peaks can be challenging\(^{20}\) |
| **AES** | Useful for quantitative analysis and can be used in conjunction with XPS\(^{16,58}\) | Same sample handling limitations as XPS\(^{16,58}\) |
| **EDX** | Qualitative and quantitative elemental analysis\(^{16,58}\)  
Vacuum equipment not as costly as UHV\(^{58}\)  
Good spatial resolution\(^{58}\) | Cannot provide information on the oxidation states of elements\(^{58}\)  
Depth profiling not an option\(^{58}\) |
| **SIMS** | Highly specific mass/charge ratio measurements\(^{16,58}\)  
High spatial resolution\(^{16,58}\)  
Depth profiling\(^{16,58}\) | Requires UHV\(^{16,58}\)  
Issues when multiple species have same mass/charge ratios\(^{58}\) |
| **EELS** | Very small sample size able to be probed\(^{59}\)  
Quantitative analysis potentially powerful for low atomic number elements\(^{59}\) | Merely 1 to 2 eV energy resolution, thus not as good as XPS at determining binding energy (oxidation state) of elements\(^{59}\)  
Typically operated in TEM between 100 to 200 KeV; thus UHV required and beam damage possible\(^{59}\) |
Table 1.5. Electrochemical analytical techniques for characterizing SEI.

<table>
<thead>
<tr>
<th>Technique</th>
<th>Advantages</th>
<th>Disadvantages/Limitations</th>
</tr>
</thead>
</table>
| EQCM      | Possible resolution of ng·cm⁻²¹⁶,⁵⁸  
Resonant frequency depends linearly on mass accumulation; thus it is possible to estimate the equivalent weight of surface species formed under different conditions of potential, concentration, and temperature¹⁶,⁵⁸  
Requires the development of special electrochemical cells¹⁶,⁵⁸  
Interpretation can be influenced by electrode roughness, electrolyte viscosity, and temperature⁵⁸  
Non-electrochemical reactions must be avoided⁵⁸  
Soluble decomposition products prevent accurate determination of equivalent weight⁵⁸ | |
| EIS       | Study the evolution of interphase resistance *in-situ*²⁰  
All processes at the electrode / electrolyte interface studied at once⁶⁰ | For complicated electrode geometries, equivalent circuits beyond simple resistance-capacitance elements must be modeled⁶⁰ |
Table 1.6. Microscopy analytical techniques for characterizing SEI.

<table>
<thead>
<tr>
<th>Technique</th>
<th>Advantages</th>
<th>Disadvantages/Limitations</th>
</tr>
</thead>
<tbody>
<tr>
<td>AFM</td>
<td>Excellent topography of surface either <em>in-situ</em> or <em>ex-situ</em>\textsuperscript{16,58} Perturbations in deflection signal correlated to hardness / softness of material\textsuperscript{29}</td>
<td>Highly specialized cell designs required for <em>in-situ</em> approach\textsuperscript{16,58} Tip may interfere with original surface morphology\textsuperscript{16,58}</td>
</tr>
<tr>
<td>STM</td>
<td>Suited for <em>in-situ</em> studies\textsuperscript{16,58} Better resolution than AFM\textsuperscript{16,58}</td>
<td>Requires electrically conducting samples; thus insulating interfacial products in SEI pose problems\textsuperscript{16,58} When electrochemical systems are highly reactive, the need to apply a bias potential may shift the system from inert to reactive\textsuperscript{58}</td>
</tr>
<tr>
<td>SEM</td>
<td>Simplest tool for morphological studies of the interface\textsuperscript{58}</td>
<td>Static charging due to electrically insulating films limits resolution\textsuperscript{58} Sensitivity of organic samples can lead to structural damage and mass loss\textsuperscript{61}</td>
</tr>
<tr>
<td>TEM</td>
<td>Very small sample sizes can be probed\textsuperscript{59} Resolution on par with the lattice of crystalline samples\textsuperscript{59} Specimens can be thin films or nanoparticles\textsuperscript{59} Combine with EELS to achieve structural, morphological, and compositional information\textsuperscript{62}</td>
<td>High energy beam can induce specimen damage\textsuperscript{59,61} Requires UHV\textsuperscript{59} Complex sample preparation if initial materials are not already thin films or nanoparticles\textsuperscript{59}</td>
</tr>
</tbody>
</table>
Table 1.7. Bulk analytical methods for characterizing SEI.

<table>
<thead>
<tr>
<th>Technique</th>
<th>Advantages</th>
<th>Disadvantages/Limitations</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>XRD</strong></td>
<td>Possibility of <em>in-situ</em> analysis(^{16,58}) Unique diffraction patterns for specific materials(^{16,58})</td>
<td>Cannot identify amorphous materials(^{59}) Exceedingly thin layers of merely several unit cells may not be visible(^{59})</td>
</tr>
<tr>
<td><strong>XRF</strong></td>
<td>Qualitative and quantitative elemental analysis No need for vacuum equipment</td>
<td>Cannot provide information on the oxidation states of elements Depth profiling not an option Not suitable for elements with low Z</td>
</tr>
<tr>
<td><strong>NMR</strong></td>
<td><em>In-situ</em> or <em>ex-situ</em> technique(^{16,58}) Integration of spectral intensities for species allows quantitative monitoring of SEI growth(^{63}) Element specific, e.g. (^{19})F, (^{13})C, (^{7})Li, with ability to enrich isotopes(^{64}) Possible to extract physical or topological information from electron-nucleus dipolar interaction(^{65})</td>
<td>Large, expensive equipment Magnetic susceptibility effects, particularly for paramagnetic materials, can complicate spectral assignments(^{66}) Orientation effects can induce peak shifts(^{66})</td>
</tr>
<tr>
<td><strong>EPR/ESR</strong></td>
<td>Good as an <em>in-situ</em> technique(^{16,58}) Identify formation and stability of radical ions formed during electrolyte decomposition(^{16,58}) Low excitation energy, thus small possibility of disturbing system by activated reaction processes(^{67}) High sensitivity(^{67})</td>
<td>Inhomogenous line broadening of randomly oriented moieties can mask homogenous broadening, thus reducing resolution(^{68})</td>
</tr>
<tr>
<td><strong>Mössbauer</strong></td>
<td>Ideally suited for thin surface layers on bulk specimens(^{59})</td>
<td>Only applicable with ferromagnetic phases(^{58})</td>
</tr>
<tr>
<td>Technique</td>
<td>Advantages</td>
<td>Disadvantages/Limitations</td>
</tr>
<tr>
<td>-----------</td>
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</tr>
<tr>
<td>Ellipsometry</td>
<td>Nondestructive and can be performed <em>in-situ</em>(^{29})</td>
<td>Ideally suited for sharp interfaces</td>
</tr>
<tr>
<td>DSC</td>
<td>Convenient means of studying reaction rates and mechanisms(^{69})</td>
<td>Difficult to make quantitative predictions about the thermal stability and reaction kinetics of large cells(^{70}) Destructive technique(^{70})</td>
</tr>
<tr>
<td>ARC</td>
<td>Near adiabatic conditions are maintained(^{70}) Suited for studying large cells(^{70}) Can be used to obtain qualitative results of the thermal stability of an electrode material in electrolyte as a function of lithium content, electrolyte type, surface area, and the initial heating temperature(^{71})</td>
<td>Destructive technique(^{70})</td>
</tr>
<tr>
<td>DEMS</td>
<td>Study gas evolution during SEI formation(^{15})</td>
<td>Issues when multiple species have same mass/charge ratios</td>
</tr>
</tbody>
</table>
1.4. Electrolytes

Candidate electrolytes for lithium and lithium-ion batteries should have the following characteristics to enable good performance and ensure safety:

- Good ionic conductivity ($> 10^{-3} \text{ S} \cdot \text{cm}^{-1}$) to minimize iR drop[11]
- A transference number, t, (Eqn. (1.15) for the lithium ion approaching unity to limit concentration polarization[11]
- Wide electrochemical stability range to withstand reducing conditions at the negative electrode and oxidizing conditions at the positive electrode[11]
- Compatibility with cell components[11]
- Low toxicity[72]
- Low cost[72]

Also of importance for liquid electrolytes are good wettability of the electrode materials, low volatility, resistance to flammability, and strong solvating ability to dissolve salts to sufficient concentration.[73] The purity of the solvent(s) for the liquid electrolyte should also be considered as trace amounts of soluble gases or soluble impurities can impact the electrode / electrolyte interfaces.[74]

A practical lithium ion battery requires that the electrochemical potential of the negative electrode is lower than the lowest unoccupied molecular orbital (LUMO) of the electrolyte components. When lithium, carbonaceous materials, or most lithium-alloys are employed as negative electrodes, the electrolyte components are decomposed because the electrochemical potential of the negative electrode is greater than the LUMO. Stable SEI must be engineered by proper solvent selection or the addition of compounds that can passivate the surface in such a
way as to kinetically stabilize it (Section 1.4.6). Conversely, the electrochemical potential of the positive electrode must be higher than the highest occupied molecular orbital (HOMO) of the electrolyte components. Otherwise, the electrolyte constituents would become oxidized by the positive electrode. The difference in the LUMO / HOMO energies is the electrochemical window of the electrolyte.[72]

Electrolytes for Li-ion batteries may be divided into the following categories: nonaqueous liquids, gels, polymers, solids, and room temperature ionic liquids (RTIL). Nonaqueous liquids are typically polar aprotic solvents such as ethers, alkyl carbonates, and esters into which lithium salts are dissolved. The nonaqueous compounds possess a polar group in its structure such as a carbonyl (C=O), nitrile (C≡N), sulfonyl (S=O), or ether-linkage (-O-) necessary to dissociate lithium salts.[73] These liquid electrolytes are wicked into a porous membrane to maintain mechanical separation of the negative and positive electrodes. Gels are formed by trapping liquid electrolyte solutions into a solid polymer matrix such as polyacrylonitrile (PAN). The liquid electrolyte solutions are immobilized by a cross-linking, gelification, or casting procedure. Conductivities as high as $10^{-3}$ S·cm$^{-1}$ at room temperature and lithium transference numbers around 0.6 have been achieved.[11] A solid polymer electrolyte (SPE) can be formed by incorporating a lithium salt into a polymer matrix such as polyethylene oxide (PEO) and casting this composite into a thin film. The inherent ionic conductivity and lithium transference numbers are low, but the SPE is usually less reactive with lithium than nonaqueous solvents and gels, and it is non-volatile.[11, 75] The SPE combines the electrolyte with the separator.[75] Electrolytes have also been based on ceramic materials such as LiPON which is one of the few solid electrolytes to withstand cell potentials approaching 4 V.[11] In general, the benefits of high temperature stability, non-volatility, and excellent shelf life of solid electrolytes are
outweighed by low conductivity (often $< 10^{-5}$ S·cm$^{-1}$) and its impact on rate performance and inability to operate at low temperatures.[11] Lastly, RTILs have negligible vapor pressures and are nonflammable. RTILs based on an aliphatic quaternary ammonium cation coupled with bis(trifluoromethylsulfonyl)imide (TFSI) exhibit sufficiently wide electrochemical windows without the need for SEI additives.[76] However, RTILs are generally quite viscous and the transference number of lithium ions is low due to strong ion-ion interactions of the molten salt.[75]

Of these electrolytes, nonaqueous solvents based largely on blends of organic alkyl carbonates will be utilized. They are described in more detail below with emphasis on their limitations at extremes in temperature and at potentials exceeding 4.5 V.

### 1.4.1 State of the art Li-ion electrolyte

After nearly two decades of research, the major constituents of state of the art electrolytes for Li-ion cells are lithium hexafluorophosphate (LiPF$_6$), a cyclic carbonate, ethylene carbonate (EC), and one or more linear carbonates including dimethyl carbonate (DMC), diethyl carbonate (DEC), and ethyl methyl carbonate (EMC). Starting with the salt, LiPF$_6$ provides the best compromise in its properties when dissociated in organic carbonate blends. It is not as conductive as LiAsF$_6$; it has a lower mobility than LiBF$_4$; it does not dissociate as well as LiTFSI; it has a relatively low thermal stability compared with most lithium salts; it has a lower anodic stability than LiAsF$_6$ or LiSbF$_6$; and LiPF$_6$ is much more sensitive to moisture than LiClO$_4$ or LiTFSI. Importantly, LiPF$_6$ aids in forming a protective film on aluminum current collectors, and it helps stabilize the SEI on the negative electrode. No other lithium salt meets the multifaceted requirements simultaneously as LiPF$_6$ does. Thus, it continues to be indispensable for the manufacture of Li-ion cells.[73]
The nonaqueous liquid employed in state of the art electrolytes is a co-solvent blend of EC with DMC, EMC, and/or DEC, typically with the EC content between 30 and 50 vol%. EC has a high dielectric constant; thus, it has a high capacity for solvating lithium salts. It aids in SEI formation, and was found to be especially important in suppressing the co-intercalation of PC with lithium ions into graphite. It also has been demonstrated to decrease the interfacial resistance on various positive electrode materials. Despite these favorable attributes, EC has a high melting point (~36°C) which restricts its use as an electrolyte solvent. The low temperature conductivity is poor owing to the sharp decrease in mobility caused by high viscosity / partial solidification. EC is therefore blended with cosolvents of linear carbonates. DMC, EMC, and DEC all help to extend the low temperature range of the electrolyte by suppressing the freezing point. Despite their lower dielectric strength, and thus lower ability to solvate lithium salts, the linear carbonates enhance the conductivity of the EC:linear carbonate blend by increasing the fluidity of the electrolyte. The complementary features of the EC and the linear carbonates yield an electrolyte which embodies the attributes of both. Several percent of additives are normally included to aid in SEI formation and to suppress flammability. The concentration is such that the LiPF₆ EC:linear carbonate cosolvent system dominates the physicochemical properties of the electrolyte.[73]

### 1.4.2 Limitations at low temperatures

The high EC content in the state of the art electrolytes becomes problematic when the temperature is reduced below 0°C because the electrolyte solidifies leading to a sharp reduction in conductivity.[77] Thus, when exploring organic carbonates for low temperature applications, the approach of decreasing the EC content and utilizing linear esters as the major solvent components was taken to lower the freezing point as well as the viscosity of the electrolyte.[78] Examples of linear esters include the aforementioned linear organic carbonates, ethyl acetate
(EA), methyl butyrate (MB), and ethyl butyrate (EB).[78] This approach improved the low temperature conductivity of LiPF$_6$ electrolytes. However, it was still crucial for the electrolyte to provide favorable chemistries for the formation of stable electrode / electrolyte interphases with reasonably facile charge transfer kinetics. The EC content was reduced but not eliminated because it was necessary for the formation of a stable SEI. Since the melting point of EC is so great (36.4°C), even a modest fraction greatly increases the liquidus of the electrolyte solvent.[79]

The charge transfer process becomes a very important parameter in determining the output potential and limiting the current output at temperatures ≤ -20°C. Through the electrochemical impedance technique, Jow et al.[80] demonstrated the de-solvation of solvated lithium ions is one of the major steps of the charge transfer process that limits the low temperature performance. The addition of ester solvents such as GBL and MB decreased the activation energy for charge transfer. The choice of electrolyte salt also impacted the low temperature performance. The charge transfer process measured with LiBF$_4$ dissolved into the same cosolvent system was found to be lower than LiPF$_6$. It may be counterintuitive to consider using an electrolyte with a lower bulk conductivity. Despite this less favorable characteristic, the LiBF$_4$ provided better low temperature performance than LiPF$_6$.[80] The charge transfer resistance of LiTFSI was also lower relative to LiPF$_6$.[77] Although the low temperature performance was improved relative to the state of the art electrolyte, the ternary[77, 78, 81] or quaternary[82] blends containing EC refrained from moving toward an entirely linear solvent system or one that utilized alternative solvents such as nitriles or ethers.
1.4.3 Limitations at elevated temperatures

The state of the art electrolyte is limited to an upper temperature of 50°C due to the accelerated hydrolysis of LiPF$_6$ with trace amounts of water and the reactivity of these products with the electrolyte solvents. If temperatures exceed 70°C, the performance is irreversibly deteriorated, and a hazardous condition becomes possible due to gas evolution and pressure build-up within the cell.[73] Changing the electrolyte salt to LiTFSI or LiBF$_4$ affords better thermal stability and more resistance to hydrolysis than LiPF$_6$.[73, 77] However, the electrolyte is still based largely on a liquid in which the vapor pressure of the cosolvent is dominated by the lower boiling component, i.e., the DMC, EMC, and/or DEC. Even if one were to consider an organic carbonate electrolyte without LiPF$_6$ that did not have too great a vapor pressure, the thermal stability of the passivation films on both the negative and positive electrodes would still keep the high temperature limit below 90°C without tailoring specific SEI chemistries.[73]

Replacement of organic carbonates with halogenated organic carbonates led to widening the liquid range of the electrolyte and increasing its flashpoint. Interestingly, the halogenated organic carbonates led to lower ionic conductivities but improved interfacial properties. The replacement of EC with GBL, particularly when also using LiBF$_4$, led to much improved thermal stability and cycling performance after storage at 85°C.[73]

Alkyl sulfones comprise a completely different class of solvents of interest for high temperature applications. Tetramethylene sulfone, aka sulfolane, is characterized by a high boiling point (280°C), high flash point (177°C), and low vapor pressure.[83] However, sulfolane is limited as a solvent at or below room temperature due to its high melting point (~28°C).[83] Addition of aliphatic groups and oligo(ethyleneglycol) segments to sulfones aids by decreasing the melting
point, but at the expense of stability at high potentials.[84] In general, the sulfones are severely limited by their high melting points and lack of ability to form effective SEI layers.[73]

Other classes of solvents that may enable better performance and safety at elevated temperatures are alkoxypropionitriles and dinitriles. An example of each is 3-methoxypropionitrile (3MPN) and adiponitrile (ADN). 3MPN has a low melting point (-57°C) and high boiling point (165°C), making it appealing for low temperature applications or cells experiencing wide temperature fluctuations.[85] ADN, representative of the other dinitrile solvents, has a high flashpoint (163°C) and high boiling point (295°C).[86, 87, 88, 89] As with the sulfones, these nitrile solvents are thermodynamically unstable on the negative electrode and do not seem to form a stabilizing SEI. However, these nitriles are liquids at room temperature.

1.4.4 Limitations at high potentials

The organic carbonate solvents are restricted to cells operating below 5 V, not including some of the transition metal layered oxides on which oxidation reactions occur ~4 V vs. Li/Li⁺.[16, 19] The organic carbonate solvents are not suitable for high voltage positive electrodes exceeding 5 V; thus, the development of high energy density batteries requires new electrolytes composed of solvents with very high HOMO levels. Two very interesting classes of solvents which exhibit high electrochemical stability are sulfones and dinitriles.

The sulfones were found to be stable up to between 5.5 V and 5.8 V vs. Li/Li⁺.[83, 84, 90] However, they are greatly limited by their high melting points and instability at the negative electrode.[73] By fluorinating the alkyl groups of the sulfone and blending with a linear carbonate cosolvent, an electrolyte was engineered possessing the high oxidation potential of
the sulfone, the ability to form an SEI layer on the negative electrode, and the fluidity at room
temperature to promote good ionic conductivity.[90]

The dinitriles are among the aprotic nonaqueous solvents with the highest reported anodic
stability limits.[86] Ue, Ida, and Mori[86] reported the anodic stability of glutaronitrile (GLN)
and ADN to 5.0 V and 5.2 V vs. a saturated calomel electrode, or roughly 8.3 V and 8.5 V vs.
Li/Li⁺. High oxidation limits were confirmed for LiTFSI electrolytes on a platinum working
electrode in GLN[91] and ADN[87]. Good conductivity on the order of $10^{-3}$ to $10^{-2}$ S·cm⁻¹ was
observed from 0°C to 80°C.[87] ADN, when paired with organic carbonate cosolvents, has been
used to evaluate the electrochemical performance and voltage profiles of fluorophosphates
positive electrodes exceeding 5 V.[92] Unlike sulfones, they are liquids at room temperature
and would thus tend to be better suited for electrochemical cells requiring both high and low
temperature operation. Both sulfones and nitriles, while exhibiting intriguing electrochemical
properties, have not been widely examined in the published literature for lithium ion battery
development.

1.5. Summary and Enumeration of Chapters

The demand for energy storage with greater energy and power densities has led to the
development of conversion materials as alternatives to intercalation materials. Many of the
conversion materials would be restricted to the negative electrode owing to their low potentials
vs. Li/Li⁺; however, the metal fluorides are uniquely suited for the positive electrode in an
electrochemical cell. Metal fluorides have been enabled by synthesizing nanocomposites. Due
to the nano-sized features of the metal fluorides, particularly in the lithiated state during which
domains of metal and lithium fluoride are formed, it is expected that any interactions occurring
with the electrolyte would potentially have a great impact on the ability of the metal fluoride
nanocomposite, and therefore the electrochemical cell, to cycle. Thus, the overarching theme of the research undertaken was to investigate the interfacial chemistry and determine if electrolyte decomposition products were formed. If, in fact, electrolyte decomposition occurred, the development of a SEI would be desirable, but this would be challenging to stabilize due to large volumetric changes during cycling of a conversion material and the rearrangement of bonds. Would an SEI or organic decomposition layer on a metal fluoride exhibit similar properties as witnessed on metal oxides and sulfides (Section 1.4.8), or would the reconversion sweep to much higher potentials induce other reactions with metal fluorides? If such reactions occurred, how can experiments be designed to show the impact of the interaction(s)? Would such interactions be beneficial or deleterious? Would interactions with metal fluoride nanocomposites be mitigated or eliminated by the proper selection of electrolyte or electrolyte additive?

Chapter 2 extends the Introduction to provide background information on the experimental apparatuses used most extensively throughout this thesis. Some examples of the instrumentation have been included.

Chapter 3 examines the cycling behavior of bismuth fluoride nanocomposites in state of the art electrolytes based on LiPF$_6$ and organic carbonate solvents. Emphasis is placed on the unexpected formation of decomposition products at potentials \( \geq 2 \text{ V vs. Li/Li}^+ \) on bismuth.

Chapter 4 expands upon the work of Chapter 3. In Chapter 3, electrolyte decomposition has been thoroughly correlated with degraded cycling performance of the BiF$_3$ nanocomposite positive electrodes. Chapter 4 details the evolution of the electrolyte decomposition products.
during the reconversion (delithiation) of the nanocomposite and its influence on the bismuth chemistry. A mechanistic link for the poor cycling is presented.

Chapter 5 explores alternative electrolyte formulations that deviate from state of the art electrolytes based on $1 \text{ M LiPF}_6 \text{ EC} + \text{ linear organic carbonate solvents}$. The cycling behavior of a well-established $4 \text{ V Li-ion configuration}$ is investigated in new electrolyte blends based on EMC, ADN, and 3MPN. Also, the chemical species formed as a result of the electrochemical reduction of monofluoroethylene carbonate (FEC), an SEI additive, are analyzed for the first time without EC and fluorinated electrolyte salts present in the electrolyte.

Chapter 6 builds off the electrolyte work of Chapter 5. Galvanostatic trials of the bismuth fluoride nanocomposites in the newly identified electrolytes were carried out to improve the long-term cycling performance. Using an unconventional electrochemical cell, good capacity retention of the bismuth fluoride nanocomposite has been achieved, thus proving the compatibility of the newly formulated nitrile electrolytes with the bismuth fluoride nanocomposite. Still, in a functional cell, the instability of the electrolytes on the negative electrode necessitates SEI additives which are also included as a preliminary study.

Chapter 7 concerns future work related to understanding the failure mechanisms of the bismuth fluoride nanocomposites. Ideas are presented that may extend to other metal fluoride conversion materials and possibly be pertinent to other disciplines.

Lastly, Chapter 8 concludes this thesis, Chapter 10 lists all references cited in this work, and Chapter 10 contains the author’s curriculum vitae.
2. Experimental techniques

A variety of analytical techniques have been used to characterize the phases of the bismuth fluoride nanocomposites, the interfacial chemistries of the electrode materials, and the electrochemical properties of the nanocomposites. The most significant used over the course of study have been X-Ray Diffraction (XRD), Attenuated Total Reflectance – Fourier Transform Infrared Spectroscopy (ATR-FTIR), X-ray Photoelectron Spectroscopy (XPS), controlled potential electrochemical techniques, galvanostatic cycling, and electrochemical impedance spectroscopy. Key elements of each have been provided below.

2.1. X-Ray Diffraction (XRD)

XRD of powders provides a means of identifying crystalline phases, weight fractions of phases in mixtures, orientation of materials, and crystallographic information such as lattice parameters, strain, and approximations for grain size. The underlying principle of XRD is satisfying the Bragg condition for diffraction which describes the diffraction maxima. The governing equation is

\[ 2d \sin \theta = n\lambda \]  \hspace{1cm} (2.1), [Ref 59]

in which \( d \) is the interplanar spacing, \( \theta \) is the angle of incidence with respect to the normal, \( n \) is an integer defining the order of diffraction (usu. \( n = 1 \)), and \( \lambda \) is the wavelength of the characteristic x-ray. The wavelength, \( \lambda \), is fixed, and the angle, \( \theta \), is controlled; thus \( d \) is determined from the relationship of Eqn. (2.1). X-rays are well suited because their wavelengths are of the same order of the interplanar distances of rows of atoms in crystalline materials, and incident x-ray beams can penetrate many micrometers into the bulk of the sample. By inspecting the diffraction pattern, it is possible to identify the structure and composition of materials.[59]
The observed intensity of diffracted beams is dictated by the polarization factor which quantifies the amount of incident radiation polarized as a function of incidence angle; the Lorentz factor which corrects for orientations of reflections and is especially important in single-crystal studies; the temperature factor which accounts for anisotropies brought about by vibrations of atoms about their equilibrium positions on the space lattice; the atomic scattering factor which may be defined as the ratio of the amplitude scattered by an atom at rest to that scattered by a single electron; the structure factor which corresponds to the atomic arrangement; the multiplicity factor which accounts for degeneracy of the lattice spacing in symmetrical crystals; and the absorption factor which corrects for the interaction of x-rays with different amounts of the bulk specimen.[93] The structure factor is really what enables the identification of the unit cell of a crystalline species. The contribution of the structure factor, \( F \), to the intensity of the diffracted beam is given as

\[
|F_{hkl}| = \sum_{n} f_n e^{2\pi i (hu_n + kv_n + lw_n)}
\]

in which \( f \) is the atomic scattering factor, \( h, k, \) and \( l \) are the Miller indices for the reflection, \( u, v, \) and \( w \) are the coordinates of the atom in the unit cell, and \( n \) is a counter for each atom at each position of the unit cell. Intensity is proportional to \( |F_{hkl}|^2 \).[59]

In a typical x-ray diffractometer (Figure 2.1), the incident wavelength is one of the characteristic wavelengths of a metal target. The metal target is bombarded with a high voltage (30-40 kV), low current (30-50 mA) beam of electrons which ejects electrons from the core orbitals of the target element. Electrons from the outer orbitals fill the vacant core levels, resulting in characteristic x-rays and a broad spectrum of x-rays (i.e. Bremsstrahlung). The x-ray beam is not truly monochromatized but it is highly discriminated to a narrow energy width through the use
of a single-filter technique in which the filter is an element whose absorption edge is just to the short-wavelength side of the characteristic wavelength of the target material. For example, a Cu target from which a CuK\textsubscript{\alpha} wavelength is produced is paired with a Ni foil filter. For K\textsubscript{\alpha} x-rays, the filter is almost always the element with an atomic number one less than the target.[93]

The x-ray source and detector, typically a solid-state energy dispersive device with high intensity gain compared to a scintillation device, are mounted on a goniometer such that the sample is as close as possible to the ideal position on the focusing circle (Figure 2.1(b)). Various modes exist in which the specimen is fixed or it is rotated, but the relative angular position of the detector with respect to the source is 2\Theta. The intensity of the diffracted signal is recorded as a function of 2\Theta, making a diffraction pattern. Digital databases enable rapid identification of many phases.[59, 93]
Figure 2.1. X-ray diffractometer used for the majority of XRD experiments. (a) Bruker D8 Advance with doors open. (b) Theta-theta goniometer. Both the source and the detector move in unison and the sample stage remains fixed.
2.2. Fourier Transform Infrared spectroscopy (FTIR)

Infrared radiation (IR) is a portion of the electromagnetic spectrum of great practical use in organic chemistry as many compounds exhibit molecular vibrational frequencies on the same order as IR. When considering a spectrum for a specific compound, a peak-by-peak correlation can identify a sample. In instances in which the exact species cannot be determined, characteristic group frequencies can be used to identify useful structural information of unknowns.\[94\]

Molecular vibrations exist as either symmetrical or asymmetrical. Symmetrical vibrations are Raman active but not IR active. Only those vibrations which yield a change in the dipole moment of the molecule are IR active. The alternating electric field produced by changing the distribution of charge accompanying the vibration is coupled with the oscillating electric field of the incident IR radiation. Vibrational modes are classified as stretching or bending depending on how the atoms move with respect to the center of gravity of the molecule or functional group. More specifically, stretching is either symmetrical or asymmetrical, and bending may be referred to as scissoring, wagging, twisting, or rocking.\[94\]

The frequency of absorption depends on the masses of the atoms of a group of atoms, the force constants of the chemical bonds, and the geometry of the atoms. A simplified treatment for stretching frequencies can be approximated by Hooke’s Law. The vibrational frequency, $\tilde{\nu}$, for a simple harmonic oscillator reported in wavenumbers [cm\(^{-1}\)], can be stated as

$$\tilde{\nu} = \frac{1}{2\pi c} \sqrt{\frac{f (M_x + M_y)}{M_x M_y}}$$

(2.3) [Ref 94]
in which \( c \) is the velocity of light (\( \text{cm} \cdot \text{s}^{-1} \)), \( f \) is the force constant of the bond, and \( M_x \) and \( M_y \) are the masses of atoms \( x \) and \( y \), respectively. Wavenumbers are reciprocally related to wavelength. Simply divide \( 10^4 \) by the wavelength [\( \mu \text{m} \)] to convert to wavenumbers [\( \text{cm}^{-1} \)]. A stronger force constant brought about by a higher degree of bonding (i.e. double or triple) or an atom with a greater atomic mass will increase the vibrational frequencies of species. Coupling of oscillators also gives rise to shifts in the observed \( \tilde{\nu} \) compared with a simple two-atom case.[94]

FTIR works by having optics split radiation such that one beam is of fixed length and the other beam is of variable length due to movement of a mirror. The varying distances of the two pathlengths result in constructive and destructive interferences and varying intensities. This interferogram is then converted from the time domain into the frequency domain via Fourier transformation (FT). A series of interferograms is made over the range of motion of the movable mirror, and the FT of each successive point gives rise to the IR spectrum.[94]

FTIR is advantageous because it is a rapid technique with high resolution. Multiple scans can be weighted or averaged to remove absorption artifacts. Depending on the phase of the sample to be analyzed, FTIR offers a range of techniques that work by transmission or reflectance of the radiation interacting with the sample. The Attenuated Total Reflectance-FTIR (ATR-FTIR) technique is well-suited for studies involving SEI on thin films (Figure 2.2). Unlike a transmission mode in which a solid is blended as a dilute material in a mull until its particle size is < 2 \( \mu \text{m} \), ATR-FTIR allows for the analysis of solids with little to no additional sample preparation.[94] ATR-FTIR is enabled by the interaction of an evanescent wave that couples with the sample when pressed firmly against a crystal of high refractive index such as zinc selenide, diamond, or
germanium. Multiple bounce variants provide better signal intensity. ATR-FTIR can shift the observed vibrational frequencies relative to those obtained through transmission techniques. Also, the relative intensities of the transmission and ATR techniques differ for the same compounds. Thus, corrections involving the refractive index and extinction coefficient as a function of wavelength for the sample are often necessary to compare and correct spectra obtained with the ATR technique.

Figure 2.2. FTIR instrument. (a) Image of instrument with single-bounce ATR stage mounted. Dashed arrows approximate the optical path of the IR radiation. (b) Front view of ATR stage showing anvil which is used to press solid samples firmly against the ATR crystal (diamond). (c) Plan view of ATR stage. In (b) and (c), anvil is drawn to the side.
2.3. X-ray Photoelectron Spectroscopy (XPS)

XPS, also known as Electron Spectroscopy for Chemical Analysis (ESCA), utilizes x-rays of high energy (usu. AlKα = 1486.6 eV, MgKα = 1253.6 eV) to eject core level electrons as photoelectrons.[20] The incident x-ray beam is collimated to a spot size between 20 and 400 μm to maintain high spatial resolution. The photoelectrons ejected from the sample are captured by an analyzer and sent to a detector. Analyzers operate in two modes, either Fixed Analyzer Transmission (FAT) or Fixed Retard Ratio (FRR). In FAT, the potentials, and hence pass energy, of the analyzer hemispheres remain constant, and the resolution is therefore constant over the entire spectrum (for a single photon source). In FRR, the analyzer potentials are varied and the electrons are retarded by a fixed amount. The resolution is dependent on the electron energy in FRR. Both modes serve to tune a specific range of photoelectrons permitted to reach the detector. For the majority of experiments, FAT is used to collect spectra to identify stoichiometric ratios of the surface species, while FRR is used when Auger electrons are monitored in conjunction with XPS. During sample analysis, the entire chamber must be kept under ultra high vacuum to prevent contamination of the surface of the specimen.[59]

The best attribute of XPS is its ability to nondestructively provide information of the surface chemistry of a sample. The photoelectrons are emitted from the outermost 10 nm of the sample surface and have energies which are not only elementally specific but also shifted by several eV to provide chemical information. When performing XPS, the binding energies, $E_B$, are reported as

$$E_B = h\nu - E_K - \varphi$$

(2.4),[Ref 59]

in which $h\nu$ is the energy of the incident x-rays, $E_K$ is the measured kinetic energy of the photoelectron, and $\varphi$ is the work function of the spectrometer. Additionally, Auger electrons
are often emitted from the surface which can be used to aid in identification of surface entities. When the incident x-ray beam is monochromatic and the energy resolution is good, fine structure peaks (e.g., multiplet splitting) are also observed.[59]

One of the issues with XPS, particularly during examination of insulating samples, is establishing an internal reference to shift the spectra. Several methods are used, and it is imperative that the exact techniques are reported such that researchers with different spectrometers can cross-reference data collected by others. Otherwise, large internal databases of compounds must be collected by each individual laboratory. With monochromatic incident x-rays and modern detectors capable of energy resolution < 0.3 eV, improper calibration or shifts due to surface charging can cause incorrect identification of surface phases. Minimization of surface charging is often done by flood gun emission of 0-5 eV electrons to compensate for residual positive charge of the surface when photoelectrons are ejected. In older spectrometers lacking this feature, a very thin layer of gold may be deposited. Spectra may then be shifted by choosing a value between 284 and 285 eV for adventitious carbon attributed to C-C and/or C-H bonds from hydrocarbon contaminants. Complications arise due to the observed adventitious carbon peak varying strongly as a function of substrate material. When using gold, it may be used as both the conductive aid and internal reference.[95]

Once a consistent value for the internal calibration has been selected, peak fitting of the core levels specific to each element is performed. The background is often a Shirley or Tougard type, and the peaks are often fit with a blend of Gaussian and Lorentzian profiles.[59] XPS is a semi-quantitative technique with an error range of approximately ±10%.[20] Several methods are used for quantifying the distribution of elements of surface species and are based on peak area
ratios and relative sensitivity factors.\[59, 95, 96\] A prevalent method and database of sensitivity factors is by Scofield.

Other features of the spectrometer include specialized compartments for heat treating samples and exposing to different atmospheres, variable angle sample stages, and ion beams for depth profiling. A variable angle stage is useful in determining the thickness of thin films and aiding in determining the material removal rate during etching. If the incidence angle is well below the critical angle for reflection, the penetration depth of the radiation is drastically reduced. This technique, termed grazing-incidence XPS, enhances the signal of the outermost surface while reducing the inelastic background underneath the recorded spectra. With this method, the determination of surface atomic positions, resolution of valence densities of states into element-specific components, and the determination of nanometer scale structures are possible.\[97\] Use of ion etching enables depth profiling, but at the expense of destroying a localized portion of the sample. Ion etching does not always ablate materials from the surface uniformly, and it may alter the chemical state of surface species.
Figure 2.3. Examples of XPS instrumentation at the Laboratory for Surface Modification at Rutgers. (a) Thermo ESCALAB 250Xi. (b) Thermo K-Alpha. The ESCALAB instrument has been shown to illustrate some of the components common to XPS analyzers. The K-Alpha was used for the majority of XPS experiments.
2.4. Electrochemical methods

Controlled potential techniques are useful for determining the electrochemical windows of electrolytes, examining the decomposition of electrolytes and additives during SEI formation, and assessing surface areas of electrodes with high roughness / porosity. The most widely used methods for applied electrochemistry of Li-ion cells involve derivatives of potentiodynamic techniques. Common to these techniques is the measurement of current in response to linear or many small, successive, step-wise adjustments of the potential. The rate of change of the potential (i.e. sweep rate) influences the current response in several ways. The pseudo-capacity of adsorbed intermediates and double-layer charging are reflected in a potentiodynamic technique by a linear proportionality with sweep rate. When mass transfer becomes limiting, the variation of the current increases with the square root of the sweep rate. One must be aware of the impact of the sweep rate on an experiment. A rapid sweep rate will cause a high degree of double-layer charging relative to the Faradaic current, resulting in a poor signal to noise ratio and distortion of the current response due to uncompensated iRelyte errors. An exceedingly low sweep rate may be necessary for kinetically slow reactions, but it may also be unnecessarily slow resulting in experimental inefficiency.[12, 14] Examples of equipment used to run controlled-potential experiments are shown in Figure 2.4 and Figure 2.5.

![Figure 2.4. MacPile (BioLogic) electrochemical testing unit capable of two techniques. Ch. 1-8: galvanostatic for controlled current experiments, typically for cell cycling trials. Ch. 9-16: potentiodynamic for controlled potential scans.](image)
Figure 2.5. Solartron Models SI 1287 and SI 1260. By itself, the SI 1287 is capable of an assortment of controlled potential and current techniques. When paired with the SI 1260, electrochemical impedance spectroscopy trials can be run. The units are controlled by a PC via GPIB running CorrWare and ZPlot (Scriber Associates).
Figure 2.6. Arbin BT2043 battery test system (with another MacPile unit mounted above). (a) External cabinet of instrument. (b) Test electrodes mounted within incubator typically set at 24°C.
Galvanostatic trials of electrochemical cells are helpful in assessing the cycling performance and quantifying parameters such as the capacity and cycling efficiency. A constant current is applied to an electrochemical cell between prescribed potentials. The current is controlled and the potential response is measured. The capacity is directly proportional to the applied current multiplied by the duration of the galvanostatic sweep. Examples of equipment used to run galvanostatic cycling trials are shown in Figure 2.4 and Figure 2.6(a). A better test for reliability and performance studies would involve running the electrochemical cell under conditions of controlled power as this would more closely mimic the discharge and charge conditions in an actual device.

Electrochemical Impedance Spectroscopy (EIS) is based largely on methods used to analyze electrical circuits. The total measured impedance, $Z$, of a cell is expressed as an equivalent circuit with resistors, capacitors, and constant phase elements organized in series and parallel arrangements. Each circuit element or sub-circuit corresponds to a portion of the electrochemical cell. Most often, the average potential of the cell is fixed at an equilibrium value and the potential is modulated by applying an alternating sinusoidal waveform of low amplitude so as not to perturb the system far from equilibrium. The frequency of the waveform is swept from high to low values.[12] The impedance spectrum is reported as a Nyquist or Cole-Cole plot (imaginary impedance ($Z_{im}$) vs. resistance ($Z_{re}$) or as a Bode phase plot (phase vs. frequency). For Li-ion data, the Nyquist or Cole-Cole complex impedance plot is predominant.

In a complex impedance plane plot, as the frequency approaches low values, the slope of the line drawn through the points of $Z_{im}$ vs. $Z_{re}$ approaches unity. This is characteristic of a diffusion-controlled electrode process. As the frequency is increased, $Z_{im}$ vs. $Z_{re}$ typically resembles a
semi-circle or an arc under which multiple semicircles can be drawn. The charge-transfer resistance becomes important at these frequencies. At very high frequencies, the resistance of the solution is apparent as the point at which the impedance data intersect the real axis.[12]

EIS affords insights into the rate-limiting areas of electrochemical cells. When a third, reference electrode is incorporated into the cell, the impedance contributions of the positive and negative electrodes can be separated. This type of measurement is especially important for layered intercalation compounds which can exhibit high charge transfer resistances toward the fully charged state (~4 V vs. Li/Li'). EIS for electrochemical cells is especially useful as a non-destructive, in-situ technique for monitoring the interfacial resistance as a function of potential to establish SEI formation and for monitoring the evolution of interfaces with time during storage trials.[16]
3. Formation, dynamics, and implication of solid electrolyte interphase in high voltage reversible conversion fluoride nanocomposites

3.1. Introduction

The transition of the reversible conversion process from chalcogenides [42] to fluorides [2, 3, 4, 5, 6, 98] represents an opportunity to develop a new pathway to very high energy density positive electrode materials for future lithium and non-lithium batteries. Although progress on a number of materials has been demonstrated, significant challenges develop for the metal fluoride nanocomposites that are foreign in mechanism to the intercalation compounds (e.g. LiCoO₂) which are ubiquitous today. Important aspects of these differences relate to the catalytic behavior of the extremely small cluster size (1–5 nm) of metals formed after reduction of the metal fluoride and also to the dynamic nature of the crystal structure (Figure 1.1). Indeed, as opposed to the stable framework of the intercalation materials during cycling, reversible conversion materials show a constant change in the crystal structures, and a number of nanophases may be present in the lithiated vs. delithiated states. Both of these aspects are especially important when it comes to the impact of electrolyte decomposition products formed on the surface of materials because the “substrate” for these reactions is in a continually dynamic state. To date there has been no discussion of solid-electrolyte interphase (SEI) relative to high voltage conversion materials although significant pieces of work exist for the low voltage chalcogenide conversion compounds with very unique polymerization reactions found to form at low potentials.[44, 50]

The catalysis for the work described in this chapter came as a result of previous work with BiF₃ nanocomposites.[4] BiF₃ nanocomposites are of interest for their very high theoretical energy density. Although the specific energy density is not especially high, BiF₃ has an exceptional
theoretical volumetric energy density of 7960 vs. 3000 Wh·L⁻¹ for today’s state of the art cathode material. Such a value exceeds that of 6090 Wh·L⁻¹ for CFₓ, the premier primary electrode for energy density. In our studies of BiF₃ nanocomposites, we have seen a very direct relationship between electrolyte solvent / salt and cycle life. The solvent aspect was especially surprising to us as the BiF₃ nanocomposites cycled better in linear carbonates vs. cyclic carbonates. This chapter explores the possibility of a relatively high voltage SEI catalyzed by the nanometal clusters, but more importantly the thrust is to show a direct link between such SEI and subsequent cycle life. In the end, the improved performance of the BiF₃ system is shown in both its prelithiated and nonprelithiated state.

3.2. Experimental

3.2.1 Materials synthesis

Raw bismuth fluoride (Alfa) was found to contain a significant amount of oxyfluoride phases; thus, a hydrofluoric acid purification procedure was developed to yield nearly 100% orthorhombic BiF₃. The bismuth fluoride nanocomposites were produced by blending 0.88 g of purified BiF₃, 0.10 g of MoS₂ (Alfa), and 0.02 g of carbon nanotubes (Advance NanoPower) in a hardened steel milling cell (Spex). The milling cell was sealed in the glovebox with helium atmosphere and then transferred outside to an 8000 series high energy mixer (Spex) for 30 min. After milling, the material was annealed for 2 h at 200°C in a hermetically sealed copper vessel. The final cathode blend was hand mixed in a mortar and pestle to have 15 wt% SP carbon (Timcal). The purified BiF₃ was always isolated from standard atmosphere in order to prevent hydrolysis, which was witnessed as splitting of diffraction peaks. Although powder blends were used exclusively for the bismuth fluoride cathodes in this study, it is worth mentioning that purified BiF₃ in contact with acetone, diethyl ether, dibutyl phthalate, and propylene carbonate (solvents commonly encountered when manufacturing electrode tapes) remained
orthorhombic, as well as material stored in a dry room (ambient temperature was 23°C with a
dew point no greater than -30°C). Bismuth metal nanocomposites were made in the same
manner except the initial charge into the milling cell was 0.67 g of 99.99% Bi powder (Aldrich),
0.275 g MoS₂, and 0.055 g carbon nanotubes. Bismuth oxide nanocomposites were made with
the same mass fractions as the bismuth fluoride nanocomposites with 99.99% Bi₂O₃ (Aldrich).
Some additional trials were performed with bismuth(III) acetate (Aldrich), bismuth(III) citrate
(Aldrich), and bismuth(III) carbonate-basic (Riedel-de Haen), and these macroblends were hand
mixed in a mortar and pestle at 85 : 15 wt ratio of bismuth compound : SP. All cathode
preparation was performed under helium in a glovebox.

Bismuth metal film was prepared in-house by thermal vacuum evaporation of 320 nm bismuth
(99.999% Bi pellets, Lesker) onto 99.999% aluminium foil (Aldrich) with a 30 nm titanium
interlayer (99.99% Ti granules, Alfa). After deposition, 12.7 mm discs were punched from the
foil in an argon filled glovebox (< 0.1 ppm H₂O, < 1 ppm O₂, MBraun), sealed in a dried glass vial,
and transferred to a helium purged glovebox (< 0.6 ppm H₂O, <0.1 ppm O₂, MBraun) until coin
cell fabrication and characterization trials.

All electrolyte materials were purchased from Ferro, stored in gloveboxes, and used without
additional treatment. 1 M lithium hexafluorophosphate (LiPF₆) solutions with dimethyl
carbonate (DMC), ethyl methyl carbonate (EMC), and propylene carbonate (PC) were blended.
1 M LiPF₆ ethylene carbonate : dimethyl carbonate (EC : DMC) 1:1 v/v, 1 M lithium
hexafluoroarsenate (LiAsF₆) EC:DMC 1:1 v/v, and 1 M lithium perchlorate (LiClO₄) EC:DMC 1:1
v/v were formulated by Ferro. The majority of experiments were conducted with 1 M LiPF₆
EC:DMC and 1 M LiPF₆ EMC electrolytes.
3.2.2 Electrochemical characterization

All batteries fabricated for studies in this chapter were aluminized 2032 coin cells made with cathodes consisting of either 3–5 mg of powder or a 12.7 mm disc of bismuth film, a Celgard porous membrane adjacent to the cathode, two layers of borosilicate glass fiber separator (Whatman) soaked with electrolyte, and a lithium foil anode (FMC). Galvanostatic cycling tests were performed on both a Maccor Series 4000 (Maccor) and MacPile II (BioLogic). Galvanostatic intermittent titration technique (GITT), potentiodynamic, and potentiostatic trials were performed on a MacPile II. Galvanostatic cells were cycled at 15 mAg\textsuperscript{-1} nanocomposite, GITT cells were reduced at 3 mAg\textsuperscript{-1} BiF\textsubscript{3} for 1 h and relaxed for 5 h, potentiodynamic cells were discharged or cycled at 20 mVs\textsuperscript{-1}, and potentiostatic cells, specifically with Bi films, were held at 1.50 V vs. Li/Li\textsuperscript{+} for 24 h. Unless otherwise specified, all electrochemical tests took place at 24°C. All potential values are referenced to lithium metal in contact with 1 M Li salt electrolyte; the lithium foil served as both anode and quasi-reference electrode.

3.2.3 Physical characterization

Prior to physical characterization, coin cells were opened in a helium purged glovebox. Except for some of the Attenuated Total Reflectance-Fourier Transform InfraRed (ATR-FTIR) trials, all Bi films were rinsed with DMC or EMC solvent to remove residual 1 M LiPF\textsubscript{6} EC:DMC and 1 M LiPF\textsubscript{6} EMC electrolytes, respectively. The films were stored in vials in heat-sealed plastic bags until characterization.

Bi films were analyzed with Field Emission Scanning Electron Microscopy (FESEM) (Zeiss), and Energy Dispersive X-ray Spectrometry (EDS) was performed with an INCAPenta FETx3 (Oxford). The films were exposed for approximately 2 min to room air when mounted in the FESEM.
ATR-FTIR of Bi films was conducted in both the MidIR and FarIR with a Smart Orbit accessory with Typella diamond crystal in a Nicolet 6700 FTIR Spectrometer (Thermo). The ATR stage was introduced into the glovebox, and each sample was mounted individually under adhesive-backed lead tape to isolate the samples from the lab atmosphere.

Raman spectroscopy was executed in a NXR FT-Raman Module (Thermo) with incident laser wavelength of 1064 nm and liquid nitrogen cooled Ge detector adjacent to the FTIR Spectrometer. Bi film samples were mounted in a custom enclosure in the glovebox to maintain an inert atmosphere.

X-Ray Photoelectron Spectroscopy (XPS) was performed in a XSAM 800 Surface Analysis System (Kratos) using a MgKα X-ray source. Samples were introduced into the UHV system via an argon purged glove bag to minimize oxidation and/or hydration effects. Due to the insulating nature of some parts of the sample, a carbon contamination peak has been chosen as a reference for the binding energy of the charging species. After a linear background subtraction, the XPS core levels were fitted using Voigt functions.

Transmission Electron Microscopy (TEM) was attempted, but we were experimentally limited by the intensity of the incident electron beam which resulted in the immediate modification of the “SEI” film. This is a common challenge and can lead to misinterpretation of the true film morphology.
3.3. Results

3.3.1 Electrochemical characterization

A typical example of the reproducible differences observed in cycling BiF$_3$ nanocomposites in cyclic or acyclic carbonate solvents is shown in Figure 3.1(a) for BiF$_3$ nanocomposites cycled in 1 M LiPF$_6$ EC:DMC vs. 1 M LiPF$_6$ EMC. Both cells were cycled between 4.50 V and 2.00 V vs. Li/Li$^+$. By the tenth cycle, the cell cycled in EC:DMC based electrolyte has already faded roughly 20% whereas the EMC based electrolyte displayed minimal capacity loss. The only difference in the fabrication of the cells in Figure 3.1(a) is that one cell used an electrolyte with a cyclic carbonate component (the EC in EC:DMC) and the other cell used a linear carbonate solvent exclusively (EMC). Similar cycling results were observed for DMC, a linear carbonate, and PC, a cyclic carbonate (Figure 3.1(b)). Investigation of the voltage profiles of these cells did not afford an explanation as to how the cycling was affected. In order to rule out interactions on the Li metal anode, additional cycling tests using LiCoO$_2$ cathodes vs. Li metal anodes were carried out, and the LiPF$_6$ EC:DMC performed similarly to the LiPF$_6$ EMC (Figure 3.2). Therefore, the bismuth fluoride nanocomposite cathode was deemed to be the site of interaction with the electrolyte.
Figure 3.1. Specific capacity as a function of cycle number of bismuth fluoride nanocomposites cycled galvanostatically between 4.50 V and 2.00 V in 1 M LiPF$_6$ based electrolytes. (a) EMC and EC:DMC gave best and worst performance, respectively. (b) DMC and PC shown for comparison. Linear carbonates performed better than cyclic carbonates.
Figure 3.2. Specific capacity of LiCoO$_2$ cells cycled galvanostatically at 15 mAg$^{-1}$ LiCoO$_2$ in 1 M LiPF$_6$ EC:DMC and EMC. Beyond the 8$^{th}$ cycle, the performance of the LiCoO$_2$ cells was nearly identical, suggesting the capacity fade of the bismuth fluoride nanocomposite in Figure 3.1 was attributable to electrolyte interaction with the cathode.

Potentiodynamic discharges of the bismuth fluoride nanocomposite in electrolytes containing 1 M LiPF$_6$ in various carbonate solvents are shown in Figure 3.3. From 2.9 to 2.5 V, bismuth fluoride is discharged, yielding Bi metal and LiF. Down to approximately 2.0 V, the discharge profiles of all the 1 M LiPF$_6$ electrolytes appear identical. A closer inspection (Figure 3.3(b)) reveals the onset potential of approximately 2 V for additional cathodic current in the cyclic-based solvents, EC:DMC and PC, which has been attributed to a mechanism beyond conversion and is of interest here. In contrast, 1 M LiPF$_6$ EMC and DMC exhibited only negligible cathodic current over the same 2.0–1.6 V; hence, it would seem as though the cyclic carbonates are the active species. Further discharge revealed the 1.15 V peak representing MoS$_2$ intercalation with Li. 1 M LiPF$_6$ DMC appears to have a decomposition peak at approximately 0.8 V, however, no such peak is shown for the DMC contained within the EC:DMC electrolyte. For EC:DMC
electrolytes, it would seem feasible that EC decomposition isolates the cathode from being reactive toward DMC once the potential reaches 1.4 V. Below 1 V, LiBi and Li$_3$Bi intermetallic formation, Li + carbon nanotube reactions, and LiAl alloying with the cathode current collector occur.

Figure 3.3. Potentiodynamic sweeps of bismuth fluoride nanocomposites in 1 M LiPF$_6$ electrolytes. (a) Entire discharge profile from initial open circuit voltage (OCV) to 0 V vs. Li/Li$^+$. (b) Region of cathodic current development beyond BiF$_3$ conversion due to decomposition of cyclic organic carbonate solvents.
To further isolate the extent of the cathodic decomposition observed in the region of 2.0 and 1.6 V vs. Li/Li⁺, GITT discharge protocols (approximately 2 month discharges) were run with 1 M LiPF₆ EC:DMC and 1 M LiPF₆ EMC electrolytes. These are shown in Figure 3.4. The theoretical discharge capacity for BiF₃ is 302.3 mAhg⁻¹. In both electrolytes, theoretical capacity was achieved after reaching an open circuit voltage (OCV) around 2.5 V. Further discharge resulted in a significant decrease of the OCV. A reaction at approximately 1.8 V developed for the EC:DMC electrolyte with a rest OCV of 2.05 V. This cathodic reaction continued to develop with discharge, more than doubling the theoretical capacity of the active material. The OCV rose back to 2.05 V for the duration of the reaction. The 1 M LiPF₆ EMC electrolyte displayed essentially no electrochemical activity until an OCV of approximately 1.5 V, and this was trivial when compared with the prolonged reaction in 1 M LiPF₆ EC:DMC. Similar featureless GITT results were also observed for the linear carbonate based electrolyte 1 M LiPF₆ DMC.
Figure 3.4. GITT discharge profiles for bismuth fluoride nanocomposites in (a) 1 M LiPF$_6$ EC:DMC and (b) 1 M LiPF$_6$ EMC.
As the conductive matrix of the BiF$_3$ nanocomposite contains potential sites of reaction with relatively high surface area, it was necessary to discount the matrix of the nanocomposite as the source of the catalysis. Milled MoS$_2$, carbon nanotubes, SP carbon, and a milled MoS$_2$ + carbon nanotube (MSCNT) matrix with SP carbon added to the bulk electrode were tested utilizing the same electrolytes as in Figure 3.3. No electrochemical reactions were recorded over the potential window from 2.0 V to 1.2 V. In Figure 3.5, a bismuth fluoride nanocomposite is contrasted against the MSCNT nanocomposite matrix with the current renormalized per gram of matrix material. This unequivocally shows that the products of the BiF$_3$ conversion are catalyzing the reaction with EC.

![Potentiodynamic sweeps of the MoS$_2$ + carbon nanotube matrix (MSCNT) and bismuth fluoride nanocomposite in 1 M LiPF$_6$ EC:DMC. The current values have been normalized per g of MSCNT.](image-url)
Within the 2.0–1.6 V window of the reactions, the BiF$_3$ nanocomposite has already been fully discharged resulting in Bi and LiF nanodomains embedded in the preprocessed MoS$_2$ + carbon nanotube matrix. As LiF is so highly insulating and presumably inactive with respect to the electrolytes, and the MSCNT matrix was discounted in the aforementioned study, potentiodynamic discharges of a bismuth metal nanocomposite were performed to isolate the source of the catalysis (Figure 3.6). The discharge profiles of the bismuth metal nanocomposite in 1 M LiPF$_6$ EC:DMC and EMC exhibited similar behavior as witnessed in Figure 3.3 with the bismuth fluoride nanocomposite. For comparison, 1 M LiPF$_6$ PC is also included. Significant reactions involving PC occurred at a slightly lower potential than EC (in EC:DMC), and the cathodic current from EMC was negligible. The bismuth metal nanocomposites did, however, exhibit currents of greater magnitude than from the electrochemically formed nanocomposite, even when the BiF$_3$ discharge profiles were re-normalized as pure Bi. Despite the larger domain size for Bi metal in the bismuth metal nanocomposite vs. the Bi metal resulting from discharge of the bismuth fluoride nanocomposite, the bismuth metal nanocomposite did not possess the 3 moles of LiF. The LiF may have isolated a significant percentage of the electrochemically formed Bi from contact with the electrolyte, thereby resulting in a lower degree of electrochemical decomposition on the Bi formed from the conversion of the BiF$_3$. 
Figure 3.6. Potentiodynamic sweeps of bismuth metal nanocomposites in 1 M LiPF$_6$ electrolytes. (a) Entire discharge profile from initial OCV to 0 V. (b) Region of cathodic current below 2.0 V related to decomposition of cyclic organic carbonate solvents on Bi metal.
In addition to LiPF$_6$ EC:DMC, alternative lithium salts in EC:DMC electrolytes were investigated to determine if the Li salt affected the reaction. Figure 3.7 shows that the onset potential for the cathodic current was identical regardless of the Li salt. It is likely that the more prominent cathodic current occurring in the LiAsF$_6$ electrolyte below 1.3 V vs. Li/Li$^+$ was due to reduction of the AsF$_6^-$ ion to form AsF$_3$ and F$^-$.[73]

![Figure 3.7](image.png)

*Figure 3.7. Potentiodynamic sweeps of bismuth metal nanocomposites in EC:DMC based electrolytes with LiPF$_6$, LiAsF$_6$, and LiClO$_4$ salts.*

In order to study the effect of the source of the converted Bi, numerous potentiodynamic discharge trials with bismuth oxide nanocomposites and extending to the bismuth (III) acetate, bismuth (III) citrate, and bismuth (III) carbonate-basic macroblends were run. All revealed that the 1 M LiPF$_6$ EC:DMC electrolyte had a prolonged, greater than theoretical discharge capacity whereas the 1 M LiPF$_6$ EMC did not. Thus, regardless of the source of the Bi metal, when coupled with any EC containing electrolyte, or PC based electrolyte for that matter, a significant
reaction occurs. To understand the reaction occurring on the surface of the Bi, the mechanism was studied using controlled thin films of Bi metal.

### 3.3.2 Physical characterization of Bi thin films

320 nm Bi films were deposited on Ti coated Al substrates. All films were handled in a He filled glovebox. The initial, as-deposited bismuth film possessed a shiny metallic luster with hues of yellow and pink under fluorescent lighting. After polarization for 24 h at 1.50 V vs. Li/Li⁺ in 1 M LiPF₆ EC:DMC, the Bi film developed a roughened surface with a gunmetal grey color. In stark contrast, polarization in 1 M LiPF₆ EMC resulted in a Bi film that did not seem to have reacted as it appeared identical to the as-deposited film. Assuming all 320 nm of the Bi was active and no LiₓBi formed at 1.50 V (a potential far greater than 0.6 V to 0.8 V vs. Li/Li⁺ at which these intermetallics have been demonstrated) the equivalent moles of Li reacted were ~15 for 1 M LiPF₆ EC:DMC vs. only 0.01 for 1 M LiPF₆ EMC. FESEM images of the polarized films are presented in Figure 3.8. Very clearly, the as-deposited (Figure 3.8(a)) and polarized films in 1 M LiPF₆ EMC (Figure 3.8(b)) look identical, while the film polarized in 1 M LiPF₆ EC : DMC (Figure 3.8(c and d)) reveals a diffuse, thick SEI-like coating on the film. Acquiring good images of the film polarized in 1 M LiPF₆ EC : DMC was difficult due to significant surface charging, indicative of a thick, insulating layer atop the metal surface. EDS was performed on all three films (Figure 3.9). The as-deposited film and film polarized in 1 M LiPF₆ EMC displayed only Bi, Ti, and Al. The film polarized in 1 M LiPF₆ EC:DMC exhibited more defined signals for C and O, and almost no F. The film was rinsed thoroughly in DMC, but there could still be a minute amount of residual electrolyte present. However, the intensity of the C and O peaks would not be expected to be as high if strictly due to residual electrolyte because of the lower x-ray fluorescence yield of these elements compared with F from the electrolyte salt. No P was witnessed in the EDS data.
Figure 3.8. FESEM images of (a) as-deposited Bi film [52kX], (b) Bi film polarized at 1.50 V for 24 h in 1 M LiPF$_6$ EMC [52kX], (c) Bi film polarized at 1.50 V for 24 h in 1 M LiPF$_6$ EC:DMC [292X], and (d) same film as (c) but at higher magnification [80kX].

Figure 3.9. EDS spectra for (A) as-deposited Bi film, (B) Bi film polarized at 1.50 V for 24 h in 1 M LiPF$_6$ EMC, and (C) Bi film polarized at 1.50 V for 24 h in 1 M LiPF$_6$ EC:DMC.
To identify the nature of the organic decomposition layer, ATR-FTIR experiments were performed for Bi films soaked in EC:DMC and EMC solvents for 24 h, soaked in 1 M LiPF₆ EC:DMC and EMC electrolytes for 24 h, and polarized for 24 h at 1.50 V in the two electrolytes. For these trials, films were monitored in duplicates, one being rinsed with DMC or EMC, and one being measured without rinsing away the residual electrolyte. This was important to establish confidence that the observed bands were truly unique and resulted from the soak or polarization and not residual electrolyte. While both MidIR and FarIR scans were conducted, the FarIR data did not provide additional bands to aid in characterization. The films soaked in both solvents and electrolytes were indiscernible from the as-deposited Bi film, all with a silvery luster with hues of yellow and pink. The FTIR spectra for these films did not exhibit any new bands. From the physical appearance as well as the lack of an FTIR signature for a new phase, it was concluded that the only means of having a reaction was by polarizing the cathode. Figure 3.10 includes a Bi film sample that was soaked for 24 h in 1 M LiPF₆ EC:DMC electrolyte (Figure 3.10, curve A) that compared well with an as-deposited Bi film (Figure 3.10, curve D).

Holding the Bi film for 24 h at 1.50 V in 1 M LiPF₆ EC:DMC (Figure 3.10, curve B) resulted in a completely different spectrum than that of the as-deposited Bi film (curve D). On the other hand, and as expected from the FESEM results, the Bi film polarized in 1 M LiPF₆ EMC (Figure 3.10, curve C) looked identical to the as-deposited film. The bands present in the FTIR spectrum for the polarized Bi film in EC:DMC were found to be distinct from a simple LiPF₆ + EC residue that was formed by allowing the DMC component to evaporate from 1 M LiPF₆ EC:DMC electrolyte. There was no doubt that EC was reacting, so various Li–C–O–H and Bi–C–O–H compounds were analyzed in the FTIR in an attempt to identify a suitable compound or functional group match. Figure 3.11 is a comparison of the polarized 1 M LiPF₆ EC:DMC Bi film
with lithium carbonate (Aldrich). The band positions as well as relative intensities are quite similar, especially the shoulder around 1465 cm$^{-1}$. However, not all of the smaller intensity peaks could be associated with Li$_2$CO$_3$. The other significant band around 1310 cm$^{-1}$ could be related to a lithium organic compound as ROCO$_2$Li was identified in work on tin anodes.[26] Lithium carbonate and lithium alkyl carbonates are common phases found in the organic decomposition products of EC with Li salts, however, ROCO$_2$Li phases are usually identified as being dominant relative to Li$_2$CO$_3$.[99] FT-Raman (not shown) was also used to investigate the Bi films, but the signal-to-noise ratio was poor. A slight peak around 1090 cm$^{-1}$ present in the 1 M LiPF$_6$ EC:DMC polarized sample and not found in the 1 M LiPF$_6$ EMC polarized or as-deposited samples further supports that the surface film is a lithium carbonate species. The same Li$_2$CO$_3$ powder as probed with ATR-FTIR was examined with FT-Raman and had its most intense peak at 1090 cm$^{-1}$ as well.
Figure 3.10. MidIR ATR-FTIR spectra for (A) Bi film soaked in 1 M LiPF$_6$ EC : DMC for 24 h, (B) Bi film polarized at 1.50 V for 24 h in 1 M LiPF$_6$ EC:DMC, (C) Bi film polarized at 1.50 V for 24 h in 1 M LiPF$_6$ EMC, and (D) as-deposited Bi film. No baseline subtraction performed.

Figure 3.11. FTIR spectra of (A) lithium carbonate powder and (B) Bi film polarized at 1.50 V for 24 h in 1 M LiPF$_6$ EC:DMC.
XPS analysis was carried out on the as-deposited Bi film (Figure 3.12 and Figure 3.13, curve A) and Bi films held at 1.50 V for 24 h in 1 M LiPF$_6$ EMC and 1 M LiPF$_6$ EC:DMC (Figure 3.12 and Figure 3.13, curves B and C, respectively). The survey scans are presented in Figure 3.12. It is evident that the 1 M LiPF$_6$ EC:DMC has a distinctly different surface phase because the O1s signal is much stronger, the Bi4d and Bi4f signals are greatly diminished, and the C1s signal appears to have split. More precise scans of individual core levels are displayed in Figure 3.13.

Figure 3.13(a) displays the C1s spectra. The as-deposited Bi film and the film polarized in 1 M LiPF$_6$ EMC exhibited nearly identical signals around -285 eV suggesting that a contaminant was present during the initial deposition of the film or that Bi-bound hydrocarbons chemisorbed during handling and storage. The C1s spectrum of the film polarized in 1 M LiPF$_6$ EC:DMC, however, displays several components. The contaminants peak at -285 eV is strongly attenuated accompanied by the presence of a broad peak centered around -288 eV attributed to C–O and hydrocarbon species. What is of greatest interest in Figure 3.13(a) is the emergence of another C1s component at higher binding energy (-290 eV), also observed in the C1s spectrum of a thin Li$_2$CO$_3$ sample (Figure 3.12 and Figure 3.13, curve D) and characteristic of carbonate species.[100]

O1s spectra are presented in Figure 3.13(b). The as-deposited Bi film exhibited a peak around -530 eV which has been attributed to a surface phase containing Bi–O bonds. Although much care was taken, the samples were transferred in non-UHV conditions, and the purity of atmosphere in which the films were stored contained as much as 1 ppm O$_2$, certainly enough to yield a chemisorbed oxide. For the film polarized in 1 M LiPF$_6$ EMC, the O1s peak has been difficult to identify as either hydration during sample transfer from the glove bag or as a possible
Figure 3.12. XPS survey scans of (A) as-deposited Bi film, (B) Bi film polarized at 1.50 V for 24 h in 1 M LiPF$_6$ EMC, (C) Bi film polarized at 1.50 V for 24 h in 1 M LiPF$_6$ EC:DMC, and (D) lithium carbonate dispersed on carbon tape.

Figure 3.13. XPS core level scans of (A) as-deposited Bi film, (B) Bi film polarized at 1.50 V for 24 h in 1 M LiPF$_6$ EMC, (C) Bi film polarized at 1.50 V for 24 h in 1 M LiPF$_6$ EC:DMC, and (D) lithium carbonate dispersed on carbon tape.
decomposition product. Recall that no significant carbonate-related peaks were witnessed in the C1s spectra (Figure 3.13(a)) for the EMC sample. On the other hand, the Bi film held at 1.5 V in 1 M LiPF$_6$ EC:DMC exhibited a strong peak at -532 eV. This peak was also measured on a thin Li$_2$CO$_3$ sample and points to the presence of a carbonate salt as the electrolyte decomposition product.[99]

Among the Bi films, a Li1s peak was only observed for the film polarized in 1 M LiPF$_6$ EC:DMC (Figure 3.13(c)). The position of the Li1s signal at -55.5 eV is identical to the one measured on the thin Li$_2$CO$_3$ layer. Furthermore, there was no indication of phosphorus in its survey scan, ruling out the possibility for residual or reacted electrolyte salt anion to be present on the surface. Indeed, based on the relative energy position of the Li1s, C1s, and O1s peaks, the surface phase for the Bi sample polarized in LiPF$_6$ EC:DMC is consistent with Li$_2$CO$_3$.

Figure 3.13(d) shows the F1s spectra collected for the two polarized films. The interpretation of the F1s lines is more problematic due to the possibility of differential charging of these inhomogeneous samples. Assuming no charging for the mostly unmodified 1 M LiPF$_6$ EMC film, the F1s core level could be interpreted as indicating the presence of LiF.[101, 102] However, due to the small Li1s cross-section, no clear Li1s counterpart was observed. In the case of the 1 M LiPF$_6$ EC:DMC film, the interpretation of the F1s spectra remains unclear at this time. Without a corresponding P signal, LiPF$_6$ has been ruled out.[103] Thus, it is speculated that the F 1s signal is due either to a minor amount of LiF or to C–F or O–F bonds incorporated within the interphase layer.
Lastly, Figure 3.13(e) displays the Bi4f spectra. The as-deposited Bi film exhibits a predominance of Bi–O (-164 eV) as opposed to pure Bi metallic bonds (-161 eV), as was observed earlier with the O1s signal. In contrast, the film polarized in 1 M LiPF₆ EMC conversely showed a predominance of Bi metal. Presumably, HF in the electrolyte etched Bi–O bonds at the surface of the Bi film, yielding Bi–F bonds. We have previously demonstrated with BiF₃-based nanocomposites that the conversion potential for BiF₃ is well above 1.5 V vs. Li/Li⁺. Hence, the fluorinated Bi film surface may result in the formation of Bi metal and LiF after polarization at 1.5 V, consistent with the Bi4f and F1s signals, respectively. The LiF was generated at the surface but in relatively small amounts (compared to the overall Bi film) as the film polarized in 1 M LiPF₆ EMC did not appear visibly or physically altered and the equivalent moles of Li reacted were merely 0.01. Finally, the Bi 4f core levels of the Bi film polarized in 1 M LiPF₆ EC:DMC were strongly attenuated due to the presence of a thick surface overlayer. The Bi 4f spectrum was indicative in this case of both a metallic Bi component and an oxide whose composition appeared more complicated than a simple oxide.

A fitting of the different core level spectra for the Bi film polarized in 1 M LiPF₆ EC:DMC corrected for cross-section effects leads to an approximate composition for the lithium oxide phase characterized by a 3:1 C:O ratio and a 1.2:1 O:Li ratio. All these factors point to the existence of a Li₂CO₃-based film as characterized by FTIR. FTIR may also suggest the presence of ROCO₂Li phases to a much lesser extent.

### 3.4. Discussion

The results clearly show a distinct SEI formation on the metal surface catalyzed by the presence of Bi metal. The aforementioned GITT results give evidence that such reactions may be initiating at voltages above 2 V vs. Li/Li⁺. Although the formation of SEI films at low potentials by cyclic
carbonates is very well known, the formation at voltages as high as 2 V is not as common, but not unprecedented. Indeed, Sn has been shown to form SEI at 1.5–1.6 V potentials\cite{26, 27, 104}, and although not discussed, the electrochemical data of Finke et al\cite{105} and Park et al\cite{106} show evidence of similar SEI formation in EC:DMC at approximately 1.6–1.8 V. During the course of the preparation of this chapter, Bridel et al\cite{24} were the first to report the presence of SEI byproducts on the surface of Bi metal in their nice study of Pb, Bi, Sn, Si, and Sb films; however, only the identification of the decomposition products on Sn was disclosed. Although similar reaction products were identified, in contrast to our work, no reaction was found with the cyclic carbonate PC. Again there is a need to reinforce the fact that the catalysis is induced by the metal. The metal sulfide and carbon components of our nanocomposite materials do not induce such formation.

The focus of this chapter is not so much as to report a detailed SEI formation study but more so to relate the formation / presence of such SEI to a direct impact of the electrochemical performance of the metal fluoride nanocomposite. The formation as shown by potentiodynamic cycling clearly reveals the majority of the film is formed at 1.6 V, and it is not at all obvious that the film is present in such amounts to influence the cycling of the BiF$_3$ nanocomposite at voltages consistent with the normal discharge cutoff voltage of 2.0 V. The first evidence of electrochemical impact can be seen if the BiF$_3$ nanocomposite is cycled galvanostatically to 1.6 V (Figure 3.14(a)). As expected, a plateau arises at 1.9 V due to the formation of the SEI. Subsequent cycling is exceptionally poor. In sharp contrast, cycling to 1.6 V in EMC reveals no film formation and the subsequent cycling is dramatically improved relative to the EC:DMC case (Figure 3.14(b)).
Figure 3.14. Bismuth fluoride nanocomposites cycled galvanostatically between 4.50 V and 1.60 V in 1 M LiPF$_6$ (a) EC:DMC and (b) EMC electrolytes. EC:DMC exhibited a plateau at 1.8 V and poor capacity utilization while EMC displayed no such plateau and good cycling.
Potentiodynamic cycling trials were limited to the 4.50–2.00 V potential range in order to provide a direct comparison with the galvanostatic tests presented in Figure 3.1. In Figure 3.15(a and c), there exist many similarities and some subtle differences between the bismuth fluoride nanocomposite cathodes cycled in 1 M LiPF$_6$ EC:DMC and EMC electrolytes. The initial discharge to 2.00 V with EC:DMC resulted in a small cathodic current feature around 2.0 V which intensifies with each cycle (Figure 3.15(b)) while the profile for 1 M LiPF$_6$ EMC remains featureless in the same region (Figure 3.15(d)). It would also appear this cathodic feature impacts the predominant reconversion reaction occurring around 3.4 V in the subsequent charge based on the splitting and broadening of the reconversion peak with each cycle. Though not included in Figure 3.15, 1 M LiPF$_6$ DMC electrolyte behaved almost identically to 1 M LiPF$_6$ EMC showing no cathodic feature at 2 V, while 1 M LiPF$_6$ PC was intermediate to that of 1 M LiPF$_6$ EC:DMC and 1 M LiPF$_6$ EMC in both the reduction occurring around 2.0 V and the peak shape of the reconversion reaction around 3.4 V. In short, there is evidence of electrolyte reduction at 2.00 V with the cyclic solvents EC and PC.
High resolution potentiodynamic characterization revealed many of the subtle features not readily apparent from the galvanostatic cycling data. In order to establish a more detailed relationship of cycling behavior as a function of electrolyte decomposition, a series of galvanostatic trials were initiated to isolate the impact of cutoff voltage and dwell time at the beginning of decomposition observed in the aforementioned potentiodynamic sweeps. Cells were cycled galvanostatically in EC:DMC and EMC based electrolytes at 15 mAg\(^{-1}\) nanocomposite to a discharge voltage cutoff of 2.25 V or 2.00 V (denoted CC 2.25 V and CC 2.00 V, respectively).
Alternatively, cells were cycled in the galvanostatic mode at 15 mAg$^{-1}$ nanocomposite until 2.25 V or 2.00 V vs. Li/Li$^+$, then held at constant potential until the current decayed to 1.5 mAg$^{-1}$ nanocomposite (CC/CV@2.25 V and CC/CV@2.00 V, respectively). All cells had a galvanostatic charge sweep at 15 mAg-1 nanocomposite to 4.50 V. In general, as shown in Figure 3.16, all cells cycling in 1 M LiPF$_6$ EMC displayed much improved cycling stability relative to the EC:DMC counterpart, consistent with the original cycling presented in Figure 3.1(a). For both electrolytes, cycling to 2.25 V gave better long-term capacity retention than cycling to 2.00 V. In EC:DMC, the CC/CV cells (2.25 and 2.00 V) both performed worse than their CC counterparts. In 1 M LiPF$_6$ EMC, the CC/CV@2.00 V cell began to diverge from the other cells presumably because the EMC is not completely inert, even at high potentials, but its reactivity is much less pronounced than that of EC:DMC. The most noteworthy result of this experiment was that a potentiostatic hold at 2.00 V in 1 M LiPF$_6$ EC:DMC gave initial discharge capacities exceeding the theoretical value of 266 mAhg$^{-1}$ nanocomposite (with BiF$_3$ as the only active component) followed by an immediate and distinct decline in discharge capacity. This result strengthens what was suggested from the potentiodynamic trials (Figure 3.15(a and b)). The reaction occurring within the EC:DMC system is active by 2.00 V and a prolonged duration at 2.00 V exacerbates the discharge capacity fade immensely. In short, the reduction of the cyclic carbonate-based electrolytes has a direct impact on the cycle life of the conversion BiF$_3$-based materials.
Figure 3.16. Cycling data of bismuth fluoride nanocomposites in 1 M LiPF$_6$ (a) EC:DMC and (b) EMC electrolytes. Cycling conditions are described in detail in text.
The results from the previous section create a very clear and direct relationship of the cathodic formation of the SEI at relatively high voltages and the degradation of the electrochemical cycling of the BiF$_3$ nanocomposite. The final question to answer is related to the mechanism by which the SEI is degrading the cycling stability of the BiF$_3$ nanocomposite. Potentiodynamic tests performed down to 1.4 V utilizing the EC:DMC electrolyte seem to indicate the SEI formed from 2.0 V to 1.7 V during discharge may partially decompose during subsequent charge at 4.4 V (Figure 3.17(a)). This anodic band did not exist in the EMC sample which had no SEI (no cathodic feature at 1.7 V) (Figure 3.17(b)). To see if the anodic decomposition feature is directly tied to the amount of SEI, one can control the amount of SEI formed by modulation of the discharge cutoff voltage and observe the impact on the anodic peak correlated to the SEI decomposition at 4.4 V. In such spirit, potentiodynamic tests were limited to 1.6 V utilizing both EC:DMC and EMC electrolytes (Figure 3.18(a and b)) and compared to the potentiodynamic studies performed to 1.4 V (Figure 3.17) and 2.0 V (Figure 3.15). The amplitude of the cathodic feature associated to the formation of the SEI occurring in the EC:DMC electrolyte increased with lowering the discharge cutoff voltage from 2.0 V, to 1.6 V, and finally down to 1.4 V. In perfect symmetry, the anodic band at 4.4 V on subsequent charge increased in amplitude as the discharge cut-off voltage decreased. Although of very small amplitude, the anodic feature at 4.4 V is clearly distinct and present in EC:DMC compared to the EMC sample, devoid of any SEI layer. Finally it should be noted that if the voltage sweep is started on charge, no distinct anodic decomposition feature is seen on the first sweep. In short, the link between the SEI formed and the anodic decomposition at 4.4 V is direct.
Figure 3.17. Potentiodynamic cycling of bismuth fluoride nanocomposite between 4.50 V and 1.40 V in 1 M LiPF$_6$ EC:DMC (a) and EMC (b). Cells were started on discharge.
Figure 3.18. Potentiodynamic cycling of bismuth fluoride nanocomposite between 4.50 V and 1.60 V in 1 M LiPF$_6$ EC:DMC (a) and EMC (b). Cells were started on discharge.
The identification of the SEI formation / decomposition bands above leads us to the question whether the formation or decomposition mechanism is tied exclusively to the Bi metal. To be as relevant as possible, we have chosen to examine whether such film formation / decomposition can be observed in another non-bismuth fluoride conversion material, FeF₂. Below 1.7 V, the EC:DMC electrolyte is exposed to nanoclusters of Fe metal with LiF.[7] Potentiodynamic cycling data at 60°C are shown in Figure 3.19. In this material, additional cathodic current, presumably due to EC decomposition on Fe nanoparticles, occurred around 1.3 V on the first discharge sweep. On the following charge sweep, anodic current was noticeable at approximately 4.3 V as a direct result of the presence of the EC:DMC (Figure 3.19(a)) as no such reactions were observed on composites cycled in the EMC solvent (Figure 3.19(b)). This is in perfect analogy with the BiF₃ case described in this chapter. These data show that the decomposition of the solvents is catalyzed by the nano-metals of various chemistries formed in the conversion process and that such SEIs can be decomposed at high voltages during the subsequent anodic sweep; however, nothing beyond that can be inferred.
Figure 3.19. Potentiodynamic cycling of iron (II) fluoride nanocomposite between 4.50 V and 1.25 V at 60°C in (a) 1 M LiPF$_6$ EC:DMC and (b) 1 M LiPF$_6$ EMC. Cells were started on discharge.
Moving back to the impact of the SEI decomposition on subsequent cycles we can refer to an extreme example. In our earlier publication, we examined the reversible conversion of $\text{Bi}_2\text{O}_3$ nanocomposites in EC:DMC.[8] In retrospect, this experiment sheds much light onto the intimacy between the SEI decomposition and the Bi chemistry. Figure 3.20 shows the discharge and charge of a $\text{Bi}_2\text{O}_3$ nanocomposite in EC:DMC electrolyte with 1 M LiPF$_6$ and LiClO$_4$ salts. Both electrolytes mirror each other almost exactly during the first discharge and charge where both the conversion of $\text{Bi}_2\text{O}_3$ and the parallel formation of the SEI layer occur. During charge, both show evidence of Bi reconversion to $\text{Bi}_2\text{O}_3$ at the 2.3 V plateau. Further charge reveals the now identified SEI decomposition at 4.4 V which is quite extensive for both samples. Of interest is the subsequent discharge (second discharge). The LiClO$_4$ sample’s voltage immediately goes to approximately 2 V associated with the conversion of $\text{Bi}_2\text{O}_3$, while the sample in LiPF$_6$ shows an electrochemical feature at approximately 3 V. The latter is consistent with the conversion of $\text{BiF}_3$ or $\text{BiO}_x\text{F}_{3-2x}$ compounds formed during charge in the LiPF$_6$-based electrolyte. We do not believe HF in the electrolyte to have simply reacted with the $\text{Bi}_2\text{O}_3$ of the bulk cathode because the subsequent discharge capacity is too high relative to the $\text{Bi}_2\text{O}_3$ reformed at 2.3 V. This shows that Bi may, in fact, interact via the SEI decomposition to form new or modified phases.
Figure 3.20. Galvanostatic cycling of bismuth (III) oxide nanocomposite between 4.50 V and 1.50 V in 1 M LiClO$_4$ and LiPF$_6$ EC:DMC electrolytes. Cells were started on discharge.

How does the Bi interact with the SEI? We will not be able to fully answer this question within this chapter; however, the first question is whether there are chemical bonds formed between the SEI and the Bi. The XPS results seemed to lend itself to this conclusion by the shift in the Bi energy consistent with a Bi–O bond development, but the results are still a bit ambiguous to definitively state the nature of the chemistry. From a mechanistic model we know that for the catalysis of the solvent during the cathodic sweep to occur, some degree of transient or permanent Bi–O chemical bonding between the catalyst and reacted species is developed, which has been observed with Bi catalysts.[107] From unpublished results, we know that such Bi–O bonds, even in the form of nanocrystalline Bi$_2$O$_3$, will simply be digested in HF containing LiPF$_6$ electrolytes and reprecipitate as a BiF$_3$-like phase. This in itself is expected to adversely affect cycle life as one would expect for dissolution–reprecipitation process. Approaching the
SEI decomposition at 4.4 V, assuming a Li₂CO₃ dominated decomposition, the following catalyzed anodic reaction of the SEI can be written:

\[ \text{Li}_2\text{CO}_3 \rightarrow 4\text{Li}^+ + 4e^- + 2\text{CO}_2(g) + \text{O}_2(g) \]  \hspace{1cm} (3.1)

We know that the SEI dominates the electrochemical reaction as a similar reaction was shown using FeF₂ based nanocomposites (Figure 3.19). Assuming some residual, unreacted Bi metal from incomplete reconversion reacts with the evolved oxygen to form Bi₂O₃, we can then realize that this fine oxide will also be attacked immediately by the LiPF₆ electrolyte to form BiF₃. Therefore, the decomposition reaction at 4.4 V may only marginally contribute to the cycle life. This is supported by unpublished results which show that cycling to 4.25 V improves cycle life, but not in an overly dramatic way. In short, we theorize the formation of Bi–O bonds induced by the SEI formation is very detrimental to the cycling via the digestion process mentioned. Indeed, we have shown that Bi–O bonds lead to poor cycle life as evidenced with bismuth oxyfluorides by partial dissolution and may be the route of the observed cycling impact.[6, 8]

In short, the utilization of both EMC-based electrolytes along with the optimal use of dense, relatively low surface area nanocomposites by the mixed conducting matrix technique we have recently introduced[5] resulted in improved cycling stability (Figure 3.16). This is a distinct relative improvement considering the original cycling stability of BiF₃ was poor (< 20 cycles). The improvements even extended to prelithiated BiF₃. Figure 3.21 provides a comparison of non-prelithiated and prelithiated bismuth fluoride nanocomposites in 1 M LiPF₆ EMC. Though the prelithiated cathode has a decreased capacity due to the additional material contained within the cathode, the capacity fade is identical, suggesting that the nature of the Bi nanodomains prior to cycling does not influence the predominant fade mechanism.
Figure 3.21. Specific capacity as a function of cycle number of prelithiated and non-prelithiated bismuth fluoride nanocomposites cycled galvanostatically between 4.50 V and 2.00 V in 1 M LiPF₆ EMC. Cells were started on discharge.

3.5. Conclusion

The catalytically induced formation of a Li₂CO₃ dominated SEI from cyclic carbonates was found in converted BiF₃ nanocomposites (3LiF + nano Bi) at voltages near 2 V vs. Li/Li⁺. This was tied directly to the presence of the nanometal as such reactions were also found on converted FeF₂ materials but not on nano-carbon or metal sulfide substrates. All linear carbonates tested did not show such a feature. A directly related SEI decomposition is shown at 4.4 V. Systematic evidence was given for the relationship of the degree of the SEI formed and the cycle life of the material.

High voltage metal fluoride nanocomposites utilized as conversion electrodes for lithium batteries are not immune to cyclic carbonate-based SEI formations by a cathodic reaction even when discharge voltages exceed 2 V. The dynamic and constantly changing bonds of the metal
fluoride conversion electrodes only exasperate the interaction between the conversion material and the electrolyte. This is the first report of such interaction, and while acyclic carbonates are a demonstrated route to distinctly improved cycling performance for bismuth based compounds, this chapter strongly supports the utilization of other non-carbonate solvents such as nitriles, ethers, or ionic liquids for use with such electrode technology.
4. Anodic decomposition of solid-electrolyte interphase leading to subsurface oxidation of nanofluoride conversion materials

4.1. Introduction

Today’s intercalation electrodes used for Li-ion batteries operate on a lithium insertion / de-insertion reaction with very little phase and volume modification during a charge / discharge cycle.\[1, 108\] In sharp contrast, conversion and displacement materials, including metal halides, nitrides, and chalcogenides, transform into two- or three-phase materials consisting of nano-sized regions of metal and lithium halide / nitride / chalcogenide salts.\[6, 40, 109\] This process reverses every cycle creating a very dynamic situation relating to phase and volume change. It has been recently noted that the metallic nanodomains formed during lithiation of certain conversion materials can be very catalytic towards the cathodic decomposition of the electrolyte at relatively high voltages of approximately 2 V vs. Li/Li\(^+\) leading to a film of lithium carbonate and lithium alkyl carbonates on the electrode material surface (Chapter 3).\[110\]

With conversion materials, one must question the eventual fate of the solid-electrolyte interphase (SEI) film, both mechanically and chemically. The mechanical question relates to the physical stability of the SEI layer while the underlying electrode materials undergo extreme changes of phase and volume during the cycling of the material. The chemical question relates to abstract evidence that the SEI may anodically decompose upon cycling the electrode to high voltages (> 4 V) incurred during normal operation. If the SEI does decompose, at the very least, it would require a reformation during the next discharge, potentially resulting in irreversible capacity loss in a Li-ion cell configuration. Much more insidious would be the local release of oxygen-related compounds that could become incorporated into the subsurface structure of the underlying metal fluoride conversion materials. Such reactions would thereby cause the metal fluoride to reconvert to metal oxide or oxyfluoride phases and affect subsequent cycling
To examine this question, we focus on bismuth fluoride conversion materials as a first example to explore whether evidence of such phenomena exists.

Bismuth fluoride nanocomposites have been evaluated for use as the positive electrode in Li-ion cells. Despite the very high theoretical gravimetric capacity (302.3 mAh g$^{-1}$) and volumetric energy density (7960 Wh L$^{-1}$) of BiF$_3$, galvanostatic cycling trials of the nanocomposites resulted in rapid capacity fade.[4, 110] The electrochemical reduction of cyclic organic carbonate solvents used as components of the electrolyte has been very strongly correlated with rapid capacity fade.[110] The Bi$^0$ resulting from the conversion (lithiation) of BiF$_3$ has been identified as the species on which the decomposition of cyclic organic carbonate solvents such as ethylene carbonate (EC) and propylene carbonate (PC) was catalyzed. At approximately 2 V vs. Li/Li$^+$, EC decomposition was initialized, and it resulted in the formation of a solid electrolyte interphase (SEI) composed predominantly of Li$_2$CO$_3$. SEI growth was correlated with increased rates of capacity loss. In electrolytes composed of linear carbonate solvents, SEI formation was not observed and long term cycling performance was better. While this initial work (Chapter 3) identified a relationship between electrolyte decomposition and poor cycling performance, the influence of SEI formation on the chemistry of the BiF$_3$ nanocomposite was not determined.

Ideally, the conversion (lithiation) of a BiF$_3$ nanocomposite should result in the formation of domains of bismuth metal and lithium fluoride during discharge, and reconversion (delithiation) should lead to the reformation of BiF$_3$ during charge (Eqn. (4.1)).

$$\text{BiF}_3 + 3\text{Li}^+ + 3\text{e}^- \Leftrightarrow \text{Bi}^0 + 3\text{LiF}$$  \hspace{1cm} (4.1)

Conversion takes place below 2.9 V, and reconversion takes place above approximately 3.3 V vs. Li/Li$^+$. In this work, the presence of the SEI formed from the decomposition of EC from the
electrolyte is considered with regard to its influence on the compounds formed during reconversion of the BiF₃ nanocomposite electrode (Eqn. (4.2)).

\[
\text{Bi}^0 + \text{LiF} + \text{SEI} \rightarrow ? \tag{4.2}
\]

First, we seek to identify whether the SEI is stable at potentials up to 4.5 V, the upper potential limit when cycling BiF₃ nanocomposites. The SEI chemistry and its electrochemical stability at high potentials vs. Li/Li⁺ will be evaluated on a relatively inert substrate, glassy carbon, to eliminate any effects of the bismuth nanocomposite. Then, we aim to determine if the SEI has any influence on the underlying bismuth chemistry during reconversion. If the SEI is removed from the electrode/electrolyte interface, does it simply disappear or does it impart new characteristics to the chemistry of the electrode? BiF₃ is an excellent vehicle to initiate such studies as it supports the formation of a number of known bismuth oxyfluoride phases. The goal is to elucidate the mechanism by which the SEI influences the capacity retention during cycling of the BiF₃ nanocomposite positive electrodes.

### 4.2. Experimental

#### 4.2.1 Materials synthesis

Glassy carbon planchets 2.7 mm thick were cut from a 6.0 mm rod (Alfa) using a diamond wire saw (MTI Corp). Debris was flushed from the cutting zone with mineral spirits. For trials in which the glassy carbon was used to probe interactions with the electrolyte, the planchets were hand polished to a mirror finish using aluminum oxide lapping film sheets (3M) from 40 to 0.3 μm. For trials in which the glassy carbon was used as the substrate for BiF₃ film deposition, the planchets were polished using 600 grit silicon carbide paper. The planchets were thoroughly cleaned to remove any lubricants and particulates by ultrasonically in methanol and acetone, successively. BiF₃ (Advanced Research Chemicals) was deposited in-house by thermal vacuum evaporation (PVD Systems) to a thickness of about 1 μm. After deposition, the BiF₃-coated
planchets were transferred directly to an argon filled glovebox (< 0.1 ppm H₂O, < 1 ppm O₂, MBraun) attached to the deposition system, sealed in a gastight bag, and transferred to a helium filled glovebox (< 0.6 ppm H₂O, < 0.1 ppm O₂, MBraun) until cell fabrication.

BiF₃ nanocomposites were fabricated by blending 0.85 g of HF treated 99.999% BiF₃ (Alfa) with 0.15 g of SP carbon (Timcal) in a hardened steel vessel (Spex). The milling cell was prepared in a helium glovebox (VAC) and then transferred outside to an 8000 series high energy mixer (Spex) for 30 min. The milling cell was reintroduced into the glovebox. The powder was annealed for 2 h at 200°C in a hermetically sealed copper vessel.

Bismuth oxyfluorides were synthesized by thoroughly mixing HF treated 99.999% BiF₃ (Alfa) and 99.99% Bi₂O₃ (Aldrich) in a 1:1 molar ratio (BiOF) or 4:1 molar ratio (BiO₀.₅F₂) in a mortar and pestle in a helium filled glovebox (VAC). 2.5 g of each powder blend was sealed in a hermetic copper vessel. The material was heat treated for 65 h at 640°C, then ground into a fine powder.

**4.2.2 Electrochemical characterization**

The electrochemical cells used for experiments with glassy carbon planchets consisted of a working electrode (polished or BiF₃-coated), a 12.7 mm diameter thin polymer membrane (Celgard), two 12.7 mm diameter layers of glass fiber separator (GF/D, Whatman) saturated with 1 M LiPF₆ EC:DMC 1:1 v/v (Novolyte), and a lithium foil counter / reference electrode (FMC). The cells were housed in stainless steel Swagelok bodies. Trials were performed between 21 and 22°C. Cyclic voltammetry (CV) studies on polished glassy carbon were conducted with a Model 1287 (Solartron) paired with CorrWare (Scribner Associates). CVs were run from 2.8 V to the lower switching potential (1600 mV, 1400 mV, ... , 400 mV) then up to 5.0 V for two cycles at 50 mV·s⁻¹. Trials involving spectroscopic studies of polished planchets were held at 1.0 V for 24
h or swept in the potentiodynamic mode at -1.25 mV / 0.006 h to 1.0 V. They were then stopped at 1.0 V and removed from the electrochemical test equipment (MacPile II, BioLogic) or swept at +1.25 mV / 0.006 h to 3.5 V, 4.0 V, 4.5 V, and 5.0 V. BiF₃ films deposited on glassy carbon were held at 1.5 V for 24 h then stopped or swept in the potentiodynamic mode at +1.25 mV / 0.006 h to 3.3 V and 4.5 V. Additionally, several of the cells containing either type of working electrode sat at rest in the open circuit condition for 24 h. After sitting at open circuit, the working electrodes were either removed from the cells or swept in the potentiodynamic mode at +1.25 mV / 0.006 h to 5.0 V (polished glassy carbon) or 4.5 V (BiF₃ film on glassy carbon). All potentials are reported vs. Li/Li⁺.

The cells used for ex-situ nuclear magnetic resonance (NMR) experiments of the BiF₃ nanocomposite were housed in stainless steel Swagelok bodies and were assembled in a similar manner as above. The working electrode was roughly 60 mg of BiF₃ nanocomposite powder. Instead of using 1 M LiPF₆ EC:DMC, the following solvents were blended: EC:EC*:DEC 1:1:2 and EC:DEC:DEC* 2:1:1 v/v/v. The starred (*) solvents were enriched with ¹³C at the C=O functional group of the ethylene carbonate (EC) and diethyl carbonate (DEC), respectively. 1 M LiPF₆ was dissolved in the enriched solvent blends. The BiF₃ nanocomposite cells were run with each ¹³C enriched electrolyte blend at ambient temperature on a BT2043 battery testing system controlled with MITS’97 software (Arbin). A set consisted of 5 individual cells, each subjected to its own electrochemical sequence. One of the cells sat at rest for 24 h (OC Rest). The other four cells were discharged in the galvanostatic mode at -5 mAg⁻¹ BiF₃ (C/60) to 2.00 V vs. Li/Li⁺. One of these cells was removed from the battery cycler (Discharge 2V); the other three automatically advanced to a potentiostatic hold at 2.00V until the current reached -1.5 mAg⁻¹ BiF₃ (C/200). After the potentiostatic hold, which lasted between 10 and 12 h, one of the cells was removed
from the battery cycler (Discharge 2V Hold), and the other two automatically advanced to a galvanostatic charge at +5 mA g\(^{-1}\) BiF\(_3\). One of these cells was charged to one-half the capacity of the galvanostatic discharge sweep (Half Reconversion). The fifth and final cell was charged to 4.50 V vs. Li/Li\(^+\) (Full Reconversion).

Supplemental potentiodynamic trials were run with the BiF\(_3\) nanocomposites in aluminized coin cells (Hohsen). These cells consisted of approximately 5 mg of BiF\(_3\) nanocomposite powder, a 19 mm diameter thin polymer membrane, two 16 mm diameter layers of glass fiber separator saturated with 1 M LiPF\(_6\) EC:DMC 1:1 v/v, and a lithium foil counter / reference electrode. The potentiodynamic trials (MacPile II) were lithiated from the open circuit potential (~3.2 V) to 2.0 V, 1.6 V, or 1.4 V, then they were delithiated to 4.5 V vs. Li/Li\(^+\). The scan rates were ±1.25 mV / 0.017 h, and the temperature was fixed at 24°C.

4.2.3 Physical characterization of bismuth oxyfluoride standards

Over the course of research, standards were needed for the identification of bismuth fluoride and oxyfluoride compounds as well as for the determination of the stability of these materials when analyzed with x-ray photoelectron spectroscopy (XPS). The x-ray diffraction (XRD) results (Figure 4.1) for BiF\(_3\), BiO\(_{0.5}\)F\(_2\), and BiOF compared favorably with powder diffraction files for orthorhombic BiF\(_3\) (PDF 01-070-2407), cubic (PDF 00-024-0147) or rhombohedral BiO\(_{0.5}\)F\(_2\) (PDF 01-089-4572), and tetragonal BiOF (PDF 01-073-1595).[111]
Figure 4.1. XRD of bismuth oxyfluoride powders used for XPS analysis.
The bismuth fluoride and oxyfluoride powders were dispersed on double-sided carbon tape for XPS analysis. The XPS instrument (K-Alpha, Thermo) was fitted with a flood gun to compensate for surface charging. Low energy, non-sputtering, charged particles were emitted from the flood gun. Monochromatic AlKα radiation was used with a spot size of 400 μm. Core level spectra were recorded using a pass energy of 50 eV and 20 scans. Analyses were conducted at room temperature. Prior to initializing the flood gun, the pressure within the analysis chamber was on the order of $5 \times 10^{-8}$ mbar. While the flood gun was operational, the analysis pressure approached $3 \times 10^{-7}$ mbar. The bismuth oxyfluoride powders were etched at 3 keV and “high” current density at 30 s intervals for a total of 2 min.† Core level spectra were recorded after each etching interval. Data was processed using Avantage v. 4.51 (Thermo). Peaks were fit with Voigt functions after Smart background subtraction (derived from the Shirley method but iteratively adjusted such that the background does not exceed the data curve).[112]

The XPS results for bismuth oxyfluorides are shown in (Figure 4.2). These samples have been subjected to a total of 120 s of ion-beam etching within the XPS analysis chamber. It is evident that some degree of instability of the bismuth compounds existed due to the gradual emergence of the Bi4f$_{7/2}$ peak at approximately 157 eV, consistent with metallic Bi. A trace of this instability has been attributed to interaction with the incident x-ray beam; the greater part of sample evolution occurred as a result of ion-beam etching. The emergence of the Bi4f signature for Bi metal was used to our advantage. The internal standard utilized for the bismuth oxyfluoride powders and BiF$_3$ films on glassy carbon was established as 157.0 eV, the Bi4f$_{7/2}$ core level for Bi.

† At 3 keV and “high” current, the equivalent etch rate of Ta$_2$O$_5$ is 2.57 nm·s$^{-1}$ assuming a continuous, uniform film of Ta$_2$O$_5$. With a nonuniform surface (in terms of smoothness and phase distribution), identifying the actual etch rate of bismuth compounds (and SEI phases) would require angle-resolved XPS studies or in-situ optical techniques.
metal. By selecting this feature as the internal reference energy, the results observed for the bismuth oxyfluoride standards would be self-consistent with those observed for the BiF$_3$ films deposited on glassy carbon. Furthermore, the use of the 157.0 eV standard avoided issues associated with possible etching instability of hydrocarbon contaminants (i.e. adventitious carbon) and convolution of this binding energy signature in subsequent electrolyte experiments.

There was a systematic increase in the binding energy of the Bi4f, O1s, and F1s core level peaks as the fluorine content of the bismuth compound was increased (Figure 4.2). This result was expected because the fluorine produces a bond of greater ionic character.[113, 114, 115] The peak positions of the Bi4f$_{7/2}$, O1s, and F1s core levels are summarized in Table 4.1. Using Scofield sensitivity factors[112], the atomic ratios for the bismuth oxyfluorides were 1.0:2.9 Bi:F for BiF$_3$, 1.0:0.4:1.9 Bi:O:F for BiO$_{0.5}$F$_2$, and 1.0:0.9:0.9 Bi:O:F for BiOF, all in excellent agreement with the target stoichiometries. Despite the formation of trace amounts of metallic Bi, the influence of the Ar$^+$ ion-beam etching on the chemistry of the bismuth oxyfluoride phases was trivial.
Figure 4.2. XPS core level spectra of bismuth oxyfluorides ion-beam etched for 2 min. Lowercase letters denote core levels: F1s (a), O1s (b), and Bi4f (c). UPPERCASE letters denote bismuth oxyfluoride sample: BiF₃ (A), BiO₀₅F₂ (B), and BiOF (C). A reference energy of 157.0 eV (Bi⁰ 4f7/2) has been applied.
Table 4.1. XPS core level peaks of bismuth oxyfluorides

<table>
<thead>
<tr>
<th>Bismuth material</th>
<th>Bi4f$_{7/2}$</th>
<th>O1s</th>
<th>F1s</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bi metal*</td>
<td>157.0</td>
<td>n/a</td>
<td>n/a</td>
</tr>
<tr>
<td>Bi$_2$O$_3$**</td>
<td>158.7</td>
<td>529.5</td>
<td>n/a</td>
</tr>
<tr>
<td>BiOF</td>
<td>159.4</td>
<td>530.0</td>
<td>683.8</td>
</tr>
<tr>
<td>Bi$_{0.5}$F$_2$</td>
<td>160.0</td>
<td>530.4</td>
<td>684.2</td>
</tr>
<tr>
<td>BiF$_3$</td>
<td>160.4</td>
<td>n/a</td>
<td>684.4</td>
</tr>
</tbody>
</table>

* Bi metal used as an internal standard for these reported values

** Results obtained with same XPS instrumentation but as part of a different study
4.2.4 Physical characterization of electrochemical cells

After electrochemical characterization, the cells were transferred to a helium filled glovebox and disassembled. The planchets were readied for x-ray photoelectron spectroscopy (XPS) analysis. They were rinsed with electrolyte grade dimethyl carbonate (DMC, Novolyte) and allowed to dry prior to being sealed in gastight sample holders. The samples were transferred to the XPS instrument. For the polished glassy carbon planchets, 284.8 eV was used as an internal standard. No Ar\(^+\) ion-beam etching was performed on the polished glassy carbon planchets. The BiF\(_3\) films were subjected to Ar\(^+\) ion-beam etching at 3 keV and “high” current density for 30 s, 60 s, 90 s, and 120 s intervals for a total of 5 min of etching.† As with the aforementioned bismuth oxyfluoride samples, the Bi4f\(_{7/2}\) core level for bismuth metal (157.0 eV) has been used as the internal reference energy, and core level spectra were recorded after each etching interval.

The BiF\(_3\) nanocomposites were not rinsed prior to packaging the powders in gastight sample bags for overnight shipment. Once received at their destination, the samples were prepared for NMR analysis in an argon glovebox without rinsing. Solid state NMR experiments were performed on all \(^{13}\)C-enriched carbonate samples under magic angle spinning (MAS) conditions. NMR experiments were performed at 7 T using a Varian S Direct Digital Drive spectrometer and a 1.6 mm double resonance probe (Varian). Single pulse spectra without proton decoupling were collected for each sample at a spinning speed of 35 kHz. An RF-field strength of approximately 60 kHz was used for all \(^{13}\)C measurements (\(\nu_0 = 75.80\) MHz). Recycle delays varied between 3 and 30 s. A total of 16,600 transients were collected for all samples. Exponential line broadening (50 Hz) was implemented before Fourier transformation. The spectra were referenced to tetramethylsilane (TMS) at 0 ppm.
4.3. Results

4.3.1 Glassy carbon electrodes

Cyclic voltammograms for a polished glassy carbon planchet are reported in Figure 4.3. As the potential was driven to successively lower values, the extent of cathodic current increased, and correspondingly, the extent of anodic current systematically increased during the subsequent oxidation sweep. There was a slight anodic current from 3.5 V up to approximately 4 V. This was followed by another anodic current increase at approximately 4.2 V. A systematic increase in the average current values from 4.7 V to 5.0 V was observed, consistent with the anodic oxidation of the electrolyte. Since the former features (< 4.7 V) of anodic current grew after cathodic decomposition of the electrolyte at values < 1.2 V, this anodic current has been surmised to be associated with the oxidative decomposition of the SEI.

Figure 4.3. Cyclic voltammograms to successively lower switching potentials from 1600 mV down to 400 mV vs. Li/Li+. Only the second cycle is reported. WE: Glassy carbon planchet. CE/RE: Li foil. Electrolyte: 1 M LiPF₆ EC:DMC 1:1 v/v. Rate: 50 mV·s⁻¹.
XPS analysis (Figure 4.4) of glassy carbon planchets corroborated the electrochemical decomposition of the SEI at high potentials vs. Li/Li$^+$. Instead of the aforementioned cyclic voltammetry, the electrochemical method for the present experiment involved a 24 h potentiostatic hold at 1.0 V followed by a potentiodynamic sweep to more positive potentials. Carbonate groups, most likely Li$_2$CO$_3$, and LiF were the predominant entities on the surface of the glassy carbon after the potentiostatic hold at 1.0 V. This was substantiated by the Li1s, C1s, O1s, and F1s core level spectra at 1.0 V (Curve C) which exhibited the strongest signals at approximately 55.5, 290, 532, and 685 eV, respectively.[100, 101] The LiF was likely a byproduct of interactions involving LiPF$_6$ which could have reacted directly with lithium carbonate phases or indirectly through HF etching.[101] After the potentiostatic hold at 1.0 V, as the potential was swept to more positive values, the observed intensities of these signals decreased. At 3.5 V (Curve D), Li$_2$CO$_3$, and to a lesser extent, LiF, remained apparent on the surface of the glassy carbon. The Li1s, C1s, and O1s peaks for Li$_2$CO$_3$ were observed, and application of Scofield sensitivity factors to these peaks resulted in ratios of very nearly 2:1:3 for Li:C:O.[112] However, by 4.0 V (Curve E), the Li1s, C1s, and O1s signatures for Li$_2$CO$_3$, particularly the 290 eV signal in the C1s core level, were greatly diminished. The observed evolution of the XPS spectra coincided with the rise in anodic current at approximately 4 V. By 5.0 V (Curve G), no Li remained on the surface of the glassy carbon, and the C1s core level spectra were similar to the glassy carbon planchet sitting in the electrolyte at open circuit (Curve B). The O1s and F1s core level spectra were shifted to higher binding energies for reasons yet to be determined.

In another trial (not shown) involving a glassy carbon working electrode, the following controlled potential sequence was applied: 24 h potentiostatic hold at 1.0 V \(\rightarrow\) potentiodynamic sweep from 1.0 V to 3.5 V \(\rightarrow\) potentiostatic hold at 3.5 V for 7.2 h. The 7.2 h duration equaled
the amount of time that would have been required for the potential to advance from 3.5 V to 5.0 V. No differences in the Li1s, O1s, C1s, or F1s core level spectra were observed when comparing this sample with Curve D in Figure 4.4. Thus, it has been concluded that the evolution of the XPS spectra was, in fact, electrochemically driven, and not a time-dependent dissolution process.
Figure 4.4. XPS core level spectra of glassy carbon electrodes. Lowercase letters denote core levels: C1s (a), Li1s (b), F1s (c), and O1s (d). UPPERCASE letters denote electrochemical sequence: no electrochemistry (A), 24 h at OCV (B), 24 h at 1.0 V (C), 24 h at 1.0 V $\rightarrow$ sweep to 3.5 V (D), sweep to 1.0 V $\rightarrow$ sweep to 4.0 V (E), sweep to 1.0 V $\rightarrow$ sweep to 4.5 V (F), 24 h at 1.0 V $\rightarrow$ sweep to 5.0 V (G), and OCV $\rightarrow$ sweep to 5.0 V (H).
4.3.2 BiF\textsubscript{3} thin film electrodes

The potentiodynamic sweep to 4.5 V for a bismuth fluoride film following a 24 h potentiostatic hold at 1.5 V is reported in Figure 4.5. During the potentiostatic hold, the BiF\textsubscript{3} was reduced to Bi\textsuperscript{0} and LiF via a conversion reaction. At potentials below 2 V, reduction of EC from the electrolyte was catalytically promoted on the Bi metal to form a thick layer composed predominantly of Li\textsubscript{2}CO\textsubscript{3} (Chapter 3).[110] During the potentiodynamic sweep from 1.5 V to 4.5 V, a small anodic signal was observed at approximately 2.9 V (Figure 4.5, inset). The origin of this electrochemical signal was unknown; its cause is hypothesized in the Discussion. At a potential above 3.5 V, the sharp anodic signal has been assigned to the reconversion of Bi\textsuperscript{0} and LiF into BiF\textsubscript{3}. The extent of reconversion was roughly one-tenth the capacity of the potentiostatic discharge. It was doubtful that the entire mass of the BiF\textsubscript{3} film was converted during discharge, and since the discharge of BiF\textsubscript{3} and decomposition of the electrolyte were concurrent below 2 V, the contributions of each to the overall capacity were not able to be isolated. Above 4.2 V, another small anodic feature appeared which was consistent with previous observations of potentiodynamic sweeps of BiF\textsubscript{3} nanocomposites in 1 M LiPF\textsubscript{6} EC:DMC 1:1 v/v (Chapter 3).[110] The potentiodynamic sweep to 4.5 V after the freshly assembled cell sat at open circuit for 24 h is shown as a direct comparison (Figure 4.5). No anodic current was observed from 3.1 V to 3.5 V. The anodic features occurring at potentials below 3.5 V have been attributed to interactions of the Bi\textsuperscript{0}, LiF, and electrolyte decomposition products (SEI) formed during the potentiostatic hold at 1.5 V.
Figure 4.5. Potentiodynamic sweeps to 4.5 V after lithiation of BiF$_3$ film to Bi$^0$ and LiF with SEI growth (24 h at 1.5 V) or sitting at rest in the open circuit condition for 24 h. Anodic features between 2.6 V and 3.4 V were revealed during reconversion after the 1.5 V potentiostatic hold. No such features were observed for the BiF$_3$ film which sat at rest. Inset more clearly shows the anodic feature at approximately 2.9 V. WE: BiF$_3$ film on glassy carbon planchet. CE/RE: Li foil. Electrolyte: 1 M LiPF$_6$ EC:DMC 1:1 v/v.

XPS analysis of the BiF$_3$ films is presented in Figure 4.6. For brevity and clarity, focus has been placed on the Bi4f core level spectra. Figure 4.6(a) shows the films without having performed ion-beam etching, thereby analyzing the very top surface of the film. These samples may have been influenced by exposure to contaminants from the glovebox, by momentary exposure to atmosphere during sample loading, and/or by electrolyte salt residue, all of which could alter the surface chemistry. The samples in Figure 4.6(b) have been subjected to a total of 5 min of ion-beam etching within the XPS analysis chamber to analyze the subsurface region that would be less affected by environmental contamination. From the excellent stoichiometric ratios of the bismuth oxyfluorides standards described in Section 4.2.3, it was assumed that the etching process did not damage the observed bismuth compounds. The Bi4f$_{7/2}$ peak for metallic Bi was
set as an internal reference energy at 157.0 eV, consistent with the aforementioned procedure for the bismuth oxyfluoride powder standards.

![Bi4f: Non-etched](image1)

![Bi4f: Etched 5 min](image2)

Figure 4.6. XPS Bi4f core level spectra of bismuth fluoride film electrodes. Lowercase letters denote degree of ion-beam etching: none (a) and 5 min (b). UPPERCASE letters denote electrochemical sequence: no electrochemistry (A), 24 h at OCV (B), 24 h at OCV → sweep to 4.5 V (C), 24 h at 1.5 V (D), 24 h at 1.5 V → sweep to 3.3 V (E), and 24 h at 1.5 V → sweep to 4.5 V (F). A reference energy of 157.0 eV (Bi\(^{0}\) 4f\(_{7/2}\)) has been applied.

4.3.3 XPS of BiF\(_3\) films, top surface analysis

In Figure 4.6(a), the as-deposited bismuth fluoride film (Curve A) and the film which sat in the electrolyte at open circuit for 24 h (Curve B) were consistent with BiF\(_3\) but were shifted to slightly lower binding energies. The sample which sat at open circuit and was then swept to 4.5 V (Curve C) had a greatly diminished Bi4f\(_{7/2}\) intensity between 158 and 161 eV that was also shifted to lower binding energies relative to Curves A and B. This was unexpected because
essentially no electrochemical processes were observed during the potentiodynamic scan. The samples reported as Curves D, E, and F each began with a potentiostatic hold at 1.5 V for 24 h. Discharge of the BiF$_3$ to Bi$^0$ + LiF and growth of the SEI (Curve D) resulted in Bi metal which did not require ion-beam etching to be detected. This sample included a small peak at approximately 159 eV in the range of where the Bi4f$_{7/2}$ peak for Bi$_2$O$_3$ would be observed. The origin was suspected to result from momentary exposure of the sample to the atmosphere while loading the XPS instrument. Discharge of the BiF$_3$ film and growth of the SEI followed by a potentiodynamic sweep to 3.3 V (Curve E) resulted in a Bi4f$_{7/2}$ peak (159.4 eV) that was intermediate to that of Bi$_2$O$_3$ and BiF$_3$. 3.3 V is prior to the onset of BiF$_3$ reconversion observed in Figure 4.5; therefore, any bismuth compound with Bi-F character was unexpected unless partially etched by the HF-containing LiPF$_6$ electrolyte. Lastly, discharge of the BiF$_3$ film and growth of the SEI followed by a potentiodynamic sweep to 4.5 V (Curve F) resulted in a Bi4f$_{7/2}$ peak (160.0 eV) that was intermediate to Bi$_2$O$_3$ and BiF$_3$; however, the peak was more so like BiF$_3$ than Bi$_2$O$_3$.

4.3.4 XPS of BiF$_3$ films, subsurface analysis

Ion-beam etching of the same samples of Figure 4.6(a) is shown in Figure 4.6(b). As expected, and in contrast to the top surface analysis, Curves A, B, and C were nearly identical and were consistent with BiF$_3$. The Bi4f$_{7/2}$ peak was 160.5 eV for all three samples. Sample C, which was directly swept to 4.5 V, did not result in a shift to a lower binding energy as was observed for the unetched sample C. When not etched, Curve D (lithiated at 1.5 V) exhibited a small peak characteristic of Bi$_2$O$_3$, but no such signal was detected after merely 30 s of ion-beam etching; only signals associated with Bi metal were observed. The sample which included a potentiostatic hold at 1.5 V followed by a potentiodynamic sweep to 3.3 V (Curve E) also had its Bi-O character etched away, although it remained intact after a significant 90 s of exposure to
the ion-beam. The Bi4f7/2 signal intensity between 158 and 161 eV for the non-etched film (Figure 4.6(a), Curve E) was relatively high compared to (Figure 4.6(a), Curve D), and a much longer duration of ion-beam etching was required to remove material exhibiting Bi4f7/2 peaks between 158 and 161 eV. Thus, the Bi-O character of the 3.3 V sample (Curve E) was more likely caused by interaction of Bi with the SEI rather than an oxide contaminant induced by exposure to atmosphere. Lastly, for the sample held at 1.5 V and swept to 4.5 V (Curve F), the Bi4f7/2 peak between 158 and 161 eV was maintained for the duration of etching. Assuming the topmost material of the 4.5 V sample (Curve F) was removed at a similar rate to the material of Curve D, any surface phases subject to contamination have been ablated after 5 min of etching. The remaining material of the 4.5 V sample (Curve F) was therefore concluded to be a reconverted bismuth compound with a Bi4f7/2 binding energy peak observed at 160.2 eV. The reconverted compound appeared not as pure BiF3 but instead as a BiOxF3−2x phase with a small amount of oxide character (Table 4.1). Also of note is the difference between Figure 4.6(b), Curves C and F. BiF3 was observed for a potentiodynamic sweep to 4.5 V without having formed Bi0, LiF, and SEI (Curve C) whereas the interaction of Bi0, LiF, and SEI resulted in the formation of BiOxF3−2x during reconversion (Curve F).

In summary, a potentiodynamic sweep from open-circuit to 4.5 V without conversion of the BiF3 and SEI growth (Curve C) resulted in BiF3; conversion of the bismuth film at 1.5 V (Curve D) resulted in Bi metal and a slight Bi2O3 contaminant that was etched away in less than 30 s; reconversion to 3.3 V (Curve E) yielded a subsurface layer of oxygen-rich bismuth oxyfluoride that was etched away after 90 s; and reconversion to 4.5 V (Curve F) resulted in the formation of a fluorine-rich BiOxF3−2x phase.
4.3.5 BiF$_3$ nanocomposite electrodes

XPS of the carbon planchets in the first section of the results clearly point to the decomposition of the SEI film at potentials exceeding 4 V. To confirm whether this decomposition also occurs with the SEI formed on converted bismuth fluoride nanocomposites, isotope enriched carbonates combined with $^{13}$C NMR were employed. The Discharge 2V Hold BiF$_3$ nanocomposite sample in the EC* enriched EC:DEC electrolyte (Figure 4.7) revealed the presence of Li$_2$CO$_3$ whereas this phase was not observed in the corresponding DEC* enriched electrolyte sample (not shown). This was in agreement with the previously identified decomposition of cyclic but not linear organic carbonates on Bi (Chapter 3).[110] For either of the samples which underwent galvanostatic charging after the potentiostatic hold at 2.00 V (Figure 4.7, Half or Full Reconversion), Li$_2$CO$_3$ was not observed with $^{13}$C NMR. The Half Reconversion sample reached a maximum potential of 3.36 V vs. Li/Li$^+$. Thus, the disappearance of Li$_2$CO$_3$, as evidenced in the $^{13}$C NMR results, occurred over a potential range far less positive than that observed on the glassy carbon planchets. The NMR observations provided more support to the idea that the anodic current observed on the BiF$_3$-coated planchet originated from electrochemical oxidation of the SEI.)
Figure 4.7. Carbonate region of $^{13}$C NMR of BiF$_3$ nanocomposites cycled in EC* enriched electrolyte. Li$_2$CO$_3$ not observed after charging the BiF$_3$ nanocomposite (both Half and Full Reconversion). The electrolyte did not decompose on the SP carbon at 2.00 V vs. Li/Li$^+$. Discharge 2V Hold sample multiplied 4x to accentuate the Li$_2$CO$_3$ signal.
Additional electrochemical trials were run in the potentiodynamic mode to mimic previous experiments in which the extent of SEI formation was intensified by sweeping the potential of the BiF$_3$ nanocomposite to lower potentials vs. Li/Li$^+$ (Figure 3.15, Figure 3.17, and Figure 3.18).[110] The electrolyte used was the non-enriched 1 M LiPF$_6$ EC:DMC 1:1 v/v. Potentiodynamic scans from 2.0 V, 1.6 V, and 1.4 V are shown in Figure 4.8, after discharge of the BiF$_3$ and SEI growth. In concert with the potentiodynamic scan for the BiF$_3$ film (Figure 4.5), an anodic signal was indicated above 2.8 V. The extent of SEI formation at potentials ≤ 2.0 V also corresponded with the increase in the anodic current observed from 2.8 V to 3.2 V (Figure 4.8). From the disappearance of the Li$_2$CO$_3$ in the $^{13}$C NMR data at potentials ≤ 3.36 V vs. Li/Li$^+$, the anodic current occurring above 2.8 V, prior to reconversion of Bi$^0$ + LiF, has been ascribed to decomposition of the SEI.

**Potentiodynamic sweeps of BiF$_3$ nanocomposites**

![Potentiodynamic sweeps of BiF$_3$ nanocomposites](image)

**Figure 4.8.** Potentiodynamic scans of BiF$_3$ nanocomposite electrodes after potentiodynamic discharge sweep to 2.0 V, 1.6 V, or 1.4 V vs. Li/Li$^+$. As the extent of SEI formation increased at potentials ≤ 2.0 V, the extent of anodic current from 2.8 V to 3.2 V increased correspondingly.
4.4. Discussion

4.4.1 Glassy carbon electrodes

The primary electrolyte decomposition products formed as a result of the reduction of the organic carbonate electrolyte were observed to be Li$_2$CO$_3$ and LiF. If either the Li$_2$CO$_3$ or LiF can be dissociated via an anodic electrochemical process, one might expect these reactions to occur on a non-catalytic substrate at potentials above 3.82 V and 6.10 V vs. Li/Li$^+$, respectively, (calculated from $\Delta G^*$ at 25°C)[116] as

$$2\text{Li}_2\text{CO}_3 \rightarrow 4\text{Li}^+ + 4\text{e}^- + 2\text{CO}_2(\text{g}) + \text{O}_2(\text{g}) \quad (4.3)$$

$$2\text{LiF} \rightarrow 2\text{Li}^+ + 2\text{e}^- + \text{F}_2(\text{g}) \quad (4.4)$$

The cyclic voltammograms in Figure 4.3 displayed an anodic current above approximately 4 V vs. Li/Li$^+$, and the XPS data (Figure 4.4) supported removal of Li$_2$CO$_3$ from the surface of the glassy carbon electrode above 4 V as well. Without the capability of directly observing the evolution of gases, reaction scheme (4.3) seemed the most plausible on the glassy carbon electrode. The trials performed on the glassy carbon supported the notion of the SEI decomposing at high positive potentials vs. Li/Li$^+$.

Since there appeared to be no lithium remaining on the surface after the potentiodynamic sweep to 5.0 V (Figure 4.4, Curve G) the results would also seem to indicate the formation and destruction of an SEI layer with replenishment of Li$^+$ back to the electrolyte from the glassy carbon electrode. The implication here is that the destruction of the SEI at high potentials could result in a reversible surface chemistry with little to no penalty of irreversible capacity loss. This also offered the question of the reactivity of the released O$_2$ and CO$_2$ with conversion materials which was the core of this research.
The XPS data for the glassy carbon electrodes after a 24 h potentiostatic hold at 1.0 V also served as an important link to previous work conducted on Bi films at 1.5 V (Chapter 3)\[^{[110]}\]. The electrolyte decomposition products formed on the glassy carbon at 1.0 V were very similar chemically to those observed on the Bi film at 1.5 V. The glassy carbon data strongly suggested the SEI can decompose at high potentials through the anodic decomposition of \( \text{Li}_2\text{CO}_3 \) above 4 V thus establishing the possibility of the removal of \( \text{Li}_2\text{CO}_3 \) from bismuth fluoride nanocomposites cycled to 4.5 V. The NMR data of \(^{13}\text{C}\) isotope enriched EC clearly confirmed that the \( \text{Li}_2\text{CO}_3 \) SEI does indeed decompose during the reconversion of the \( \text{BiF}_3 \) nanocomposite (at potentials below 3.4 V) and confirmed that we can make such a link.

### 4.4.2 Trials with bismuth fluoride films and proposed mechanisms for the formation of \( \text{BiO}_x\text{F}_{3-2x} \)

The samples which underwent extensive ion-beam etching supported the formation of an oxygen-rich bismuth phase at 3.3 V and \( \text{BiO}_x\text{F}_{3-2x} \) at 4.5 V. Ion-beam etching helped to discern between oxygen that was incorporated into the reconverted film through an electrochemical process vs. oxygen that originated as an artifact of sample handling. Despite possible ambiguities, it was still absolutely plausible to consider interactions of the SEI with \( \text{Bi}^0 \) that would yield bismuth compounds with a high degree of oxygen incorporation.

Reversible conversion reactions have been observed for polyatomic anion groups including oxalates\[^{[35, 36]}\], carbonates\[^{[35, 37, 38]}\], and formates\[^{[39]}\]. It is conceivable that below the potential necessary for the reconversion of \( \text{BiF}_3 \) from \( \text{Bi}^0 + \text{LiF} \), \( \text{Bi}^0 \) could interact with \( \text{Li}_2\text{CO}_3 \) of the SEI to yield a new bismuth compound containing \( \text{Bi}, \text{O} \), and/or \( \text{C} \). No known \( \text{Bi}_2(\text{CO}_3)_3 \) compound exists as a bulk phase. Instead bismuth oxide subcarbonate, \( \text{Bi}_2\text{O}_2\text{CO}_3 \), could be formed as a result of partial \( \text{CO}_2(\text{g}) \) evolution during reconversion of \( \text{Bi}^0 \) with \( \text{Li}_2\text{CO}_3 \) (Eqn. (4.5)).
\[2\text{Bi}^\circ + 3\text{Li}_2\text{CO}_3 \rightarrow \text{Bi}_2\text{O}_2\text{CO}_3 + 2\text{CO}_2(\text{g}) + 6\text{Li}^+ + 6\text{e}^- \quad (4.5)\]

If the CO\textsubscript{2} was completely evolved during the reaction of Bi\textsuperscript{0} and Li\textsubscript{2}CO\textsubscript{3}, Bi\textsubscript{2}O\textsubscript{3} could be formed above 2.96 V vs. Li/Li\textsuperscript{+} (calculated from ΔG\textsuperscript{o} at 25°C)[116] (Eqn. (4.6)).

\[2\text{Bi}^\circ + 3\text{Li}_2\text{CO}_3 \rightarrow \text{Bi}_2\text{O}_3 + 3\text{CO}_2(\text{g}) + 6\text{Li}^+ + 6\text{e}^- \quad (4.6)\]

Eqns. (4.5) and (4.6) consider bismuth oxide phases that do not rely on the decomposition of Li\textsubscript{2}CO\textsubscript{3} according to Eqn. (4.3). Instead, conversion reactions involving Bi\textsuperscript{0} occur.

If instead of by a conversion reaction as proposed in Eqns. (4.5) and (4.6) we consider a scenario in which bismuth catalyzes the decomposition of Li\textsubscript{2}CO\textsubscript{3} in such a way as to shift the potential of Eqn. (4.3) to values much lower than 3.82 V vs. Li/Li\textsuperscript{+}. If this were to occur, the spontaneous interaction of Bi\textsuperscript{0} with O\textsubscript{2}(\text{g}) and CO\textsubscript{2}(\text{g}) evolved from Li\textsubscript{2}CO\textsubscript{3} would yield Bi\textsubscript{2}O\textsubscript{3} or Bi\textsubscript{2}O\textsubscript{2}CO\textsubscript{3}. So long as the potential of the positive electrode exceeded 2 V, the Bi\textsubscript{2}O\textsubscript{3} and Bi\textsubscript{2}O\textsubscript{2}CO\textsubscript{3} phases would be stable. During the potentiodynamic sweep from 1.5 V, the anodic feature highlighted in Figure 4.5 coincided with the calculated potential of Eqn. (4.6). Therefore, a reaction scheme like that in Eqn. (4.6) seemed more probable on the Bi\textsuperscript{0} than that of Eqn. (4.3).

It has been shown that bismuth oxyfluoride phases react in a stepwise fashion during discharge. First, above 2.6 V vs. Li/Li\textsuperscript{+}, the Bi-F bonds are converted, leaving Bi\textsubscript{2}O\textsubscript{3}, Bi\textsuperscript{0}, and LiF. Then, below 1.8 V, the Bi\textsubscript{2}O\textsubscript{3} is converted to Bi\textsuperscript{0} and Li\textsubscript{2}O, and the overall specific capacity of the oxyfluoride phase is attained. During reconversion of the Bi\textsuperscript{0}, LiF, and Li\textsubscript{2}O, the reaction proceeds first by reforming Bi\textsubscript{2}O\textsubscript{3}, then at higher potentials, the bismuth oxyfluoride is reconstructed.[8] It would therefore seem possible that a fully converted bismuth fluoride phase which has a portion of its Bi\textsuperscript{0} in direct contact with Li\textsubscript{2}CO\textsubscript{3} from the SEI could undergo a stepwise reconversion sequence first to Bi\textsubscript{2}O\textsubscript{3} and then to BiO\textsubscript{x}F\textsubscript{3-2x} instead of a pure BiF\textsubscript{3} phase (Eqn. (4.7(a))).
$\text{Bi}^0 + (3-2x)\text{LiF} + x\text{Li}_2\text{CO}_3(\text{SEI}) \rightarrow x\text{Bi}_2\text{O}_3 + 2x\text{Li}^+ + 2xe^- + (1-2x)\text{Bi}^0 + (3-2x)\text{LiF} + x\text{CO}_2(\text{g}) \uparrow \quad (4.7(a))$

$$x\text{Bi}_2\text{O}_3 + 2x\text{Li}^+ + 2xe^- + (1-2x)\text{Bi}^0 + (3-2x)\text{LiF} \rightarrow \text{BiO}_x\text{F}_{3-2x} + 3\text{Li}^+ + 3e^- \quad (4.7(a))$$

Eqn. (4.7(a)) would proceed at potentials between 2 and 3 V, and Eqn. (4.7(a)) would proceed above 3.4 V vs. Li/Li$^+$ (observed potential of BiF$_3$ reconversion). First, Eqn. (4.7(a)) results in a bismuth phase rich in oxygen, then, incorporation of fluorine in Eqn. (4.7(a)) yields a fluorine-rich oxyfluoride phase. This is perfectly consistent with the XPS data of this study. Reconversion to 3.3 V exhibited an oxygen-rich bismuth compound. As the samples were converted towards more positive potentials, an increase of the fluorine vs. oxygen content of the BiO$_x$F$_{3-2x}$ was observed. The evolution of the chemistry of the BiF$_3$ as a function of its state of charge during the first cycle is depicted in Figure 4.9.

$E \sim 3.2 \text{ V}$  
$E \leq 2.0 \text{ V}$  
$2.0 \text{ V} < E \leq 3.3 \text{ V}$  
$E \rightarrow 4.5 \text{ V}$

![Figure 4.9](image_url)

**Figure 4.9.** Schematic showing the evolution of BiF$_3$ to BiO$_x$F$_{3-2x}$ during the first discharge/charge cycle of BiF$_3$ thin film electrode on glassy carbon substrate in a cyclic carbonate electrolyte such as 1 M LiPF$_6$ EC:DMC. (a) Open circuit condition. (b) After discharge $\leq 2$ V, SEI growth on Bi$^0$. (c) During delithiation (reconversion), SEI and Bi$^0$ interact to yield oxygen-rich Bi compound. (d) At the completion of reconversion to 4.5 V, BiO$_x$F$_5$ + Bi$^0$ + LiF form F-rich BiO$_x$F$_{3-2x}$. 
4.4.3 Ramifications of BiO$_x$F$_{3-2x}$ formation

Though it was previously speculated that a relatively low oxygen content may enhance the electrochemical activity of the electronically insulating BiF$_3$, the formation of BiOF and BiO$_{0.5}$F$_2$ has been shown to have a detrimental impact on the cycling performance of bismuth nanocomposite positive electrodes. Beyond this, the gradual evolution of the bismuth fluoride phase towards a bismuth oxyfluoride phase has its own ramifications. The typical discharge protocol for BiF$_3$ nanocomposites is limited to 2.0 V. The stepwise reaction sequence of bismuth oxyfluorides will permit reduction of Bi-F bonds with Li$^+$, but 2.0 V is above the potential at which Bi$_2$O$_3$ reduction occurs. There is a loss of capacity of the positive electrode because some of the bismuth of the initially active BiF$_3$ becomes electrochemically inactive through the formation of Bi-O bonds. As additional interactions of the Bi$^0$ and SEI occur during subsequent cycling, a greater extent of Bi-O bonding results. With LiPF$_6$, the typical salt utilized in state of the art electrolytes, a different mechanism of capacity fade related to enhanced dissolution of oxygen-rich bismuth compounds may very well occur. Bismuth oxyfluorides have previously been demonstrated to cycle very poorly, possibly due to HF attack from the electrolyte. Despite not identifying the exact mechanism of capacity fade, a clear correlation exists for the presence of electrolyte decomposition products, and hence the likelihood for oxygen incorporation into the reconverted bismuth compound, and the long term cycling performance of the nanocomposite positive electrodes. SEI formation, observed on Bi from cyclic carbonates but not linear carbonates, was directly correlated with poorer cycling (Chapter 3).

4.5. Conclusion

Li$_2$CO$_3$ SEI, formed by electrochemical reduction of EC, has been found to be unstable on a glassy carbon electrode at potentials exceeding 4 V vs. Li/Li$^+$. XPS analysis revealed the disappearance
of Li₂CO₃ from the glassy carbon, and $^{13}$C NMR revealed the disappearance of Li₂O₃ from reconverted BiF₃ nanocomposites. Anodic SEI decomposition during the reconversion of bismuth fluoride nanocomposite positive electrodes has been concluded. Bismuth oxyfluoride powders have been examined with XPS and served as standards to aid in the determination of the bismuth compounds resulting from interactions amongst Bi⁰, LiF, and Li₂CO₃ during reconversion. After a potentiostatic hold at 1.5 V followed by potentiodynamic sweeps to 3.3 V and 4.5 V, XPS analysis revealed bismuth compounds which incorporated oxygen from the decomposition of the SEI. For the 4.5 V sample, reconversion yielded a BiOₓF₃₋₂ₓ phase with a fluorine content between BiOₐF₂ and BiF₃. This phase was likely induced by the formation of a bismuth compound rich in oxygen between 2 V and 3 V followed by the conversion of Bi⁰ and LiF to yield BiOₓF₃₋₂ₓ.

A mechanistic link has been established between the recently identified relationship of poor cycling of bismuth fluoride nanocomposites with SEI formed from the cathodic decomposition of cyclic carbonate electrolytes on Bi⁰ (Chapter 3).[110] During reconversion, the decomposition of the SEI leads to the formation of BiOₓF₃₋₂ₓ instead of BiF₃. Despite not identifying the exact reaction pathway by which oxygen incorporation occurs, this work has deepened our understanding of the intricacies of the interfacial chemistry during the reconversion process. Several plausible schemes have been proposed based on our electrochemical, XPS, and NMR observations paired with thermochemical data.
5. High concentration dinitrile, 3-alkoxypropionirile, and linear carbonate electrolytes enabled by vinylene carbonate and monofluoroethylene carbonate additives

5.1. Introduction

The voltage and thermal stabilities of electrolytes as well as their ionic conductivities and interfacial properties with electrodes and current collectors must be considered when assigning Li-ion batteries to new applications. The most prevalent classes of solvents used to formulate nonaqueous liquid electrolytes for Li-ion batteries are organic carbonates, esters, and ethers.[73] Device performance and safety would be difficult to achieve with these classes of solvents if wide temperature fluctuations or cell voltages greater than 5 V were demanded.

The electrolytes most commonly used in Li-ion batteries contain lithium hexafluorophosphate (LiPF₆) dissolved in binary or ternary mixtures of ethylene carbonate (EC) with dimethyl carbonate (DMC), ethyl methyl carbonate (EMC), and/or diethyl carbonate (DEC).[73, 117] The EC content is typically between 30 and 50 vol%. A high EC content is problematic when the temperature is reduced below 0°C because the electrolyte solidifies leading to a sharp reduction in conductivity.[77] Thus, when exploring organic carbonates for low temperature applications, the approach of decreasing the EC content and utilizing linear esters as the major solvent components was taken to lower the freezing point as well as the viscosity of the electrolyte.[78] This approach improved the low temperature conductivity of LiPF₆ electrolytes. However, it was still crucial for the electrolyte to provide favorable chemistries for the formation of stable electrode / electrolyte interphases and reasonably facile charge transfer kinetics. The EC content was reduced but not eliminated because it was necessary for the formation of a stable electrode / electrolyte interphase. Since the melting point of EC is so great (36.4°C), even a modest fraction greatly increases the liquidus of the electrolyte solvent.[79] Regarding the
charge transfer process, lithium tetrafluoroborate (LiBF₄) was measured to have a lower activation energy than LiPF₆ at -20°C. The charge transfer resistance of lithium bis(trifluoromethylsulfonyl)imide (LiTFSI) was also lower relative to LiPF₆.

Linear aliphatic carbonates (DMC, EMC, and DEC) have been demonstrated to be well-suited as co-solvents due to their low reactivity. EMC was found to be the most stable of the three with respect to both the positive and negative electrodes. Additionally, when comparing the melting points of the linear aliphatic carbonates, $mp_{DEC} (-74.2^\circ C) < mp_{EMC} (-54.5^\circ C) < mp_{DMC} (5.5^\circ C)$. As opposed to making ternary or quaternary blends of organic carbonates, we sought to use EMC as the principal solvent in the electrolyte.

Alternative classes of solvents beyond organic carbonates, esters, and ethers that may offer enhanced attributes are alkoxypropionitriles and dinitriles. An example of each is 3-methoxypropionitrile (3MPN) and adiponitrile (ADN). 3MPN has been evaluated on numerous occasions in dye-sensitized solar cells as a lower volatility alternative to acetonitrile and as a gel electrolyte. Although rarely evaluated in Li-ion cells, Grätzel et al. found that 3MPN afforded better rate capability in cells using $Li_4Ti_5O_{12}$ as the negative electrode relative to organic carbonates due to lower charge transfer impedance at the negative electrode. This was despite these electrolytes having nearly identical viscosity and ionic conductivity values at room temperature. This nitrile has a very low melting point (-57°C) and high boiling point (165°C), making it appealing for low temperature applications or cells experiencing wide temperature fluctuations.
ADN has several attributes favorable for Li-ion batteries. It is among the aprotic solvents with the highest reported anodic stability limits.[86] Its physicochemical properties, chiefly its high flashpoint (163°C) and boiling point (295°C), would be well-suited for applications in which Li-ion batteries will experience high temperatures.[86, 87, 88, 89] Another key attribute of ADN is its foreseeable low cost as it is a precursor in the industrial manufacture of nylon.[120] Upwards of a billion kilograms of ADN are produced annually.[121] Conductivity measurements as a function of temperature and cycling trials in a 4 V system have been conducted.[87] ADN, along with other dinitrile solvents, has recently been used as a co-solvent with organic carbonates to evaluate the electrochemical performance and voltage profiles of > 5 V fluorophosphate cathodes.[92]

The few published reports utilizing nitrile solvents are of interest because the positive electrodes exhibited good cycling performance, and impressively, the dinitriles were stable above 5 V. However, both the 3MPN and ADN solvents are thermodynamically unstable at low potentials (3MPN: -2.7 V vs. SCE[86] or ~0.6 V vs. Li/Li⁺; ADN: -2.9 V vs. SCE[86] or ~0.4 V vs. Li/Li⁺) and do not seem to offer the ability to form a stabilizing SEI on carbonaceous anodes with relatively low potential vs. Li/Li⁺. Accordingly, the electrochemical evaluation of 3MPN utilized Li₄Ti₅O₁₂ as the negative electrode.[85] This effectively reduced the electrolyte operating window by 1.5 V and avoided the highly reducing interfacial environment found on Li metal or lithiated carbon. The ADN was examined using co-solvent systems in which the organic carbonate was 50 vol% of the electrolyte blend.[87, 89, 92] The stability of ADN was not evaluated with the nitrile existing as the primary solvent in systems using Li foil[89, 92] or carbon[87]. LiBOB was examined as an SEI promoter in an ADN electrolyte in a cell employing a
carbon negative electrode, but the cell faded rapidly also in the absence of ethylene carbonate as a 1:1 v/v co-solvent.[87]

While the mechanisms of formation and specific chemistries of the solid electrolyte interphase (SEI) are subject to continued scientific inquiry, there is little doubt that without an effective SEI, graphitic carbon electrodes would be unable to be utilized in lithium-ion batteries. The SEI imparts stability to electrolyte reduction on the highly negative lithiated carbon electrode. In systems in which electrolyte solvent decomposition, gas evolution, co-intercalation of solvents, and/or exfoliation of graphitic carbon occur, a well-formed SEI effectively limits these undesirable reactions, thus enabling good cyclability.[20] In this work, therefore, we sought to determine if additives could enable stability of the EMC, 3MPN, and ADN on carbon electrodes while maintaining an EMC or nitrile-rich solvent. Specifically, vinlylene carbonate (VC) and monofluoroethylene carbonate (FEC) were examined.

VC contains a polymerizable vinyl functionality and is a highly strained cyclic allyl carbonate.[73, 122] It has been found to decompose irreversibly between 0.8-1.1 V vs. Li/Li$^+$ on graphite.[122, 123] VC decomposition on the negative electrode yielded polymeric species and a high content of alkyl carbonate functionalities leading to a reduction of the irreversible capacity loss, greater stability of the SEI at elevated temperatures, and improvement of the cycle life performance in commercial Li-ion cells.[73] FEC (4-fluoro-1,3-dioxolan-2-one) is structurally similar to ethylene carbonate (1,3-dioxolan-2-one). The effect of FEC on the cycling performance of a lithium-ion battery with a graphite anode has been demonstrated in EC/PC-based electrolytes.[124] FEC addition to 1 M LiPF$_6$ EC:EMC 3:7 v/v has led to lower interfacial impedances than the
electrolyte without FEC and improved thermal properties of the SEI.[125] Lastly, FEC, especially with the co-additive vinyl sulfone, exhibited better swelling inhibition properties than VC.[126]

It should be noted that in Chapter 3, cyclic organic carbonates were found to have a detrimental impact on the cycling performance of bismuth fluoride nanocomposite positive electrodes.[110] It was partially our aim to develop electrolytes which may enable better performance of metal fluoride nanocomposites in addition to the more general interest of identifying suitable electrolyte solvents which are not based on combinations of cyclic and linear organic carbonates. The present work focuses on LiCoO$_2$ vs. synthetic graphite Li-ion cells as a well understood system for electrolyte evaluation.

5.2. Experimental

5.2.1 Materials fabrication

The solvents utilized for blending electrolytes were EMC (Novolyte), 3MPN (Fluka), ADN (Novolyte), VC (Ferro), FEC (Novolyte), and EC (Aldrich). With the exceptions of 3MPN and ADN, the solvents were battery or electrolyte grade and were delivered with < 20 ppm H$_2$O. The ADN was used as-received with a manufacturer reported water content of 87.5 ppm. The 3MPN initially had a water content of approximately 700 ppm as measured by coulometric Karl Fischer titration (Model 684, Metrohm). The 3MPN was treated in the following manner to reduce its water content. Molecular sieves (3 Å, Aldrich) were dried overnight in vacuo at 120°C in glassware. 3MPN was stored over the molecular sieves for 7 d with a ratio of 3 mL of 3MPN for each 1 g of molecular sieves. This treatment routinely yielded < 10 ppm H$_2$O.

The salts used in this study were LiPF$_6$ (Ferro), LiBF$_4$ (Ferro), LiTFSI (HQ-115, 3M), and lithium perchlorate (LiClO$_4$, Aldrich). The LiPF$_6$ was selected for use in the EMC electrolytes because
many of the previous studies in organic carbonates used this salt. The LiTFSI and LiBF₄ were blended as 1 M LiTFSI + 0.25 M LiBF₄. First, as mentioned above, both were identified as better alternatives to LiPF₆ for low temperature applications. Second, the adiponitrile was found to not solvate LiPF₆, but it could host 1 M LiTFSI + 0.25 M LiBF₄ with gentle stirring and heating. Third, if considering high temperature operation, both LiTFSI and LiBF₄ are more thermally stable and resistant to hydrolysis than LiPF₆.[73, 77] Lastly, LiTFSI is incompatible with aluminum current collectors. A co-salt such as LiPF₆ or LiBF₄ would aid in suppressing corrosion.[127] Please note that although 3MPN has the ability to solvate at least 0.5 M LiBF₄ with 1 M LiTFSI, studies were restricted to 0.25 M due to this being the maximum solubility of LiBF₄ in ADN. Table 5.1 lists all the electrolyte blends considered in this study.

<table>
<thead>
<tr>
<th>Electrolyte blend</th>
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<tr>
<td>1 M LiPF₆ EMC no additive, + 5 vol% VC, + 5 vol% FEC</td>
</tr>
<tr>
<td>1 M LiTFSI + 0.25 M LiBF₄ EMC no additive, + 5 vol% VC, + 5 vol% FEC</td>
</tr>
<tr>
<td>1 M LiTFSI + 0.25 M LiBF₄ ADN no additive, + 5 vol% VC, + 5 vol% FEC</td>
</tr>
<tr>
<td>1 M LiTFSI + 0.25 M LiBF₄ ADN + 5 vol% EC</td>
</tr>
<tr>
<td>1 M LiTFSI + 0.25 M LiBF₄ ADN + 0.5 vol% FEC</td>
</tr>
<tr>
<td>1 M LiTFSI + 0.25 M LiBF₄ 3MPN no additive, + 5 vol% VC, + 5 vol% FEC</td>
</tr>
<tr>
<td>1 M LiClO₄ EMC no additive, + 5 vol% FEC</td>
</tr>
</tbody>
</table>

Positive electrodes were cast in a dry room (dewpoint < -30°C) using LiCoO₂ (C-22, Seimi), polyvinylidene difluoride (PVdF) resin (Kynar Flex 2801, Arkema), and conductive carbon black (SuperP, Timcal) with 89:6:5 wt % loading. The PVdF resin was dissolved with acetone, and propylene carbonate was used as a plasticizer. Negative electrode tapes were fabricated in a similar manner but with mesocarbon microbeads (MCMB-2528, Osaka Gas) as the active material with wt % 88:6:6 loading. Prior to coin cell assembly, diethyl ether was used to extract
the plasticizer. Freestanding electrode tapes were dried briefly at 70°C in the dry room before being transferred to a helium filled glovebox with H₂O and O₂ < 1 ppm.

5.2.2 Carbon vs. Li half cells
Stainless steel 2032-type coin cells (Hohsen) were used. The cell was comprised of a 12.7 mm disc of MCMB electrode, two glass fiber separators (GF/D, Whatman) saturated with electrolyte, and Li foil (FMC). These cells were examined on a MacPile II (BioLogic) in the potentiodynamic mode at a fixed temperature of 24°C. Each step was ±1.25 mV/0.006 h, or approximately 58 μVs⁻¹ if estimated to run in a continuous mode. The cells were swept from the open circuit voltage (OCV) which was approximately 3 V to 0.05 V to 3.00 V (all half-cell potentials reported vs. Li/Li⁺) for two cycles to examine the effectiveness of additives on stabilizing the interface of the MCMB electrode and electrolyte.

12.7 mm spectroscopically pure (impurities < 2 ppm) graphite planchets (Ted Pella) were used instead of MCMB tape electrodes to avoid the overlapping signals of the PVdF binder and SP carbon during XPS investigations, particularly in the F1s and C1s core levels. Swagelok-type cells using stainless steel plungers were assembled in a similar fashion as the half cells above. These cells were swept from OCV to 1.00 V and stopped, or they were swept to 0.05 V and back to 1.50 V. After electrochemical testing, the graphite planchets were removed from the Swagelok bodies. Unless otherwise stated, the planchet was thoroughly rinsed with dimethyl carbonate (DMC, Novolyte) to remove as much of the residual electrolyte as possible.

5.2.3 LiCoO₂ vs. MCMB Li-ion cells
2032-type coin cells (Hohsen) were assembled with 12.7 mm discs of both the positive and negative electrodes and glass fiber separators saturated with electrolyte. The mass ratio of the active components was 2.20±0.05:1 LiCoO₂:MCMB. Aluminum-clad stainless steel positive
electrode current collectors were used exclusively with LiPF<sub>6</sub>-containing electrolytes, while non-aluminized stainless steel was used with LiTFSI + LiBF<sub>4</sub> electrolytes. All the formulations listed in Table 5.1 were used in the Li-ion cells with the exception of the LiClO<sub>4</sub> EMC-based electrolytes. Coin cells were cycled in the galvanostatic mode between 3.50 V and 4.15 V vs. the negative electrode on a MacPile II at a fixed temperature of 24°C. The charge/discharge rates were C/5 except for cycles 51 through 60 which were 1C and cycles 71 through 80 which were C/2. The impedance was measured for the initially assembled cell and at the end of the 50<sup>th</sup>, 60<sup>th</sup>, 70<sup>th</sup>, 80<sup>th</sup>, and 100<sup>th</sup> discharge sweeps with Models SI 1260/1287 (Solartron) and ZPlot (Scribner Associates). The frequency was swept from 1 MHz down to 1 Hz with a 10 mV amplitude at 0 V vs. open circuit. After monitoring the impedance at the end of the 100<sup>th</sup> cycle, the cell was discharged at C/50 to 1.50 V to extract as much Li<sup>+</sup> as possible from the negative electrode. The coin cell was reintroduced into the glovebox and disassembled. The negative electrodes were retrieved from each cell and cut in half. One half was rinsed with DMC for several minutes to remove the excess electrolyte. The other half received no such treatment. Both halves were sealed individually in gastight sample holders until x-ray photoelectron spectroscopy (XPS) analysis was performed.

5.2.4 Surface characterization

The XPS instrument (K-Alpha, Thermo) was fitted with a flood gun to compensate for surface charging. Low energy, non-sputtering, charged particles were emitted from the flood gun. Monochromatic AlKα radiation was used with a spot size of 400 μm. Core level spectra were recorded using a 50 eV pass energy and 20 scans. Analyses were conducted at room temperature. Prior to initializing the flood gun, the pressure within the analysis chamber was on the order of 5 x 10<sup>-8</sup> mbar. While the flood gun was operational, the analysis pressure approached 3 x 10<sup>-7</sup> mbar. Data was processed using Avantage v.4.51 or v.4.67 (Thermo). 284.8
eV was used as an internal standard; uncorrected spectra were within several tenths of an eV for all scans.

5.3. Results

5.3.1 Cyclic voltammetry of MCMB vs. Li half cells
Potentiodynamic scans of MCMB half cells in 1 M LiPF₆ EMC-based and 1 M LiTFSI + 0.25 M LiBF₄ EMC-, ADN- and 3MPN-based electrolytes are shown in Figures 5.1-5.4, respectively. It would appear that EMC (Figure 5.1 and Figure 5.2) without any additives may be stable with respect to graphitic carbon as the well known cathodic and anodic lithium intercalation into graphite at potentials < 0.5 V showed good initial reversibility from cycle 1 to cycle 2 and a fairly well pronounced SEI formation wave at < 0.8 V (approximately 0.5 V) for the neat solvent. In sharp contrast, ADN (Figure 5.3) exhibited a poorly defined reversible sweep after a large decomposition wave in the first cycle with no subsequent reversibility, and 3MPN (Figure 5.4) showed a large decomposition reaction at approximately 0.8 V with no evidence of Li⁺ intercalation into graphite. Examination of the nitrile cells after testing revealed yellowish-brown decomposition products across both electrolyte separators, consistent with nitrile decomposition.

In each of the four electrolyte groups containing VC and FEC additives, a small amount of VC and FEC decomposed on the surface of the MCMB during the first reduction sweep. For VC additives, the cathodic decomposition occurred within a voltage range of 0.8-1.1 V for all electrolytes investigated, consistent with previous reports with non-nitrile solvents.[122, 123] For FEC the cathodic decomposition was found within the range of 1.0-1.6 V. While the FEC reduction in LiPF₆ EMC (Figure 5.1) compared favorably with LiPF₆ in a blend of carbonate solvents[128], an explanation for the wide variation in the reduction potential for FEC as a
function of salt or solvent (Figures 5.1-5.4) cannot be given at present. Below 0.5 V, Li⁺ insertion into MCMB occurred, followed by extraction of Li⁺ during the sweep to higher potentials. On the second reduction sweep, no current was observed between 0.8 and 1.7 V. This is consistent with the formation of a stable SEI. Li⁺ insertion of the MCMB occurred to the same extent as the first reduction sweep. The VC and FEC additives effectively stabilized the interfacial region in a manner that prevented decomposition of the EMC, ADN, and 3MPN solvents and enabled lithiation / delithiation to occur at low additive concentrations.
Figure 5.1. Potentiodynamic scans of MCMB half cells in 1 M LiPF$_6$ EMC with (a) no additive, (b) 5 vol% VC, and (c) 5 vol% FEC. Insets have been included to show effective SEI formation on the first reduction sweep.
Figure 5.2. Potentiodynamic scans of MCMB half cells in 1 M LiTFSI + 0.25 M LiBF<sub>4</sub> EMC with (a) no additive, (b) 5 vol% VC, and (c) 5 vol% FEC. Insets have been included to show effective SEI formation on the first reduction sweep.
Figure 5.3. Potentiodynamic scans of MCMB half cells in 1 M LiTFSI + 0.25 M LiBF$_4$ ADN with (a) no additive, (b) 5 vol% VC, and (c) 5 vol% FEC. Insets have been included to show effective SEI formation on the first reduction sweep.
Figure 5.4. Potentiodynamic scans of MCMB half cells in 1 M LiTFSI + 0.25 M LiBF₄ 3MPN with (a) no additive, (b) 5 vol% VC, and (c) 5 vol% FEC. Insets have been included to show effective SEI formation on the first reduction sweep.
5.3.2 Cycling of LiCoO$_2$ vs. MCMB Li-ion cells

Figure 5.5 shows the performance of the Li-ion cells fabricated with the electrolyte blends listed in Table 5.1. They have been separated by both the salt (1 M LiPF$_6$, 1 M LiTFSI + 0.25 M LiBF$_4$) and the type of solvent (EMC, ADN, 3MPN). Beginning with the 1 M LiPF$_6$ EMC shown in Figure 5.5(a), galvanostatic cycling was not possible without having a SEI promoting additive in the electrolyte. This contrasted with the potentiodynamic result in Figure 5.1 in which EMC, at least initially, exhibited reversible Li$^+$ insertion. However, with only a 5% addition of VC or FEC, good cycling on par with internal results using 1 M LiPF$_6$ EC:DMC 1:1 v/v was achieved. The best performance was achieved for the 5% VC solvent.

The cycling performance in 1 M LiTFSI + 0.25 M LiBF$_4$ EMC electrolytes is summarized in Figure 5.5(b). Similarly to the LiPF$_6$ data in Figure 5.5(a), the EMC was unstable unless VC or FEC was added. However, in the LiTFSI + LiBF$_4$ system, EMC + 5% FEC was found to be far superior to VC in stabilizing the electrolyte. In Figure 5.5(b), the only suitable electrolyte blend, based on exhibiting good capacity retention after 100 cycles was the EMC + 5% FEC.

Figure 5.5(c and d) show the cycling performance of cells utilizing ADN and 3MPN electrolytes, respectively. Without additives, the pure nitrile solvents showed no ability to support reversible intercalation thereby resulting in poor cycling behavior. With only 5% VC or FEC additive, a dramatic improvement in cycle life was observed. This was consistent with the aforementioned potentiodynamic scans. Unlike the 1 M LiTFSI + 0.25 M LiBF$_4$ EMC blends, VC was a functional additive in both nitriles. Remarkably, at only 5% additive, the full cells exhibited capacity retentions in both the ADN and 3MPN electrolytes that were nearly as good as the 1 M LiPF$_6$ EMC blend after 100 cycles.
Figure 5.5. Galvanostatic cycling results of LiCoO$_2$ vs. MCMB Li-ion cells in (a) 1 M LiPF$_6$ EMC electrolytes, (b) 1 M LiTFSI + 0.25 M LiBF$_4$ EMC electrolytes, (c) 1 M LiTFSI + 0.25 M LiBF$_4$ ADN electrolytes, and (d) 1 M LiTFSI + 0.25 M LiBF$_4$ 3MPN electrolytes.
Figure 5.5, the 1C rate of cycling was relatively poor and has been attributed to the high thickness of the separator within the coin cells. The impedance data collected for all the cells of Figure 5.5 revealed that for those which exhibited good long-term cycling, the complex impedance plane data for cycles 50, 60, …, 100 appeared unaltered as a function of cycle number. An example is shown in Figure 5.6 for ADN with 5% FEC. On the other hand, for cells which experienced rapid capacity fade, particularly 1 M LiTFSI + 0.25 M LiBF₄ with EMC + 5% VC, the recorded impedance (not shown) at later stages of cycling showed possible evidence of electrolyte degradation as the solution resistance value increased by a factor of 2. Further confirmation beyond the poor cycling and evolution of the impedance data was found upon dismantling the coin cell. Examination of the cell cycled in 1 M LiTFSI + 0.25 M LiBF₄ EMC + 5% VC revealed a grey powdery material between the MCMB and the glass fiber separator. The discoloration was isolated to the negative electrode halves. Since the C/5 data from cycles 60 through 70 showed a non-recoverable decline in capacity vs. cycle 50, the grey material was believed to be mossy lithium.

![Impedance data for LiCoO₂ vs. MCMB Li-ion cell cycled in 1 M LiTFSI + 0.25 M LiBF₄ ADN + 5% FEC.](image)

Figure 5.6. Impedance data for LiCoO₂ vs. MCMB Li-ion cell cycled in 1 M LiTFSI + 0.25 M LiBF₄ ADN + 5% FEC.
The first cycle irreversible capacity losses and capacity retentions of the aforementioned Li-ion cells are summarized in Table 5.2. The initial charge sweeps all ranged from 135-145 mAhg\(^{-1}\) LiCoO\(_2\) with the exceptions of the 1 M LiPF\(_6\) EMC, 1 M LiTFSI + 0.25 M LiBF\(_4\) ADN, and 1 M LiTFSI + 0.25 M LiBF\(_4\) 3MPN without additives. When the first discharge capacity values were compared for galvanostatic cycling trials in which the electrolytes contained additives, the first cycle irreversible capacity losses were 16.9 ± 1.6 mAhg\(^{-1}\) of LiCoO\(_2\) or 12.1 ± 1.0% for the balanced cell (Table 5.2). A 1 M LiPF\(_6\) EC:DMC benchmark electrolyte exhibited a 12.0% first cycle capacity difference. This is slightly higher than a typical Li-ion cell and is due to the presence of a higher SP carbon black content in the negative electrode and slightly lower than theoretical matching ratio. The only outlier beyond one standard deviation was the 3MPN + 5% FEC cell (20.6 mAhg\(^{-1}\)), and it was among the best cells in terms of its capacity retention after 100 cycles and its performance at rapid rates of cycling. The differences among FEC, VC, and EC, if not attributable to the early stages of SEI formation, have been surmised to result from differences of the chemistries of the electrolyte and SEI over the course of cycling.
<table>
<thead>
<tr>
<th>Electrolyte</th>
<th>mAhg⁻¹ LiCoO₂</th>
<th>Capacity loss / %</th>
<th>Discharge capacity retention / %</th>
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</thead>
<tbody>
<tr>
<td></td>
<td>Cycle 1</td>
<td>Cycle 1</td>
<td>Cycle 1 vs. 50</td>
</tr>
<tr>
<td><strong>1 M LiPF₆</strong></td>
<td></td>
<td></td>
<td></td>
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<td>EMC</td>
<td>79.5</td>
<td>39.9</td>
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<tr>
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<td>121.7</td>
<td>13.2</td>
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<tr>
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<td>13.4</td>
<td>93.8</td>
</tr>
<tr>
<td><strong>1 M LiTFSI + 0.25 M LiBF₄</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>EMC</td>
<td>89.4</td>
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<td>11.4</td>
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<tr>
<td>EMC + 5 vol% VC</td>
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<td>12.0</td>
<td>81.0</td>
</tr>
<tr>
<td>EMC + 5 vol% FEC</td>
<td>125.2</td>
<td>10.9</td>
<td>86.2</td>
</tr>
<tr>
<td>ADN</td>
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<td>83.4</td>
<td>0.8</td>
</tr>
<tr>
<td>ADN + 5 vol% VC</td>
<td>119.5</td>
<td>11.6</td>
<td>94.1</td>
</tr>
<tr>
<td>ADN + 5 vol% EC</td>
<td>119.1</td>
<td>11.4</td>
<td>84.4</td>
</tr>
<tr>
<td>ADN + 5 vol% FEC</td>
<td>119.6</td>
<td>12.5</td>
<td>93.7</td>
</tr>
<tr>
<td>ADN + 0.5 vol% FEC</td>
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<td>12.3</td>
<td>92.0</td>
</tr>
<tr>
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<td>0.0</td>
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<tr>
<td>3MPN + 5 vol% VC</td>
<td>126.7</td>
<td>11.3</td>
<td>92.0</td>
</tr>
<tr>
<td>3MPN + 5 vol% FEC</td>
<td>124.6</td>
<td>14.2</td>
<td>90.5</td>
</tr>
</tbody>
</table>
XPS analysis of MCMB negative electrodes after electrochemical trials proved difficult to interpret because of the overlapping signals, particularly within the C1s and F1s core level binding energies. MCMB, SP, PVdF, LiTFSI, and anticipated solvent decomposition products all exhibit C1s signals in the range of 284 to 294 eV. Furthermore, PVdF, LiTFSI, LiBF₄, LiPF₆, and possibly the decomposition products of FEC can each contribute to the F1s signal. Figure 5.7 shows the F1s, O1s, C1s, and Li1s core level spectra for raw MCMB tape, non-rinsed MCMB tape after 100 cycles, and rinsed MCMB tape after 100 cycles for ADN-based electrolytes containing 5% VC and 5% FEC additives. Peaks have been appropriately labeled in Figure 5.7 based on extrinsic powder standards analyzed with the K-Alpha XPS instrument. By rinsing the cycled electrodes with DMC, residual LiTFSI (Li1s: 56.0 eV, C1s: 293 eV, O1s: 533 eV, F1s: 689 eV) was removed from the surface, exposing what would appear to be lithium fluoride (Li1s: 55.5 eV, F1s: 685 eV) and a carbonate surface group (O1s: 532 eV). Residual LiBF₄ was ruled out due to the lack of a 57.0 eV peak in any of the Li1s core level spectra. The Li1s peak for the rinsed MCMB tape was better approximated by LiF (55.5 eV) as opposed to LiTFSI (56.0 eV) for the non-rinsed sample. The F1s core level spectra for rinsed tapes showed a definitive LiF peak (685 eV) and PVdF peak (688 eV) compared with the non-rinsed and raw MCMB tape samples. The C1s spectra were complex for all core level scans, making a conclusive identification of the carbon chemical entities of the SEI difficult. The LiTFSI (293 eV) was effectively rinsed away and some new surface entity likely existed on the negative electrode tape based on the diminished peak for adventitious carbon (284.8 eV). The O1s spectra for the rinsed MCMB tapes were consistent with a carbonate species (532 eV).

The XPS results of Figure 5.7 showed that the addition of SEI promoting entities (i.e. VC, FEC) into the electrolyte resulted in the development of new phases on the surface of the negative
electrode. The Li1s and F1s core level spectra appeared to be dominated by LiTFSI (non-rinsed samples), LiF (rinsed samples), and PVdF binder (rinsed samples). It was anticipated that the FEC additive would contribute more fluorine to the SEI, thus it was unexpected for the XPS spectra for negative electrodes with VC and FEC additives to be nearly identical. It was not possible to determine from the F1s spectra (Figure 5.7) whether FEC decomposition had occurred or if its decomposition products were commingled with phases due to electrolyte salt. For electrolytes containing LiPF$_6$ or LiBF$_4$, LiF precipitation occurs, forming an integral inorganic part of the SEI.[20,129] Though residual LiBF$_4$ was not directly observed in the XPS spectra, it was still a component of the electrolytes under study and could have certainly led to LiF formation. In summary, there exists a significant similarity between the results of the VC and FEC additives suggesting that the spectra are dominated by the presence of the binder and decomposition products of a fluorinated salt.
Figure 5.7. XPS spectra for MCMB negative electrode tapes cycled 100 times vs. LiCoO2. Curve A (· · ·): plain MCMB electrode tape, no electrochemical treatment. Curve B (- - -): MCMB tape, cycled, non-rinsed. Curve C (—): MCMB tape, cycled, rinsed with DMC. Upper row: ADN + 5% VC. Lower row: ADN + 5% FEC.
5.3.3 XPS of graphite planchets

To more confidently assign the peaks observed in each of the core levels obtained from XPS, electrochemical trials with binder free, spectroscopically pure graphite planchets and 1 M LiClO₄ EMC electrolytes were performed. The latter was essential to enable a clear identification of F from the decomposition of FEC. Since the use of VC for SEI promotion is well documented[30, 73, 130, 131, 132], it was omitted from this spectroscopy study. The aim was to identify the decomposition products of FEC.

Figure 5.8 shows the results of XPS analysis for four specimens: raw carbon planchet (Curve A), 1 M LiClO₄ EMC + 5% FEC at OCV for 24 h (Curve B), 1 M LiClO₄ EMC + 5% FEC swept to 1 V (Curve C), and 1 M LiClO₄ EMC swept to 1 V (Curve D). As expected, the signal from the raw carbon planchet (Curve A) exhibited mostly C-C bonding (284.8 eV) with merely a trace of oxygen, making it an ideal substrate. Contrasting curves B, C, and D in Figure 5.8, it was evident that sweeping the potential to 1 V vs. Li induced decomposition of the FEC additive. The only trial to exhibit a distinct C1s spectrum was the EMC + 5% FEC swept to 1 V (Curve C). Not coincidentally the strongest F1s signal was also displayed with this electrolyte. Although a trace of F existed in the LiClO₄ as a stabilization aid, all things being equal, the intensities of the F1s spectra for Curves B and D were very similar. Whether by allowing a cell containing FEC in its electrolyte to sit at rest or by sweeping an electrolyte free of FEC to 1 V, the F1s signal intensities on the carbon planchet were nearly identical and were caused by a residual F-containing species associated with the base LiClO₄ EMC electrolyte. Furthermore, the Cl2p spectra for Curves C and D were similar for both electrolytes swept to 1 V, but the electrolyte intentionally doped with a fluorine containing entity (i.e. FEC) exhibited a substantial F1s signal. Lastly, merely having the FEC additive in the electrolyte (Curve B) did not yield a strong F1s signal; it was only produced by
sweeping the electrolyte with FEC to 1 V (Curve C). From the significant contrast in the F1s core level for the FEC additive swept to 1 V as well as the C1s data, it has been concluded that the F on the surface of the carbon planchet was, in fact, due to cathodic electrochemical decomposition of FEC. The chemical entities resulting from the decomposition of FEC would appear to be lithium methyl carbonate[100] (C1s: 287 eV and 290 eV, O1s: 532 eV) and lithium fluoride[101] (Li1s: 55.5 eV, F1s: 685 eV).

Figure 5.8. XPS spectra for spectroscopically pure carbon planchet working electrodes. Curve A (—, hairline): raw carbon planchet. Curve B (- - -): 1 M LiClO4 EMC + 5% FEC at OCV for 24 h. Curve C (—, bold): 1 M LiClO4 EMC + 5% FEC swept to 1 V. Curve D (· · ·): 1 M LiClO4 EMC without FEC swept to 1 V. Care was taken to have approximately the same signal intensity over the survey spectrum for each of the four samples.
5.4. Discussion

To the best of our knowledge, this work demonstrated, for the first time, the successful implementation of electrolytes which were based *predominantly* on EMC, 3MPN, and ADN solvents for use in 4 V Li-ion cells. While we have only explored these electrolytes at a fixed temperature of 24°C, the fact that we have verified good cycling performance in a Li-ion system with a balanced, finite amount of lithium was promising. With the exception of 1 M LiTFSI + 0.25 M LiBF$_4$ EMC + 5% VC, the VC and FEC were effective at preventing solvent decomposition on the carbon negative electrode, and the SEI were relatively stable once formed, not continuously consuming quantities of Li$^+$ during each cycle. This was directly supported by the good capacity retention (Figure 5.5 and Table 5.2) and inferred from similar impedance measurements for cycles 50 through 100 (Figure 5.6). When the 1 M LiTFSI + 0.25 M LiBF$_4$ salt blend was utilized in EMC (Figure 5.5(b)), the performance of FEC was superior to VC as additives. Although the fluorinated electrolyte salts do contain fluorine components, FEC may lead to a rapid inclusion of a stable F component in the chemistry of the SEI before other deleterious solvent decomposition can begin. In addition, in exploring the efficacy of any SEI, it is important that the organic component of the SEI does not swell allowing solvent transport under the SEI and leading to further decomposition regardless of the SEI thickness. Indeed the SEI must be not only stable in but impermeable to the ambient solvent environment. As such, the FEC induced SEI may be more resistant to organic solvent penetration,[126]

Curiously, VC was effective in nitriles but not carbonates when using 1 M LiTFSI + 0.25 M LiBF$_4$. VC may be very similar to carbonates and offer no overt added benefit although it is known that VC does impart advantages in carbonate solvents under more extreme testing conditions.[123, 130] Despite the similar XPS spectra for cells cycled in ADN (Figure 5.7) from which one might
anticipate that VC and FEC would yield the same SEI chemistry across a range of electrolyte systems, FEC appeared to be effective in all electrolyte solvents examined whereas VC was not. In order to examine the difference of having a fluorinated SEI additive vs. a non-fluorinated one, we examined EC (1,3-dioxolan-2-one), a molecule of similar chemistry to FEC (4-fluoro-1,3-dioxolan-2-one).

As in Figures 5.1-5.4 above, potentiodynamic scans were performed for a MCMB vs. Li half cell containing 1 M LiTFSI + 0.25 M LiBF$_4$ ADN + 5 vol% EC. The potentiodynamic data (Figure 5.9) suggested that EC in ADN was not as effective a SEI former as FEC. Whereas FEC effectively coated the carbon negative electrode during the first reduction sweep, the EC did not appear to have fully passivated the surface during the first reduction sweep because the second reduction sweep in Figure 5.9 showed another cathodic wave at approximately 0.7 V vs. Li/Li$^+$. This wave has been attributed to more EC decomposition. Perhaps the EC was not as effective at providing coverage over the entire interface during the first reduction sweep due to swelling of its SEI. Or, possibly some component of the EC decomposition product was soluble into the electrolyte, exposing fresh surface which subsequently reacted with the EC on the second reduction sweep. Despite the less effective SEI stabilization, the results of Figure 5.9 did not preclude an ADN + 5% EC electrolyte from being studied in a full cell configuration.
Figure 5.9. Potentiodynamic scans of MCMB half cells in 1 M LiTFSI + 0.25 M LiBF$_4$ ADN + 5% EC. The inset has been included to more clearly show the current associated with EC solvent reduction.

Figure 5.10. Galvanostatic cycling performance of LiCoO$_2$ vs. MCMB Li-ion cells in 1 M LiTFSI + 0.25 M LiBF$_4$ ADN comparing EC and FEC as additives.
Galvanostatic cycling trials with ADN + 5% EC and 5% FEC were compared in Figure 5.10. Based on its less effective stabilization (Figure 5.9), it was expected that the 5% EC cell would not maintain as good capacity retention through 100 cycles as its 5% FEC counterpart in ADN. The ADN + 5% EC additive did not exhibit as good cycling performance at rapid rates of charge/discharge as ADN + 5% FEC. Upon opening the coin cell after the 100th cycle, the glass fiber separator adjacent to the MCMB negative electrode was discolored with a faint yellow hue which may have been caused by a small quantity of ADN reacting undesirably with the negative electrode. The separator in the ADN + 5% FEC cell remained white.

Our observations would seem to indicate that the various interactions occurring amongst solvent decomposition products, electrolyte salts, and side-products introduced from impurities are not so easily generalized from one electrolyte system to another. Each electrolyte system may require specific engineering with its own nuances. FEC appeared to be an excellent candidate across all electrolytes studied (Figure 5.5 and Figure 5.10). When using 1 M LiTFSI + 0.25 M LiBF₄, VC was unsatisfactory in EMC yet VC worked well in nitriles, and EC worked marginally in ADN (Figure 5.5 and Figure 5.10). FEC and VC were both excellent when using LiPF₆ (Figure 5.5(a)).

LiF can be identified as the common species in the SEI across all the electrolytes that exhibited good cycling performance. With LiPF₆, equilibria involving H₂O impurities leads to the presence of HF, which can react with carbonate phases in the SEI to yield LiF.[20, 73, 129] LiF is incorporated into the SEI, but it is an indirect process which requires etching of an already established carbonate phase. However, by using FEC as an additive, lithium methyl carbonate and lithium fluoride can be formed directly on graphitic carbon via electrochemical reduction.
One must be careful here in identifying LiF as highly desirable without also identifying the quantity and distribution in the SEI chemistry. For example, an abundance of LiF may lead to a highly resistive film[73], but as shown by Profatilova et al[125], FEC can beneficially reduce the interfacial resistance. The results of this study suggested that some LiF was necessary to provide good performance. The exact mechanism for enhanced performance and the distribution of LiF throughout the SEI remain to be determined. The improved chemical compatibility appeared to be strongly correlated with the LiF resulting from the decomposition products of FEC, a fluorinated SEI-promoter, while not inherently occurring with EC or VC additives.

We believe this work has lead to the strongest evidence that the decomposition products of FEC yielded a fluorinated phase. In all previous studies in which XPS was used to characterize the SEI formed with FEC, LiPF$_6$ was used as the electrolyte salt.[25, 125, 128] The interaction of the fluorinated salt, whether by LiPF$_6$ decomposition to LiF and PF$_5$ or hydrolysis to yield HF, likely influenced the observed F1s signals during XPS analysis. Since we utilized LiClO$_4$ while also excluding any F signals from the electrode material, we believe our work to be the first truly conclusive evidence for FEC decomposition yielding a fluorinated phase (i.e. LiF). Furthermore, since the working electrode substrate utilized in this chapter was free of any overlapping C1s signals, and we did not use a cyclic carbonate solvent (e.g. EC) in our XPS investigations, we are the first to conclusively report lithium methyl carbonate as the other predominant phase formed as a result of FEC decomposition. This contrasts with the results published by Profatilova et al[125]. In their work, it was suggested that carbonate and alkyl carbonate moieties existed on the surface of the graphite anodes; however, the XPS data did not reveal them as distinct when comparing the C1s core level spectra of 1 M LiPF$_6$ EC:EMC 3:7 v/v with...
and without FEC. The F1s core level spectra did indicate a relative intensity ratio shift of the LiF to PVdF signal in the F1s core level to favor LiF. The LiF content increased from 7 to 10 to 14% when the FEC content increased from 0 to 10 to 30%.[125] Our work showed a definitive growth in the F content without having to consider reactions attributable to LiPF₆. As a result of using LiClO₄ in our work, the Li1s and O1s core level spectra were influenced by the perchlorate salt; however, we believe the C1s and F1s spectra have provided very strong evidence for the lithium methyl carbonate and lithium fluoride phases.

Lastly, the electrolytes investigated in this study were blended with 5 vol% additive, a relatively large amount considering the excess electrolyte within the two glass fiber separator discs. The coin cells contained 90 μL of electrolyte, which meant that 4.5 μL of SEI promoting additive was in each cell. This equated to 3.5 μLcm⁻² additive per geometric surface area of the negative electrode. Previous research has shown successful cycling of isocyanate additives in propylene carbonate with only 0.64 μLcm⁻², an order of magnitude below the value in our electrolytes.[133] An ADN + 0.5% FEC cell was constructed to determine if the volume percent additive could be lowered yet remain effective. Comparable performance to the ADN + 5% FEC electrolyte was exhibited (Table 5.2), and the glass fiber separator remained white. Thus, an electrolyte solvent containing merely 0.35 μLcm⁻² additive has been proven to stabilize the interface in a 4 V Li-ion cell.
5.5. Conclusion

Electrolytes consisting predominantly of EMC, a linear organic carbonate solvent, 3MPN, an alkoxypropionitrile solvent, and ADN, a dinitrile solvent, were successfully implemented in a 4 V Li-ion system with merely 5 vol% of SEI additive. In the majority of cases, especially when using 1 M LiTFSI + 0.25 M LiBF$_4$ as the salts within the electrolyte, FEC proved to be better than VC and EC when considering the capacity retention over 100 cycles. A third contribution of this work conclusively proved that in otherwise nonfluorinated electrolytes, FEC imparted a fluorinated compound (LiF) at the interface of the electrolyte and graphitic carbon negative electrode as a result of its cathodic electrochemical decomposition. It has been surmised that the LiF contained within the SEI derived from the FEC provides better stability when using 1 M LiTFSI + 0.25 M LiBF$_4$ as the Li$^+$ salts in the electrolyte. FEC has been shown to be a good SEI-promoter across a variety of electrolyte solvents and salts. FEC would be especially appealing when considering the stability of SEI derived from FEC-containing electrolytes up to 120°C and the lower interfacial impedances enabled by using FEC as an SEI additive.[125]

We have not yet explored the cycling performance of the electrolytes studied herein at either very low or elevated temperatures. However, the reasonably good capacity utilization observed at 24°C, particularly in the 1 M LiPF$_6$ EMC, 1 M LiTFSI + 0.25 M LiBF$_4$ ADN, and 1 M LiTFSI + 0.25 M LiBF$_4$ 3MPN electrolytes was promising. The findings of this study serve as a platform for future research for these challenging areas. EMC would be suitable for low to moderate temperature applications. 3MPN would offer the widest range in temperature of the three solvents studied. ADN would be best for moderate to high temperature operation as well as cells exceeding 5 V.
6. Improved cycling performance of bismuth fluoride nanocomposite positive electrodes enabled with nitrile-based electrolytes

6.1. Introduction

The theoretical gravimetric (302.3 mAh g⁻¹) and volumetric capacities (7960 Wh·L⁻¹) coupled with a reasonably high potential (~3.1 V vs. Li/Li⁺) make BiF₃ an attractive candidate for use as a rechargeable positive electrode material in Li-ion batteries.[4, 110] When aggressively milled into a nanocomposite, this metal fluoride conversion material has demonstrated near-theoretical capacities and a relatively flat discharge plateau at moderate to very fast (3C) rates of cycling.[4, 110] However, the BiF₃ nanocomposites have been plagued by rapid rates of capacity fade. Initially, the capacity loss was correlated with the decomposition of electrolyte solvents on the positive electrode. Nanodomains of Bi⁰, formed as a result of the discharge (lithiation) of BiF₃, were identified to catalyze the electrochemical reduction of cyclic organic carbonate solvents, notably ethylene carbonate (EC), from the electrolyte (Chapter 3).[110] Recently, the species formed from the electrochemical reduction of EC at the positive electrode / electrolyte interface have been found to decompose during reconversion (delithiation), and the formation of BiOₓF₃₋₂ₓ through interactions of the Bi⁰, LiF, and solid-electrolyte interphase (SEI) was evident (Chapter 4).

Ethyl methyl carbonate (EMC) and dimethyl carbonate (DMC), examples of linear organic carbonate solvents, were not observed to decompose on the lithiated BiF₃ nanocomposites or on Bi films (Chapter 3).[110] It was hypothesized that other straight-chained aprotic solvents such as dinitriles and 3-alkoxypropionitriles would behave similarly. Novel electrolyte blends composed predominantly of EMC, adiponitrile (ADN, a dinitrile), and 3-methoxypropionitrile (3MPN) have recently been demonstrated in a 4 V Li-ion configuration (Chapter 5).[134] When
blended with suitable soluble salts such as 1 M lithium bis(trifluoromethylsulfonyl) imide + 0.25 M lithium tetrafluoroborate (1 M LiTFSI + 0.25 M LiBF₄), none of these nitrile electrolytes were inherently able to stabilize the graphite negative electrode / electrolyte interface. This necessitated the addition of a small amount of the SEI-forming compounds, vinylene carbonate (VC) and monofluoroethylene carbonate (FEC).[134]

SEI additives are necessary to effectively passivate the negative electrode to prevent continual decomposition of the electrolyte. Additives are reduced on the negative electrode through reactions that typically involve the saturation of C=C double bonds and polymerization or the formation of radical anions through ring-opening mechanisms, both of which yield insoluble phases.[21] The SEI additive is typically reactive at potentials more positive than necessary for the electrochemical reduction of the main solvent(s) of the electrolyte; thus, the negative electrode is passivated before deleterious interactions of the electrolyte solvents can occur. Of the cyclic organic carbonates, VC was found to have the most positive reduction potential which is of great importance when considering it as an additive to promote SEI formation.[15] This would suggest that VC would be even more susceptible than EC to electrochemical reduction on the catalytic Bi⁰ formed during lithiation of BiF₃ nanocomposites. This suspected trait of VC led to the inclusion of cycling trials in which a variety of additives was compared. The additives were selected with regard to their molecular shapes, functional groups, solubility, and availability. The compounds are categorized by their functional groups, and key references are included with respect to their electrochemical properties and usage as additives in Li-ion cells (Table 6.1 and Table 6.2).
Table 6.1. Additives containing C=O and/or C=C functional groups.

<table>
<thead>
<tr>
<th>Common Name</th>
<th>IUPAC Name</th>
<th>Abbr.</th>
<th>CAS Number</th>
<th>Chemical Formula</th>
<th>Molecule[135]</th>
<th>Refs.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ethylene Carbonate</td>
<td>1,3-Dioxolan-2-one</td>
<td>EC</td>
<td>96-49-1</td>
<td>C₃H₄O₃</td>
<td></td>
<td>73</td>
</tr>
<tr>
<td>Monofluoroethylene Carbonate</td>
<td>4-Fluoro-1,3-dioxolan-2-one</td>
<td>FEC</td>
<td>114435-02-8</td>
<td>C₃H₃FO₃</td>
<td></td>
<td>125, 134</td>
</tr>
<tr>
<td>Propylene Carbonate</td>
<td>4-Methyl-1,3-dioxolan-2-one</td>
<td>PC</td>
<td>108-32-7</td>
<td>C₄H₆O₃</td>
<td></td>
<td>73</td>
</tr>
<tr>
<td>Vinyl Ethylene Carbonate</td>
<td>4-Ethenyl-1,3-dioxolan-2-one</td>
<td>VEC</td>
<td>4427-96-7</td>
<td>C₅H₆O₃</td>
<td></td>
<td>136</td>
</tr>
<tr>
<td>Ethyl Methyl Carbonate</td>
<td>Carbonic acid, ethyl methyl ester</td>
<td>EMC</td>
<td>623-53-0</td>
<td>C₄H₈O₃</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Vinylene Carbonate</td>
<td>1,3-Dioxol-2-one</td>
<td>VC</td>
<td>872-36-6</td>
<td>C₃H₂O₃</td>
<td></td>
<td>73, 130</td>
</tr>
<tr>
<td>Dimethyl Vinylene Carbonate</td>
<td>4,5-Dimethyl-1,3-dioxol-2-one</td>
<td>DMDO</td>
<td>37830-90-3</td>
<td>C₅H₆O₃</td>
<td></td>
<td>137</td>
</tr>
</tbody>
</table>
Table 6.2. Additives containing S=O or N=C=O functional groups.

<table>
<thead>
<tr>
<th>Common Name</th>
<th>IUPAC Name</th>
<th>Abbr.</th>
<th>CAS Number</th>
<th>Chemical Formula</th>
<th>Molecule[135]</th>
<th>Refs.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ethylene Sulfite</td>
<td>1,3,2-Dioxathiolane 2-oxide</td>
<td>ES</td>
<td>3741-38-6</td>
<td>C\textsubscript{2}H\textsubscript{4}O\textsubscript{3}S</td>
<td><img src="https://example.com/image1.png" alt="Image" /></td>
<td>138, 139</td>
</tr>
<tr>
<td>Ethylene Sulfate or Glycol Sulfate</td>
<td>1,3,2-Dioxathiolane 2,2-dioxide</td>
<td>DTD</td>
<td>1072-53-3</td>
<td>C\textsubscript{2}H\textsubscript{4}O\textsubscript{4}S</td>
<td><img src="https://example.com/image2.png" alt="Image" /></td>
<td>140, 141</td>
</tr>
<tr>
<td>Propanediol Cyclic Sulfate</td>
<td>1,3,2-Dioxathiane 2,2-dioxide</td>
<td>PDCS</td>
<td>1073-05-8</td>
<td>C\textsubscript{3}H\textsubscript{6}O\textsubscript{4}S</td>
<td><img src="https://example.com/image3.png" alt="Image" /></td>
<td>142, 143</td>
</tr>
<tr>
<td>1,3-Propane Sultone</td>
<td>1,2-Oxathiolane 2,2-dioxide</td>
<td>PS*</td>
<td>1120-71-4</td>
<td>C\textsubscript{3}H\textsubscript{6}O\textsubscript{3}S</td>
<td><img src="https://example.com/image4.png" alt="Image" /></td>
<td>144, 145</td>
</tr>
<tr>
<td>1,4-Butane Sultone</td>
<td>1,2-Oxathiane 2,2-dioxide</td>
<td>BS</td>
<td>1633-83-6</td>
<td>C\textsubscript{4}H\textsubscript{8}O\textsubscript{3}S</td>
<td><img src="https://example.com/image5.png" alt="Image" /></td>
<td>146</td>
</tr>
<tr>
<td>Ethyl Isocyanate</td>
<td>Isocyanatoethane</td>
<td>EtNCO</td>
<td>109-90-0</td>
<td>C\textsubscript{3}H\textsubscript{5}NO</td>
<td><img src="https://example.com/image6.png" alt="Image" /></td>
<td>133, 147</td>
</tr>
</tbody>
</table>

*PS in this work is not propylene sulfite [4-Methyl-1,3,2-dioxathiolane 2-oxide; 1469-73-4], an additive possessing the same chemical formula as 1,3-propane sultone. Propylene sulfite, also commonly abbreviated PS, was explored by Wrodnigg et al[148]
The ideal SEI additive would stabilize a graphite/lithium/alloy negative electrode and cathodically form at voltages below that of the operation of BiF$_3$. In essence, the ideal additive would not form an SEI on the catalytic surface of Bi$^0$.

There are three criteria the SEI additive must meet when using BiF$_3$ nanocomposites as the positive electrode.

(1) First and foremost, the SEI additive must stabilize the negative electrode / electrolyte interface.

With respect to the BiF$_3$ nanocomposite positive electrode / electrolyte interface, there are two criteria for the SEI additive.

(2a) Ideally, the SEI additive would not be electrochemically reduced on the positive electrode, thus avoiding any deleterious Li$^+$ and electrolyte consumption while also completely avoiding possible interactions of the Bi$^0$ with the SEI during reconversion (Chapter 4).

(2b) A near-ideal scenario would involve the electrochemical reduction of the SEI additive during only the first lithiation of the BiF$_3$ nanocomposite. This would require that the SEI layer remain stable to oxidation over potentials ranging from 2 V to 4.5 V vs. Li/Li$^+$ and that the SEI layer not influence the reconversion reaction by becoming incorporated into the reformed BiF$_3$. (2b) is dubious for several reasons. Very large volumetric changes inherent to the BiF$_3$ conversion electrode (the unit cell volume for BiF$_3$ is 55.7 Å$^3$ vs. 84.4 for Bi$^0$ + 3LiF), would likely permit the electrolyte to contact newly exposed Bi$^0$ during subsequent lithiation, leading to additional SEI
growth. The SEI layer would have to be very resilient. The formation of BiO$_x$F$_{3-2x}$ observed from Bi$^0$, LiF, and SEI in 1 M LiPF$_6$ EC:DMC has been implicated as a mode to rapid capacity fade through accumulation of Bi-O bonds which are not converted above 2 V vs. Li/Li$^+$ and/or dissolution of BiO$_x$F$_{3-2x}$ into HF-containing electrolytes (Chapter 4).

(3) The SEI additive must possess a high oxidative stability, or else the additive will anodically decompose on the BiF$_3$ nanocomposite positive electrode. The potential defining the end of delithiation is typically 4.5 V vs. Li/Li$^+$.

In this chapter, we first attempt to prove the intrinsic stability of BiF$_3$ in additive-free nitrile electrolytes by cycling vs. a counter electrode which is stable with the nitrile solvents (ADN and MPN). From there, we commence an investigation to identify an optimal class of additives that will stabilize the nitrile solvents vs. low voltage negative electrodes without resulting in deleterious effects on the BiF$_3$ nanocomposite conversion electrode material.

### 6.2. Experimental

#### 6.2.1 Materials synthesis

The methods of producing BiF$_3$ nanocomposite powders and Bi metal films have been described previously (Section 3.2.1). LiCoO$_2$ (LCO) tape electrodes were fabricated in a dry room (dew point < -30°C) by dispersing 0.600 g of LCO (C-22, Seimi), 0.320 g of polyvinylidene difluoride (PVdF) resin (Kynar Flex 2801, Arkema), 0.128 g of conductive carbon black (SuperP, Timcal), and roughly 0.4 g of dibutyl phthalate (DBP) in acetone. The suspensions were thoroughly mixed for 15 to 20 min before tapes were cast. After the acetone evaporated, the DBP plasticizer was extracted by soaking the tapes in diethyl ether. The tapes were vacuum dried overnight at
120°C prior to transfer to a helium filled glovebox (< 0.6 ppm H₂O, < 0.1 ppm O₂, MBraun). The final active loading of LCO was 57.2 wt%.

With the exception of 1 M lithium hexafluorophosphate (LiPF₆) EC:DMC 1:1 v/v (Novolyte), all electrolytes were blended in-house in a helium filled glovebox. The salts and solvents utilized for blending base electrolytes were LiPF₆ (Ferro), LiTFSI (HQ-115, 3M), LiBF₄ (Ferro), EC (Aldrich), DMC (Novolyte), EMC (Novolyte), 3MPN (Fluka), and ADN (Alfa). With the exceptions of 3MPN and ADN, these chemicals were battery or electrolyte grade, were delivered with < 20 ppm H₂O, and were used as-received. The 3MPN and ADN initially had water contents of approximately 700 ppm and 820 ppm, respectively, as measured by coulometric Karl Fischer titration (Model 684, Metrohm). The 3MPN and ADN were treated in the following manner to reduce their water contents. Molecular sieves (3 Å, Aldrich) were vacuum dried overnight at 120°C in glassware. The 3MPN and ADN were stored over the molecular sieves for 7 d with a ratio of 3 mL of solvent for each 1 g of molecular sieves. This treatment routinely yielded < 10 ppm H₂O for the 3MPN and < 15 ppm H₂O for the ADN.

One of the base electrolytes was made by adding LiPF₆ to EMC to 1 M concentration. 5 vol% of the additive VC (Ferro) was added to the 1 M LiPF₆ EMC electrolyte. 1 M LiTFSI + 0.25 M LiBF₄ was used as the salt combination for the remainder of the electrolytes. EC and DMC were mixed in a 1:1 v/v ratio. EMC and the dried 3MPN were used as base electrolytes to which 10 vol% VC was added. The base electrolyte composed of 1 M LiTFSI + 0.25 M LiBF₄ in dried ADN was blended with the following SEI additives, also at 10 vol%: EC, FEC (Novolyte), PC (Ferro), VEC (Aldrich), EMC, VC, DMDO (TCI America), ES (Aldrich), DTD (Aldrich), PDCS (Aldrich), PS (Aldrich), BS (Aldrich), and EtNCO (Aldrich). For compounds that were solids at room temperature, the
equivalent mass was added that would result in 10 vol% additive when dissolved into the ADN electrolyte.

### 6.2.2 Electrochemical characterization

2032-type coin cells (Hohsen) were assembled with non-metalized (1 M LiTFSI + 0.25 M LiBF₄ electrolytes) or aluminized (1 M LiPF₆ electrolytes) stainless steel current collectors. For galvanostatic cycling trials, cells contained 5-6 mg of BiF₃ nanocomposite powder as the working electrode (WE), a porous membrane (Celgard) adjacent to the WE, and two layers of borosilicate glass fiber separator (GF/D, Whatman) saturated with electrolyte. The counter electrode (CE) / reference electrode (RE) for half cells was lithium foil (FMC). For Li-ion cells, the CE / RE was LCO tape with a LiCoO₂:BiF₃ weight ratio of 3.5:1.0. Galvanostatic trials of these cells were run on a BT2043 battery testing system controlled with MITS'97 software (Arbin). Trials were run at ±15 mAg⁻¹ BiF₃ between 2.00 and 4.50 V (CE / RE = Li) or -1.95 and 0.55 V (CE / RE = LCO) at 24°C. The voltage plateau of LCO was 3.95 V vs. Li/Li⁺.

Several three-electrode cells were assembled. These were used to justify the mass ratio and cycling parameters of the two-electrode BiF₃ / LCO cells above. The WE was BiF₃, the RE was a ring (12.7 mm OD x 11.1 mm ID) of 316L stainless steel mounted to a partially bored-through stainless steel Swagelok body, and the CE was either LCO tape or Li. SS was used as a quasi-RE (qRE) after several failed attempts with Ag. When sitting in the cell at rest, the open circuit potential of Ag vs. Li/Li⁺ was nearly constant at 2.9 V, but during cycling of the BiF₃ nanocomposite, the Ag RE drifted from 2.9 V to 3.35 V vs. Li/Li⁺. This swing was consistent with the plating of Bi⁰ on the Ag RE. No such fluctuation was observed with the SS; thus, it was used as a qRE. The upper and lower potentials were established as 4.50 V and 2.00 V vs. Li or 0.55 V and -1.95 V vs. LCO. It is important to note that the RE was not used to control the applied
current; the potential difference of the WE and CE was used for this purpose. Galvanostatic cycling trials were run at ±15 mA g⁻¹ BiF₃ on a MacPile II (BioLogic) in a dry room.

Potentiodynamic scans in the 1 M LiTFSI + 0.25 M LiBF₄ ADN + 10 vol% additive electrolytes were run from the open circuit potential (approximately 3 V) to 1.00 V vs. Li/Li⁺ at -1.25 mV / 0.017 h on a MacPile II at 24°C. Stainless steel coin cells were assembled in a similar manner as BiF₃ nanocomposite vs. Li half cells, but with a 12.7 mm disc of bismuth film serving as the WE.
6.3. Results and Discussion

Galvanostatic cycling results of BiF$_3$ nanocomposite positive electrodes presented in Figure 6.1 show that superior cycling was identified in LiPF$_6$ EMC vs. LiPF$_6$ EC:DMC. This result was consistent with previous observations, and highly reproducible (Chapter 3).[110] The presence of EC (cyclic carbonate) as a 50 vol% co-solvent with DMC (linear carbonate), or VC (cyclic carbonate) as a 5 vol% additive to EMC (linear carbonate), had a detrimental impact on the long-term capacity retention of the BiF$_3$ nanocomposite. The VC was included in this plot because EMC was observed as stable on Li but not on synthetic graphite negative electrodes in a Li-ion configuration (Figure 5.5(a and b)); thus, a true Li-ion configuration employing BiF$_3$ positive electrodes would require an additive. The VC, though present to a far lesser extent, likely behaved in a similar manner as EC on the catalytically active Bi$^0$ formed during the lithiation of the BiF$_3$(Chapter 3).[110] In Figure 6.1(b), the capacity values of EC:DMC and EMC faded more rapidly in the 1 M LiTFSI + 0.25 M LiBF$_4$ electrolytes than in the 1 M LiPF$_6$ electrolytes. The BiF$_3$ nanocomposites did not cycle well in EMC, ADN, and 3MPN-based electrolytes without a co-solvent or SEI additive present in the electrolyte. The 3MPN decomposed rapidly on the Li negative electrode (indicated by yellowish-brown discoloration of the electrolyte adjacent to the Li), and the ADN only endured several cycles before the cell was nonfunctional. The addition of 10 vol% VC aided in stabilizing the electrolytes from continual decomposition at the negative electrode. The ADN provided the best long-term capacity retention of the 1 M LiTFSI + 0.25 M LiBF$_4$ electrolytes containing 10 vol% VC, consistent with previous studies reported on LiCoO$_2$ vs. graphite Li-ion cells (Chapter 5).
Figure 6.1. Specific capacity of BiF₃ nanocomposites cycled galvanostatically between 4.50 V and 2.00 V vs. Li. (a) 1 M LiPF₆ carbonates. (b) 1 M LiTFSI + 0.25 M LiBF₄ electrolytes. Best cycling overall with 1 M LiPF₆ EMC and 1 M LiTFSI + 0.25 M LiBF₄ ADN + 10 vol% VC when using Li as negative electrode.
From the LiPF₆ data (Figure 6.1(a)), an electrolyte devoid of SEI additives was concluded to provide the best capacity retention. However, in the 1 M LiTFSI + 0.25 M LiBF₄ electrolytes (Figure 6.1(b)), all of the electrolytes free of EC or VC were unstable on the Li negative electrode. It was not possible to determine how much of the capacity fade was inherent to the main solvent (i.e. EMC, ADN, or 3MPN) when VC was added. Therefore a methodology to examine the stability of the additive-free electrolytes vs. BiF₃ during cycling was needed.

In order to examine the electrolytes in a VC-free condition, LiCoO₂ (LCO) was used as the counter / reference electrode in a two-electrode Li-ion cell. LCO was greatly positive with respect to the reduction of the electrolyte solvents, and it was expected to be below the anodic limit of the solvents as well.[73, 86] With LCO, no additive is required to enable stability of the electrolyte solvents as required with Li metal. In addition, the BiF₃ nanocomposites were in the fully charged condition and required Li⁺ to be discharged (lithiated). The use of LCO enabled BiF₃ to be extensively tested in a Li-ion configuration. Any loss of Li⁺ due to a parasitic reaction with BiF₃ will be accounted for and not replaced as is the case with Li metal half cells.

The data from three-electrode cells in which the CE was either Li foil (Figure 6.2(a)) or LCO (Figure 6.2(b)), and the qRE was SS are presented. After roughly 8 cycles, the three-electrode trials (Figure 6.2) revealed that the potentials of the BiF₃ nanocomposite WE vs. SS qRE were similar for the two counter electrodes. The capacities were comparable, the potentials of BiF₃ vs. SS at the ends of lithiation and delithiation were almost identical, and the degrees of hysteresis in the reconversion of BiF₃ were comparable. The voltage profile (Figure 6.2(a)) did indicate that the SS qRE drifted ~100 mV during cycling trials. If the potentials of the Li CE and LCO CE vs. qSS RE (~-3.11 V (Figure 6.2(a)) and +0.82 V (Figure 6.2(b))) are considered, despite
running in two different cells, the combined average potential of LCO vs. Li was 3.93 V. This is completely consistent with the observed discharge potential of LCO in a typical half cell configuration. Overall, it was possible to cycle the BiF₃ in an unconventional fashion against LCO, and the three-electrode trials justified the series of two-electrode cells in which the WE was BiF₃ and the CE / RE was LCO.

![Graph](image)

**Figure 6.2.** Similarities observed in the voltage profiles of BiF₃ in three-electrode cells in which the counter electrode was Li (a) or LCO (b). WE: BiF₃ nanocomposite. RE: SS. Electrolyte: 1 M LiTFSI + 0.25 M LiBF₄ ADN. The electrolyte in (a) contained a small amount of additive (VC) to stabilize the interface with the Li.
The results of cycling BiF$_3$ nanocomposites in 1 M LiTFSI + 0.25 M LiBF$_4$ electrolytes against LCO CE/RE are presented in Figure 6.3. Similarly to the 10 vol% VC data in Figure 6.1(b), the ADN electrolyte exhibited the best long-term capacity. Remarkably, the discharge capacity of the BiF$_3$ nanocomposite in the additive-free ADN electrolyte was 183 mAh g$^{-1}$ nanocomposite after 100 cycles with a flat cycling profile indicating that cycling could continue for a considerably longer period of time. To date, this has been the best reported cycling of a BiF$_3$ nanocomposite positive electrode. It unequivocally demonstrated that good capacity retention was achievable with the BiF$_3$ nanocomposite utilizing a conversion mechanism to store energy, and it simultaneously highlighted the importance of identifying compatible electrolytes. Clearly, cycling in an electrolyte free of an additive (or co-solvent) susceptible to electrochemical reduction on Bi$^{0}$ provided superior results. It is, however, problematic for the development of a Li-ion cell of BiF$_3$ vs. a negative electrode such as synthetic graphite. The susceptibility of the additive to electrochemical reduction at potentials greater than the bulk electrolyte solvent(s) is the very property that is exploited when selecting functional additives. Without additives (or EC as a co-solvent), cycling of Li-ion batteries would not be possible, but with these types of additives, the interactions occurring with the BiF$_3$ nanocomposite lead to a significant degradation of performance.

Trials involving the VC-free electrolytes were momentarily cycled at a lower rate (±3 mAg$^{-1}$ BiF$_3$) around cycles 50 to 55 (Figure 6.3). The ADN, and especially the 3MPN, electrolytes showed a fair amount of recovery of the discharge capacity. Upon increasing the cycling rate to the original value (±15 mAg$^{-1}$ BiF$_3$), the ADN provided the best long-term capacity retention. The EMC, though previously identified to be quite nonreactive with the BiF$_3$, did not follow the same trend as the ADN and 3MPN electrolytes. This was surprising as EMC was believed to show low
reactivity at the converted BiF$_3$ nanocomposite, and it is not expected to be unstable with respect to LCO. The electrolytes containing VC also exhibited poorer performance than their VC-free counterparts. This has been attributed to VC decomposition on the BiF$_3$ electrodes and the progressive loss of Li$^+$ from the LCO electrode.

Figure 6.3. Specific capacity of BiF$_3$ nanocomposites cycled galvanostatically between 0.55 V and -1.95 V vs. LCO. Best cycling overall with 1 M LiTFSI + 0.25 M LiBF$_4$ ADN. 1 M LiPF$_6$ EC:DMC included as a comparison to highlight the rapid capacity fade when using 50 vol% EC.
Of the electrolyte solvents considered in this study, the best long-term cycling performance of the BiF$_3$ nanocomposites was observed in ADN. While 1 M LiPF$_6$ EMC may have afforded slightly higher discharge capacities over the first 20 cycles, cycling in 1 M LiTFSI + 0.25 M LiBF$_4$ ADN (BiF$_3$ vs. LCO) has consistently been better to 100 cycles. Therefore, ADN was selected as the base electrolyte to which 10 vol% SEI promoting species was added. The SEI additives were required to stabilize the negative electrode / electrolyte interface to prevent the decomposition of the ADN on Li. The 10 vol% SEI additive concentration was established after blending 1 M LiTFSI + 0.25 M LiBF$_4$ ADN with 1 M LiTFSI + 0.25 M LiBF$_4$ VC in the following ADN:VC volumetric ratios and running galvanostatic cycling trials of BiF$_3$ nanocomposite half cells: 100:0, 95:5, 90:10, 75:25, 50:50, 25:75, and 0:100 v/v (Figure 6.4). Even at an ADN:VC ratio of 75:25, the VC does not continually decompose on the Li electrode. While there is an abundance of SEI additive in these blends, if the interfaces are effectively passivated, additive decomposition should cease and the additive should remain in the electrolyte. On the other hand, 5 vol% VC in the ADN electrolyte seemed to be too low to effectively stabilize the negative electrode / electrolyte interface. Using 10 vol% concentration of various additives as a starting point in our investigations, the cycling performance of BiF$_3$ nanocomposite / Li metal half cells in ADN solvent were investigated in ADN + 10 vol% additive electrolytes (Figure 6.5 and Figure 6.6).
Figure 6.4. Specific capacity of BiF$_3$ nanocomposites cycled galvanostatically between 4.50 V and 2.00 V vs. Li in 1 M LiTFSI + 0.25 M LiBF$_4$ ADN:VC electrolytes. 10 vol% was selected as the additive concentration to be used in subsequent cycling trials.
Figure 6.5. Specific capacity of BiF₃ nanocomposites cycled galvanostatically between 4.50 V and 2.00 V vs. Li in 1 M LiTFSI + 0.25 M LiBF₄ ADN electrolytes.
Figure 6.6. Voltage profiles of BiF₃ nanocomposites plotted as a function of capacity. First two cycles shown for samples cycled galvanostatically between 4.50 V and 2.00 V vs. Li in 1 M LiTFSI + 0.25 M LiBF₄ ADN electrolytes. The theoretical capacity is 266 mAh g⁻¹ nanocomposite. Note the different x-axes for panels (e), (h), and (i). (a) no additive, (b) 10 vol% EC, (c) 10 vol% FEC, (d) 10 vol% PC, (e) 10 vol% VEC, (f) 10 vol% EMC, (g) 10 vol% VC, (h) 10 vol% DMDO, (i) 10 vol% ES, (j) 10 vol% DTD, (k) 10 vol% PDCS, (l) 10 vol% PS, (m) 10 vol% BS, and (n) 10 vol% EtNCO.
After 40 cycles, the two best ADN electrolytes contained the additives VC and FEC (Figure 6.5). Both of these additives have been proven to form effective SEI on Li negative electrodes[130, 139] as well as on synthetic graphite when added to nitrile solvents (Chapter 5). VC has already been shown to detrimentally impact the long-term cycling performance of BiF₃ nanocomposites in 1 M LiPF₆ EMC (Figure 6.1(a)) and 1 M LiTFSI + 0.25 M LiBF₄ ADN electrolytes (Figure 6.3) compared with EMC and ADN electrolytes free of additives. It was anticipated that in at least one of the other ADN electrolytes, the BiF₃ would perform better than in ADN + 10 vol% VC. Contrary to expectations, no improvement was observed with the other additives considered (Figure 6.5). None of the sulfite, sulfate, or sultone compounds provided any benefit over the carbonate additives. However, all conclusions are preliminary as we have not expanded the investigation to include variation in additive content (vol %) or voltage cutoff (e.g. Figure 3.16). Examination of the potential profiles of BiF₃ in electrolytes with the sulfur-containing compounds (Figure 6.6) revealed decomposition of these additives at or above 2.0 V vs. Li/Li⁺. This was especially apparent during the first discharge in ADN + 10 vol % ES, and evident in ADN + 10 vol% DTD, PDCS, PS, and BS by the lack of sharpness of the potential profiles toward the end of second discharge (Figure 6.6). The electrochemical reduction of these sulfur-containing compounds was also observed at or above 2.0 V vs. Li/Li⁺ during potentiodynamic scans of Bi films (not shown). Thus, Bi⁰ has been established as catalytic toward the reduction of cyclic organic compounds containing either C=O (and now) S=O functional groups. The S=O analogs of C=O cyclic organic compounds are likely more reactive with the Bi⁰. In our work, the potential for ES reduction was observed to be more positive than EC. Theoretical investigations involving ES, DTD (reported as GS in [140]), EC, PC, and VC, have shown the reductive decomposition by lithium atoms in order of the most energetically favorable to be ES ~ DTD > EC ~ PC > VC for the first lithium addition.[140] This substantiated the reduction of cyclic organic
compounds containing S=O functional groups at more positive potentials than those containing C=O functional groups.

Cyclic carbonates were expected to be poor candidates for electrolyte additives. EC, and to a lesser extent PC, have previously been established as reactive on Bi$^0$ and detrimental to the cycling performance of BiF$_3$ nanocomposites (Chapter 3).[110] All the candidate additives were suboptimal, yet the best capacity retention was observed in ADN electrolytes containing cyclic carbonate additives based on the EC molecule (Table 6.1). Of the four molecules possessing a five-membered ring of 1,3-dioxolan-2-one, the VEC was most reactive on Bi$^0$. This has been attributed to the ethenyl (vinyl) group extending from the ring. VEC was found to decompose at approx. 2.4 V vs. Li/Li$^+$ during lithiation of the BiF$_3$ nanocomposite positive electrode (Figure 6.6(e)). The extent of VEC decomposition was large enough to cause the specific capacity of the nanocomposite to exceed the theoretical maximum (266 mAh g$^{-1}$), and subsequent discharge capacities were drastically reduced. In ADN + 10 vol% PC and FEC, potentiodynamic scans of Bi films (not shown) from approximately 3.0 V to 1.0 V revealed the extent of cathodic current to be very similar to 2.0 V vs. Li/Li$^+$. The galvanostatic cycling of BiF$_3$ nanocomposites was therefore anticipated to be similar in ADN containing these two additives, yet it was superior with 10 vol% FEC. It is unknown if the difference between the two additives was attributable to their stabilities on the negative electrode or the different chemistries of the SEI formed on the BiF$_3$ nanocomposite. However, it is known that the decomposition of FEC results in a significant inorganic component of LiF at the negative electrode (Chapter 5).[134] We have not examined whether decomposition to LiF is apparent at the higher voltages.
VC was observed to be the best SEI additive in the ADN electrolyte. If VC does form an SEI during the first lithiation of the BiF₃ nanocomposite, perhaps its ability to polymerize aids in forming an interfacial layer capable of accommodating the large volumetric expansion of the conversion electrode. Also, perhaps an SEI that favors polymeric chains as opposed to carbonate moieties is more stable to anodic decomposition or has a much lesser tendency to interact with Bi⁺ through a conversion mechanism as has been observed for SEI formed from EC (Chapter 4). DMDO, the most chemically similar molecule to VC in this study (Table 6.1), was completely unsatisfactory as an additive in the ADN electrolyte. It failed to meet criterion (3). A prolonged anodic current was observed during galvanostatic cycling above 4.3 V vs. Li/Li⁺ (Figure 6.6(h)).

The most intriguing additive was EtNCO (Figure 6.6(n)) despite its inability to provide the best long-term cycling performance. It was among those samples which exhibited the most consistent voltage profiles and the least difference of the discharge and charge capacities. These attributes were common to EC (Figure 6.6(b)), FEC (Figure 6.6(c)), PC (Figure 6.6(d)), EMC (Figure 6.6(f)), VC (Figure 6.6(g)), and EtNCO Figure 6.6(n)). These same additives yielded the best cycling of BiF₃ in ADN (Figure 6.5). Compared with VC and FEC, the two best additives, EtNCO yielded a substantially lesser extent of charge capacity at potentials above 3.5 V during cycle 2 (Figure 6.6(n)). The reactions occurring at potentials exceeding 3.5 V are indicative of inefficiencies during the reconversion of Bi⁺LiF to BiF₃. These inefficiencies may be attributed to interaction of the conversion chemistry with the SEI or the oxidative decomposition of SEI species. Furthermore, the electrochemical reduction of EtNCO on a Bi film was identified to occur at approximately 1.7 V vs. Li/Li⁺, a value more negative than the lower potential limit during galvanostatic cycling trials. During potentiodynamic scans (not shown), ADN + 10 vol%
EtNCO exhibited the second lowest magnitude of current at 2.0 V of all the ADN electrolytes. The current was second only to the additive-free ADN electrolyte. Either the EtNCO was the least reactive during the lithiation of the BiF$_3$ nanocomposite positive electrode, or it required the fewest Coulombs to effectively passivate the Bi. Spectroscopic studies are underway to address whether EtNCO imparts any changes to the surface chemistry of Bi at 2.0 V vs. Li/Li$^+$. Independent of whether EtNCO decomposes on the BiF$_3$ positive electrode, the poor long-term cycling performance of BiF$_3$ nanocomposites in ADN + 10 vol% EtNCO could also arise from an ineffective stabilization of the lithium / electrolyte interface. At present, the behavior leading to rapid capacity loss of BiF$_3$ nanocomposites during galvanostatic cycling in ADN + 10 vol% EtNCO remains under investigation.

Overall, this study has not succeeded in improving the cycling performance of BiF$_3$ nanocomposite positive electrodes when paired with a negative electrode of low potential (i.e. Li) relative to that of the VC additives we have previously identified. However, it has succeeded in expanding the list of solvents, whether as the main constituents of the electrolyte or as additives, to avoid when formulating electrolytes. The electrochemical reduction of cyclic organic solvents possessing C=O or S=O functional groups has been catalyzed on Bi$^0$, leading to rapid rates of capacity fade. Solvents containing ethenyl (vinyl) functional groups were also subject to decomposition on Bi$^0$. This has very serious repercussions and poses many difficulties to developing electrolytes suitable for use with bismuth nanocomposites. The vast majority of compounds identified for use as SEI additives in Li-ion cells are, in fact, based on these very same chemistries. Unless their addition to electrolytes can be effectively reduced to the absolute minimum required to passivate the negative electrode, these SEI additives will degrade the performance of the BiF$_3$ positive electrode. For the safety of the electrochemical device, this
is really not an option because a reserve of additive must always be present to repair the SEI, if damaged.

The additive must therefore be completely non-reactive with Bi\(^0\) (criterion 2a) in its normally cycled voltage range or somehow withstand large volumetric changes, possible incorporation into the conversion material during delithiation, and/or possible anodic decomposition of the SEI during delithiation (criterion 2b). Preliminary observations would suggest isocyanates to be prime candidates. On synthetic carbon, a widespread negative electrode in industrially manufactured cells, SEI layers were proven to form.[133, 147] Regarding the BiF\(_3\) nanocomposite positive electrode, preliminary results suggested the EtNCO to be relatively inert on Bi\(^0\). EtNCO is a linear molecule with a different functional group than S=O, C=O, or C=C. Improved cycling of the BiF\(_3\) nanocomposite, a fundamentally different type of positive electrode, requires the identification of electrolyte chemistries radically different than those presently established.

**6.4. Conclusion**

Cycling trials of BiF\(_3\) nanocomposites in additive-free ADN indisputably showed that good capacity retention was attainable for a nanocomposite utilizing a conversion mechanism to store energy, and it simultaneously highlighted the importance of identifying compatible electrolytes. Superior results were yielded when the electrolyte was devoid of any additives or co-solvents which are both susceptible to electrochemical reduction on Bi\(^0\). The reactivity of additives with the BiF\(_3\) nanocomposites poses problems for the development of a Li-ion cell. The susceptibility of the additive to be electrochemically reduced at potentials more positive than the bulk electrolyte solvent(s) is the very property that is exploited when selecting functional additives to stabilize the negative electrode / electrolyte interface. However, the
catalytic surface of the Bi\textsuperscript{0} also promotes the electrochemical reduction of the electrolyte additives with deleterious effects on the long-term capacity. It would thus seem that the ideal electrolyte additive for use in solvents such as ADN would (1) stabilize the negative electrode / electrolyte interface, (2) be nonreactive with the catalytic Bi\textsuperscript{0}, and (3) be able to withstand the relatively high positive potentials of the BiF\textsubscript{3} nanocomposite during reconversion.

Of the additives considered in this preliminary study, cyclic organic compounds containing C=O, S=O, or ethenyl (vinyl) functional groups were all subject to decomposition on Bi\textsuperscript{0}. Future trials with these compounds would involve lowering the additive concentration and studying the influence of the switching potential during discharge. From the observed voltage profiles (Figure 6.6(n)) and its unique chemistry, EtNCO and other isocyanates may be best suited as electrolytes additives compatible with BiF\textsubscript{3} nanocomposites.
7. Future work

Over the course of this investigation, observations were made which fell outside the scope of the research project, were beyond the capabilities of the accessible experimental equipment, and/or would have required a great deal of additional time and finances. The following sections highlight these observations and propose methodologies to explain their origins or implications.

7.1. Future work relevant to BiF$_3$ nanocomposites

In Chapter 4, the SEI layer that formed as a result of the electrochemical reduction of EC decomposed when the nanocomposite positive electrode was delithiated. It was apparent that the product of this reaction was a bismuth compound rich in oxygen, but the origin of this phase was split between two mechanisms. Either the decomposition of the SEI, which was composed predominantly of Li$_2$CO$_3$, occurred at potentials far less positive than 3.82 V vs. Li/Li$^+$ to yield gaseous oxygen local to the Bi$^0$ of the lithiated BiF$_3$, or, the Bi$^0$ reacted with the SEI in a conversion reaction to yield a phase such as Bi$_2$O$_3$ or Bi$_2$O$_2$CO$_3$. At present, NMR studies involving naturally abundant $^{13}$C (non-$^{13}$C enriched) and $^{209}$Bi are underway to determine the NMR signatures of nanocomposites of BiF$_3$, BiO$_{0.5}$F$_2$, BiOF, Bi$_2$O$_3$, and Bi$_2$O$_2$CO$_3$. These standards will aid in the identification of the species formed in the nanocomposites at varying degrees of delithiation (reconversion). To fully elucidate the reaction mechanism, a combination of EQCM with either DEMS or gas chromatography would be well-suited for studying the potentials at which gaseous species are evolved from the nanocomposite electrode.

A troubling observation involved the deposition of bismuth metal at the negative electrode. To date, the amount of this bismuth has not been quantified, nor has it been correlated with interactions of the electrolyte. Regardless of the mechanism by which it was deposited at the negative electrode, any bismuth located there will no longer be able to contribute to the
capacity of the cell. It is irreversibly lost from the positive electrode. Furthermore, if the morphology is such that the bismuth does not plate uniformly, the risk of shorting is greatly increased. A series of preliminary cycling and storage trials at 24°C were run that accounted for the number of cycles, the storage condition (initially fabricated cell, fully lithiated BiF₃, one full lithiation/delithiation of BiF₃), and the electrolyte (1 M LiPF₆ EC:DMC, 1 M LiTFSI + 0.25 M LiBF₄ EC:DMC, and 1 M LiTFSI + 0.25 M LiBF₄ 3MPN + 5 vol% VC). The lithium foil negative electrodes were recovered from each cell. The idea was that the lithium foils would act as a getter for all the soluble bismuth species in the electrolyte. Either through atomic emission (flame or inductively-coupled plasma) or electrochemical methods, the mass of Bi⁰ could be accurately determined from solutions formed by dissolving the negative electrodes in nitric acid (Li forms Li⁺ and OH⁻, metallic Bi is soluble in nitric acid). The goal would be to quantify the total Bi loss from the positive electrode and correlate with the storage and cycling conditions. Ideally, this total Bi loss would directly correspond to the observed capacity loss. If this occurred, it would demonstrate that the effectiveness of the conducting matrix was maintained. If the total Bi loss underestimated the observed capacity loss, then other failure modes such as electrochemical grinding, particle ripening, or electronic isolation of the active materials of the positive electrode are concurrent with the formation of soluble Bi species.

In conjunction with trials to quantify the amount of Bi deposited on the negative electrode, a merged electrochemical and spectroscopy experiment would be ideal. The envisioned apparatus would actually combine two sets of working, counter, and reference electrodes in a transparent vessel (Figure 7.1). The counter and reference electrodes will be assumed to be lithium foil. One set of the electrodes would involve either galvanostatic cycling or slow potentiodynamic scans of the BiF₃ nanocomposite electrode. The other set of electrodes would
comprise a silver or platinum mesh used to electrochemically reduce ("plate out") the Bi from solution before it diffuses to the lithium at the far end of the vessel. If the potential of the mesh electrode is set negative in relation to the reduction potential of Bi species from the electrolyte, Bi\(^0\) will be deposited on the mesh electrode surface. A fixed quantity of charge will be transferred. So long as the Bi\(^0\) is not spontaneously soluble from the mesh into the electrolyte, the extent of electrons transferred to the mesh should directly correspond to the mass of Bi\(^0\) deposited, and hence, the amount of Bi loss from the BiF\(_3\) electrode. In the proposed design, it is imperative that the lithium electrodes are positioned on only one side of the cell. Otherwise, soluble Bi species will plate out spontaneously on the lithium instead of through electrochemical reduction on the mesh electrode. Since the vessel will be transparent, spectrophotometric or FTIR techniques can be used to probe the electrolyte and identify the chemical entities of the soluble Bi species. The chemistry may, in fact, be quite rich owing to the possibility of forming complexes with the solvent and/or salt anions. Bi has been observed to complex in acetonitrile, another common aprotic solvent, in the presence of hexafluorides.[150] In acidic media, soluble fluoride complexes such as (BiF\(_2\))\(^+\) and (BiF\(_3\))\(^2+\) are possible.[151] And, when paired with strong fluoride acceptors, complexes and adducts can occur through strong fluorine bridging.[152]
Figure 7.1. Schematic of a proposed vessel combining electrochemical and spectrophotometric techniques.
It has been thoroughly established that cyclic organic carbonate solvents are unsatisfactory for use as electrolytes with BiF₃ nanocomposites (Chapters 3 and 6). In Chapter 6, ADN was examined with a variety of SEI additives, but to date, no additive has exceeded the performance of ADN + 10 vol% VC. It would be ideal to identify an additive that would either (a) be completely non-reactive with the BiF₃ nanocomposite or (b) form a resilient SEI layer that did not decompose or influence the underlying bismuth chemistry. In addition to aprotic solvents, several other types of electrolytes should be considered. Room temperature ionic liquids have been suggested, but improvements in their ionic conductivities must be realized before they can be successfully implemented in Li-ion cells. A solid polymer electrolyte may not permit the migration of Bi species, or if such species are more favorably complexed by aprotic solvents, the solid polymer electrolyte could diminish the likelihood of their formation. Solid state ionic conductors could be useful for this purpose as well.

At the outset of the research project, identifying the origin of the hexagonal bismuth phase observed after delithiation of the bismuth fluoride nanocomposite was proposed as a plan of study. To date, its origin remains undetermined. In Chapter 4, the formation of BiOₓF₃₋₂ₓ was concluded from XPS observations and thermochemical considerations. In the nanocomposite, an oxygen content of x≈0.02, and possibly lower, would result in the formation of hexagonal, Tysonite-like bismuth oxyfluoride.[153] From the XPS observations (Chapter 4), the binding energy shift of the sample swept to 4.5 V would support at least this amount of oxygen incorporation. Several electrochemical trials were run with 1 M LiPF₆ EMC (a linear carbonate electrolyte with no cyclic compounds to decompose during lithiation) and 0.25 M LiBF₄ ADN (LiTFSI was purposefully excluded to minimize oxygen containing chemicals from the electrolyte). The ex-situ XRD results for BiF₃ nanocomposites galvanostatically cycled once still
yielded a hexagonal bismuth phase. It was not possible to differentiate a hexagonal polymorph of pure BiF$_3$ from the Tysonite-like BiO$_x$F$_{3-2x}$ due to the extremely similar diffraction patterns and peak broadening of the nanoparticles. More work involving high resolution *in-situ* techniques, theoretical studies, and/or calculations that account for surface energies and coherency strains, would be necessary to elucidate the reason for the formation of a hexagonal phase. Its origin may lie in the thermodynamics or kinetics and is inherent to BiF$_3$ in the nanocomposite, or it may be triggered from an external source such as impurities in the electrolyte.

**7.2. Future work relevant to other metal fluoride conversion materials**

In BiF$_3$ nanocomposites, the incorporation of oxygen is detrimental. In other metal fluoride materials including FeF$_3$ and FeOF, the Fe$^0$ formed as a result of full lithiation may be catalytic with respect to the electrochemical reduction of electrolyte solvents (e.g. Figure 3.19). It would be very interesting to consider the possibility of oxygen incorporation into fluorides or oxygen enrichment of oxyfluoride conversion materials. If this were to be identified, how would the long-term cycling capacity be impacted, if at all? If considering metal fluorides in which the metal is a p-block element (Sn, Pb), a tendency exists to form SEI at potentials similar to those observed on Bi. This is based on observations on Sn and suggested from electrochemical trials on Bi in 1 M LiPF$_6$ EC:DMC.[24, 26] (Please note that in Refs. 24 and 26, the metals were not formed as result of lithiation of a nanocomposite positive electrode. Rather, the metals were being investigated for use as lithium alloy negative electrodes.) It is therefore expected that nanocomposites based on SnF$_2$ and PbF$_2$ would also be susceptible to the detrimental impacts of SEI formation. Future studies with EMC, ADN, and 3MPN electrolytes would also be interesting for all metal fluoride nanocomposite positive electrode materials.
7.3. Future work relevant to Li-ion batteries

The work of Chapter 5 was a departure from experiments directly pertaining to BiF₃. The initial results of electrolytes based predominantly on EMC, ADN, and 3MPN were promising because of the good capacity retention of the LiCoO₂ positive electrodes and the finite amount of lithium available in the full cells. However, the trials were performed at a fixed temperature of 24°C. If these formulations will be suitable for the development of cells capable of performing at exceedingly low and/or high temperatures, the properties of these electrolytes must be characterized and cycling trials must be performed over a range of temperatures. Some preliminary conductivity trials from -20°C to 30°C are displayed in Figure 7.2. It is not evident from the conductivity data alone, but the 3MPN electrolyte is, in fact, superior at temperatures below -10°C. Both the 1 M LiPF₆ EC:DMC 1:1, indicative of today’s state of the art electrolyte, and the 1 M LiTFSI + 0.25 M LiBF₄ EC:DMC 1:1, partially solidified whereas the 3MPN remained a liquid. The ADN electrolyte solidified below 0°C.

![Figure 7.2. Conductivity data for EC:DMC, ADN, and 3MPN electrolytes. Data collected with Solartron SI 1260 and 1287, Metrohm conductivity cell, and Haake programmable temperature circulating bath. At temperatures ≤ -10°C, both EC:DMC 1:1 electrolytes partially solidified. 3MPN is the solvent best suited for low temperature operation.](image-url)
7.4. Future work extending beyond Li-ion batteries

The catalytic nature of the Bi\(^0\) formed as a product of lithiation of BiF\(_3\) nanocomposite is interesting. This result was unexpected, but it has inspired the idea of using conversion materials systems to generate metals with catalytic properties. Heterogeneous catalysts are often metals. Surface area maximization and tuning of the energies of the catalyst surface through preferential faceting and alloying are employed to yield the greatest amount of desirable product while requiring the least amount of catalyst material. Through an electrochemical reaction, nanodomains of metal can be formed on an electronically conductive substrate. Depending on both the anion of the catalytic metal compound to be electrochemically reduced and the cation of the electrochemical reaction (e.g. MeF\(_x\) with Li\(^+\), MeCl\(_x\) with Na\(^+\)), the salt formed during the electrochemical reduction of the metal compound can be left intact or dissolved away. This can either maximize the surface area or destroy the nanocomposite completely such that the metallic nanoparticles could be collected for later use. While this would require extensive time and added processing steps, it may, in fact, be able to yield unique structures and provide a novel method for tuning the properties of catalysts in ways previously not possible with other development techniques.
8. Summary

For much of this thesis, the interaction of the bismuth fluoride nanocomposite with the electrolyte was studied specifically from the perspective of interphase development and the incorporation of interfacial / interphase byproducts during the reconversion reaction. Initial investigations of BiF₃ nanocomposites were conducted in organic carbonate solvents. It was discovered that the Bi⁰ metal produced through the discharge reaction of BiF₃ was a catalytically active site for the electrochemical reduction of ethylene carbonate (EC) at potentials exceeding 2 V vs. Li/Li⁺. Li₂CO₃ was the predominant SEI product formed from the decomposition of EC. EMC, a linear organic carbonate solvent, was not observed to form a SEI layer. Systematic evidence was provided for the degree of SEI formation and the impact on cycle life of the BiF₃ nanocomposite material.

We succeeded in correlating SEI formation with the observed detrimental impact on cycling of the BiF₃ nanocomposite electrode. The mechanism by which the SEI impacts the chemistry of the reconverted bismuth nanocomposite was more thoroughly examined. In LiPF₆ EC:DMC, the growth of an SEI layer on Bi⁰ corresponded to additional anodic current at potentials negative relative to Bi⁰ + LiF reconversion or the observed oxidative decomposition of Li₂CO₃. Through XPS analyses of glassy carbon and BiF₃ thin film electrodes, NMR of BiF₃ nanocomposite powder electrodes, and thermochemical calculations, we have demonstrated the instability of the SEI layer during reconversion. Whether by anodic decomposition of Li₂CO₃ with gas evolution or by a reconversion reaction involving Bi⁰ and carbonate species of the SEI, BiOxFₓ is formed between 2 V and 3.3 V. Then above 3.4 V, the BiOxFₓ and remaining Bi⁰ + LiF interact, yielding BiOxF₃₋₂ₓ in a stepwise reaction sequence. The implication of oxyfluoride formation on the capacity fade has been discussed.
The apparent lack of reactivity of EMC, a linear organic carbonate, on Bi\(^0\) led to work involving straight-chained nitrile solvents. For the first time, EMC, ADN and 3MPN were formulated into high concentration electrolyte blends. Stability of these electrolytes at the negative electrode (synthetic graphite) was enabled through the use of VC and FEC additives, and good cycling performance was observed in a 4 V Li-ion configuration. Overall, this initial research showed promise toward the development of electrolytes capable of operation at low temperature, at high temperature, and/or with > 5 V positive electrode materials. Furthermore, for the first time, the decomposition products of FEC were identified without the presence of either EC or LiPF\(_6\), a fluorinated salt, in the electrolyte. FEC was electrochemically reduced to lithium alkyl carbonate and lithium fluoride.

Adapting the nitrile electrolyte work to BiF\(_3\) was challenging due to the lack of an ability of the nitriles to form a stable SEI layer intrinsically. Using an unconventional method involving a LiCoO\(_2\) counter electrode, cycling BiF\(_3\) nanocomposites in additive-free nitrile electrolytes yielded a distinct improvement over organic carbonates. In fact, the best capacity retention to date was observed for a BiF\(_3\) vs. LiCoO\(_2\) cell with an ADN electrolyte. ADN was surveyed with a series of additives in order to make a functional cell that would ideally be stable with respect to the negative electrode and be non-reactive with the BiF\(_3\) nanocomposite positive electrode. The initial observations of EC were found to extend to other cyclic organic solvents with C=O and S=O functional groups as these were also observed to decompose through electrochemical reduction on the catalytically active Bi\(^0\). These preliminary results highlight the challenges of finding suitable additives for use with bismuth nanocomposites. Without any additives, the electrolytes are unstable on the negative electrode; however, the inclusion of the additives examined has unfavorably impacted the positive electrode when discharged to 2 V vs. Li/Li\(^+\).
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