PHYSICAL AND ELECTROCHEMICAL STUDY OF HALIDE-MODIFIED ACTIVATED CARBONS

By

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ABSTRACT OF THE DISSERTATION

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Dissertation Director: Prof. Glenn G. Amatucci

The current thesis aims to improve the electrochemical capacity of activated carbon electrodes, which enjoy prominent position in commercial electrochemical capacitors. Our approach was to develop electrochemical capacity by developing faradaic pseudocapacitance in carbon through a novel mechanochemical modification using iodine and bromine.

Various commercial carbons were mechanochemically modified via solid-state iodation and vapour phase iodine-incorporation. The halidation-induced changes in the structure, composition, morphology, electrical and electrochemical properties of carbon materials were studied using different characterization techniques encompassing XRD, XRF, XPS, Raman spectroscopy, BET study, TEM, SAXS and electrochemical testing followed by an intensive battery of physical and electrochemical characterization. The introduction of iodine into carbon system led to the formation of polyiodide species that were preferentially reacted within the micropore voids within the carbon leading to the development of a faradaic reaction at 3.1V. In spite of the lower surface area of modified carbon, we observed manyfold increase in its electrochemical capacity. Parallel inception of non-faradaic development and faradaic pseudocapacitive reaction led to promising gravimetric, surface area normalized and volumetric capacity in iodated carbons. With promising electrochemical improvement post halidation process, the chemical halidation method was extended to different class of carbons and halides. Carbons ranging from amorphous (activated) carbons to crystalline carbons (graphites, fluorographites) were iodine-modified to gain further insight on the local graphite-iodine chemical interaction. In addition, the effect of pore size distribution on chemical iodation process was studied by using in-house fabricated microporous carbon. A comparative study of commercial mesoporous carbons and in-house fabricated microporous carbons showed higher iodineuptake ability and larger volumetric capacity development in case of microporous carbons. For halides, bromine was also tested in activated carbons, which showed similar set of physical and electrochemical modification, but to a smaller degree.

Carbon-polyhalide nanocomposites form a very interesting system both for fundamental research and as new electrode systems for asymmetric hybrid capacitor and low-voltage high power battery type applications.

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"Everything Grows With Gratitude." -----OSHO

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Life and science goes on.



"The five essential entrepreneurial skills for success are concentration, discrimination, organization, innovation and communication."

----- Michael Faraday

"Just do it!" ----- Nike®

"The best way to get a good idea is to get lots of ideas". ----- Linus Pauling

"....Don't Stop Till You Get Enough!" ----- Michael Jackson

"Keep punching." ----Sylvester Stallone (Rocky)

"Life is short. Play hard .No Guts, No Glory! Never give up. Remember: Even a blind squirrel will someday find a nut". ---- Robert J Cava, Princeton Univ, NJ.

"Never say NEVER!"

---- Jean-Marie Tarascon, UPJV, France.

"Seek for true impact of the research work, not the impact factor of research publication". -----Glenn G Amatucci, Rutgers University, NJ

"The opposite of Success is not Failure....Its Quitting. The opposite of Failure is not Success...Its Continuing." ----- Anonymous

"There are only two ways to live your life. One is as though nothing is a miracle. The other is as though everything is a miracle." ----- Albert Einstein

> "The finest steel has to go through the hottest fire". ----- John N Mitchell

"Awake, Arise and Stop not till the goal is reached. The goal is life, not empty dreams". ----- Swami Vivekananda

> "The success is not in the trophy won, but in the race run. The glory lies not in quarry, but in chase. Plan out the Work....And Work out the Plan. Know what to do...and do it yourself. Do the best...and leave the rest. And Remember.....Even this will pass away!" -----Swami Chinmayananda

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1.1 Introduction to energy-storage devices

The ever-increasing scientific progress, technological development and global commercialization of electronic and automobile technologies over last five decades have resulted in 'energy and environment' crisis worldwide. As pointed by eminent Nobel laureate Prof. Richard E Smalley, energy is going to the biggest challenge for international scientific community for next century [1]. This alarming energy-crisis is driving exponential growth in technical effort to combat the energy-harvesting, supply, energy-storage and energy-delivery in eco-friendly ways. In this sector, electrochemical energy storage devices are attracting significant attention these days. These electrochemical devices can serve applications ranging from portable electronics (e.g. cellular phones, laptop computers, digital cameras etc), bio-medical devices to hybrid electric vehicles. Various electrochemical devices have different combination of energy-density and power-density, which can be represented in form of Ragone plot (Figure 1.1). Typical electrochemical properties of these devices are summarized in table 1.1



Fig 1.1: Ragone's plots showing various zones related to energy-storage devices with different combination of energy-density and power-density.

Electrochemical Characteristics	Batteries	Carbon Supercapacitors	Electrolytic capacitors
Specific energy (Wh/kg)	10-100	1-10	<0.1
Specific power (W/kg)	<1000	500-10000	>>10000
Discharge time	0.3-3 h	s~min	$10^{-6} \sim 10^{-3} \text{ s}$
Charge time	1-5 h	s~min	$10^{-6} \sim 10^{-3}$ s
Charge-discharge efficiency	70-85%	85-98%	~100%
Cycling stability (cycles)	~1000	>500000	Infinite
Maximum voltage determinant	thermodynamics of phase reactions	electrode/ electrolyte stability window	Dielectric thickness
Charge storage determinant	active mass and thermodynamics	electrolyte/ electrode microstructure	electrode area

Table 1.1: Comparison of electrochemical properties of typical supercapacitors and batteries [1]

As shown, the battery and capacitor form the two extremes of the plot having high energy density and high power-density respectively. Electrochemical capacitors (here onwards referred as supercapacitors) form an interesting device with a unique combination of energy density and power-density [2-4]. This chapter provides a summary of science and technology of electrochemical capacitors (supercapacitors).

1.2 Comparison between battery and supercapacitors

Battery and *Supercapacitor* are adjacent to each other in Ragone plot having advantage in energy-density and power-density respectively. This section briefly draws a comparison between these two classes of secondary energy-storage devices.

There are two fundamental ways to store electrical energy by electrochemical means. First, it can be stored indirectly as potentially available chemical energy, which delivers charge with faradaic redox reaction of electrochemically active electrodes. Second, it can be stored directly as electrostatic charge on two electrode interfaces, which deliver charge involving non-faradaic reaction. While battery is based on first method, supercapacitor employs the latter method. The evolution of electrostatic charge storage in supercapacitor is briefly described below.

Any conventional capacitor store oppositely charged carriers (electrons) on the surface of two conducting electrodes. The resulting charge separation creates a potential difference (voltage) between the two electrodes, which can be exploited in an external circuit. The net capacitance (C) of this arrangement can be expressed as:

$$C = \frac{\varepsilon A}{d}$$
 where, ε = permittivity of air,

A = surface area of electrode plate, and d = distance between electrodes.

The net energy stored by the electrostatic capacitor depends upon the net charge stored (C) and the corresponding potential difference (V). The capacitance can be developed by increasing surface area and decreasing the electrode distance. The potential difference is often limited by the dielectric breakdown potential of the electrodes. Various dielectric materials can be inserted between oppositely charged electrodes to improve the voltage and energy storage ability of capacitors. The modified capacitance can be expressed as:

$$C = \frac{\varepsilon_o \varepsilon_r A}{d}$$
 where, ε_r = relative permittivity of dielectrics.

Using dielectric spacers with higher permittivity values, electrostatic capacitors can be made with capacitance exceeding several hundred microfarads (μ F).

On the other hand, electrochemical capacitors (or supercapacitors) store electrostatic energy at electrode interface via reversible adsorption of electrolyte ions. The electrolyte ions form diffused double layer at electrode surface. The thickness of this ionic double layer can be expressed as [5]:

Double layer thickness =
$$\kappa^{-1} = \left(\frac{\varepsilon_r \varepsilon_0 k_B T}{F^2 \sum N_i Z_i^2}\right)^{1/2}$$

where, ε_r = dielectric constant of electrolytic solution,

 ε_0 = permittivity of free space,

 k_B = Boltzmann constant, N_i = concentration of ion in solution,

F = Faraday constant and $Z_i =$ number of charge of ionic species.

This double layer thickness is very small, which corresponds to small distance (d, in nm) between centre of electrolyte ion and electrode surface. Further, electrochemical capacitor involves very high surface area (A) (>1000 m²/g) electrodes. Combining these two parameters, electrochemical capacitor gives rise to extremely high capacitance values (>100 F/g).

The fundamental reaction mechanisms lead to reversibility difference in battery and supercapacitor. In supercapacitors, the formation/ dissolution of electrochemical double layers at electrode-electrolyte interface does not involve any chemical changes in electrodes. Any such chemical change involves strain due to phase/ structural variation that lead to electrode failure over long cycling. The nonfaradaic reaction affirms very high degree of reversibility and cycling stability.

However, in case of (lithium-ion) batteries, the electrochemical energy storage involves faradaic chemical conversion (or phase changes) of electrode materials via intercalation reaction as shown in Fig 1.2. Intercalation process involves reversible insertion of guest species (Li⁺ ions) into a host structure having vacant sites and diffusion pathways. During discharge, Li dissociates into Li⁺ ions and electrons (at negative electrode). These ions move to positive electrode via electrolyte and electrons move through external circuit. The Li⁺ ions intercalate into and reduce the host (metal-oxide) structure. Upon charging, the reverse reaction occurs oxidizing the host structure.

 $x Li^+ + x e^- + MO_y \leftrightarrow Li_x MO_y$ (intercalation process)

As battery involves (bulk) intercalation reaction with valence electrons of each atom (1 electron per atom), it gives more energy-density, whereas supercapacitor charge

storage is mostly interfacial with less energy-density (0.2 electrons involved per atom). However, this bulk reaction involves huge strain, irreversible loss and slower reaction kinetics of charge storage and cycling stability.



Figure 1.2: Schematic representation of (bulk) intercalation reaction involved in lithium-ion battery, also known as rocking chair batteries.

In case of supercapacitors, the energy required to charge an electrode to voltage V is the Gibb's free energy (an electrostatic free energy) expressed as:

$$G = H - TS = \frac{1}{2}CV^2 = \frac{1}{2}QV$$

where, H = enthalpy of charging process, T = temperature of operation, V = voltage,

 $S = entropy arising from temperature dependence of '<math>\varepsilon$ ' of ionic double layer.

 ε = dielectric constant of electrochemical double layer, Q = Charge.

In case of battery, the Gibb's free energy involved is the product of charge (Q) and potential difference (ΔE), between the Nernstian reversible potentials of two electrodes. This leads to the expression: $G = Q\Delta E = QV$.

Comparing these Gibbs free energy equations, it is evident for a fixed voltage range (V), the energy stored by a two-electrode battery involving a faradaic charge Q at voltage ΔE or V, is twice that of energy stored in supercapacitor. While charging a battery, a thermodynamic potential exists independent of the degree of charging, thus

delivering a constant potential difference (ΔE) throughout the discharge cycle. But, in supercapacitors, a certain amount of work has to be done against the existing charge density (around the electrode) in order to add any additional element of charge. This phenomenon progressively increases the electrode potential difference.



Fig 1.3: Upper diagram showing the comparison between the ideal voltage profiles of battery and supercapacitors. Bottom diagrams show the energy stored (area covered in Q-V diagram), battery having double energy-density [6].

The difference between battery and supercapacitor discharge profiles are shown in figure 1.3. While the voltage of supercapacitor gradually decreases with the extent of charge, the voltage of battery remains constant throughout the process. As the area under Q-V curve denotes energy-density, supercapacitors have lower energydensity due to decreasing voltage profile. Battery and supercapacitor have their own advantages and shortcomings that find different specific applications.

1.3 Applications and world-wide market for Supercapacitors:

Supercapacitors find plethora of applications requiring high power density, long cycling stability and low-voltage pulse power applications (milliseconds range).



Figure 1.4: Some commercially available supercapacitor products of different size/ capacity, manufactured by Maxwell, Cap-XX and NEC Inc.

Supercapacitors were commercially introduced first by Panasonic/Matsushita with trade name Gold Capacitors (1978) [7] and by NEC/Tokin with trade name Supercap [8]. By late eighties, ELNA Inc and Seiko Inc [9] entered into commercial markets. These Supercapacitors are targeted for consumer electronics usages. In early nineties, two Russian companies (ECond Inc with product PSCap, ELIT Inc [10] with product SC) made successful entry to commercial market. Panasonic produced cylindrical capacitors (1500 F, 2.3 V) and Maxwell [11] produced prismatic capacitors (2700 F, 2.3 V). Some commercial supercapacitors are sold annually, which form 1% of world market for electrical energy storage [12]. However, the recent progressive advances in improved performance, decreasing cost and long cycling are leading to an exciting future for electrochemical supercapacitors.



Figure 1.5: .The use of supercapacitors in (a) backup to a battery-powered device, (b) protecting the critical load from large voltage drops.

From application point of view, consumer electronics consume the largest number of supercapacitors, serving as a backup power for memories, microcomputers, clocks, system boards etc. Here, Supercapacitors back up the primary power sources (battery or AC source) as shown schematically in figure 1.5. Some current generation applications of electrochemical supercapacitors are listed below.

- (a) Car audio system/ taximeter: back up (4 hours to 4 days) for radio station memory, taxi fare programmes etc, while the radio/ meter are taken out of car.
- (b) Video recorders, TV satellite: back up for clock time, channel setting etc.
- (c) Photo cameras/ video cameras, pocket calculators, electronic organizers, mobile phones, pagers etc. Here, supercapacitors provides back up during battery replacement.
- (d) Electronic toys: Supercapacitors are used in toys due to long cycling and high power density. They are usually quickly charged by the battery for operation.
- (e) Starter usages: Electrochemical supercapacitors are used to provide pulse power to start locomotives. It is charged from lead-acid battery within a

minute and gives the pulse power to ignite the engine. It reduces the battery size by 50%, as batteries are tasked with much less pulse currents.

- (f) Fail-safe positioning: Electrochemical supercapacitors provide power for open/ close positioning in case of power failures.
- (g) Solar cells complementary devices: In recent days, solar power generating devices are using supercapacitors as a complementary device for power storage. They are charged by solar cells and once charged, they can supply power for solar lanterns, solar watch etc for few days. The long cycling of capacitors makes it favourite for solar cells installed in remote locations.

Apart from these consumer usages, Supercapacitors are seriously being considered for electric vehicles (EV), hybrid electric vehicles (HEV) and fuel cell vehicles [13]. Here, Supercapacitors will be used for power back-up system and to store energy from regenerative braking, which can be used for subsequent acceleration of vehicles (Figure 1.6). The regenerative nature helps extending the lifetime of primary power source (battery, combustion engine) in motor vehicles with many go-stop intervals. It can reduce the energy consumption by 20-30% in urban areas, which reduces oil consumption by thousands of gallons annually.



Figure 1.6: Schematic diagram showing the driveline of a hybrid electric vehicle employing supercapacitors as energy-storage device for regenerative braking set-up. The arrows indicate the flow of energy from the combustion engine to wheel.

Apart from applications in personal vehicles, supercapacitors can find similar applications in people-movers at fairs, carriers in hospitals, airport buses, wheelchairs, amusement minicars etc. It can use the frequent stopping-braking energy at very fast rate.

In addition, supercapacitors are moving towards telecommunications usages. Along with battery, supercapacitors can be used to improve power output and cycling life [14, 15]. Additionally, some industrial processes (chemical production, paper/ textile industry, semiconductor and pharmaceuticals industry) always tend to avoid short interruption/ disturbance of power supply. Supercapacitors, in conjunction with battery, can be useful in these industries.

Many actuators usages need high power and energy back-up, which can be delivered by supercapacitors. Some of these possible uses are enlisted here.

- (a) magnetic medium/ high voltage switch-gear system,
- (b) pace makers, defibrillators and X-ray generators,
- (c) actuators for flood-control in submarine system,
- (d) starting of military tank/ trucks in very hot/cold environment,
- (e) bridge power for submarine computer systems, detonators, pulse lasers.
- (f) Power-storage related to solar cells, wind-turbines, wave-energy devices.

As shown here, electrochemical Supercapacitors have tremendous potential for research and applications. Table 1.2 enlists some major world-wide research efforts on different kinds of supercapacitors. The electrochemical performances of some current and future generation supercapacitors are captured in table 1.3. Supercapacitors have no movable parts, are safe to operate and needs no cooling/ auxiliary installations. The exceptional cycle life and cheaper electrode materials
make it very economic in large scale production. Also they are eco-friendly with no hazardous/ heavy metals. Thus, it is envisioned, that in the near future electrochemical supercapacitors will affect wide range of industries, from consumer electronics to electric vehicles.

Country	Company/ Lab	Description of the technology	Energy density (Wh/kg)	Power density (W/kg)
Carbon par	ticulate composites	S		
Japan	Panasonic	Spiral wound, particulate with binder, Organic electrolyte	3-4	200-400
France/ US	A SAFT/Alcatel	Spiral wound, particulate with binder, Organic electrolyte	, 3	500
Australia	Cap-XX	Spiral wound/ monoblock, particulate with binder. Organic electrolyte	6	300
Japan	NEC-Tokin	Monoblock, multi-cell, ticulate with binder, organic electrolyte	0.5	5-10
Russia	ELIT	Bipolar, multicell carbon with H_2SO_4	1	9
Carbon fibr	re composites			
USA	Maxwell	Monoblock carbon cloth on Al foil, Organic electrolyte	3-5	400-600
Sweden	Superfarad	Monoblock multicell carbon cloth On Al foil, organic electrolyte	5	200-300
Carbon Aa	rogals			
USA	PowerStor S	piral wound, aerogel carbon with binde Organic electrolyte	er, 0.4	250
Conducting	nobmer films			
USA	Los Alamos National Lab	Single cell, conducting polymer on carbon paper, organic electrolyte	1.2	2000
Mixed meta	el oxides			
USA	Pinnacle Research	Bipolar, multicell, RuO ₂ on Ti foil, sulfuric acid electrolyte	0.5-0	.6 200
USA U	JS Army Research	Hydrous RuO ₂ , bipolar, multicell Architecture, H ₂ SO ₄	1.5	4000
Hybrid Sup	ercapacitors			
Russia	Evans	Double layer/ Faradaic monoblock,	8-10) 100
USA	ESMA	Multiple cell, Carbon/ NiO/ H ₂ SO ₄ Double layer/electrolytic, single cell, monoblock, RuO ₂ / Ta powders/ H ₂ SO ₄	0.1	30000

Table 1.2: World-wide research and development activities on supercapacitors [1]:

Type Ele		trode/ Electrolyte	Present status		Future	Future goals	
			Energy	Power	Energy	Power	
			density	density	density	density	
			(Wh/kg)	(W/kg)	(Wh/kg)	(W/kg)	
Double-1	aver	Carbon/ aqueous	1.0	1.0	15	2.0	
Double	luyer	Carbon/ organic	5-6	0.5	8-10	1-1.5	
Pseudocapacitance		Anhydrous RuO_2 (aq.)	0.6	0.5-2.0	1.0	2-3	
	1	Hydrous RuO_2 (aq.)			8-10	4-6	
Mixed metal oxides (aq)					1.5	2-3	
Doped metal oxide (organic)		8-12	1-2	
Doped conducting polymers (orga			ic) 1.0	1.8	8	4	
Hybrid	1	Carbon/NiO/Aqueous	1.5	0.3	8-10	2-3	
		Carbon/ PbO ₂ / Aqueous			10-20	2-3	

Table 1.3: Summary of present and future performance of various supercapacitor technologies [1]:

1.4 Different types (taxonomy) of supercapacitors

Electrochemical supercapacitors can be fabricated using different types and combination of electrodes, which involve various electric charge storage mechanisms. Broadly, supercapacitors can be divided into two categories based on their operating principles (a) electrical double layer capacitors (EDLC) and (b) pseudocapacitors. Further, recently hybrid capacitors have evolved as a special class involving unique electrode combination. Figure 1.7 enlists three major types of supercapacitors. They are briefly explained below.

1.4.1 Electrochemical double layer capacitors (EDLC):

Whenever a solid material is exposed to an ionic solution, a separation of ionic/ electronic charges arises across the solid-liquid interface. If the solid member is charged, oppositely charged ions are attracted towards its interface forming a dense, adsorbed layer (known as Stern layer). Following this surface layer, a diffused layer of ions is formed to complete the charge balance (Diffused layer). These two layers

collectively give rise to 'interfacial double layer', which stores electrostatic charge. This concept is used in electrochemical double layer capacitors (EDLC), where energy is electrostatically stored as ionic double layer formed at the interface between solid electrode surface and liquid electrolyte trapped in electrode pores.



Figure 1.7: The taxonomy of three main types of supercapacitors.

The ions displaced in forming the double-layers within the pores are transferred between the electrodes via diffusion through the electrolyte. The amount of charge stored (ΔQ) in EDLC is related to the potential difference (ΔV) across the

interface, so it establishes a capacitance $C_{DL}=\Delta Q/\Delta V$ (double layer capacitance). The energy and charge stored in EDLCs are $\frac{1}{2}$ CV² and CV respectively. Here, the capacitance is primarily dependent upon the morphological characteristics of the electrode materials (BET surface area and pore size distribution). The thickness of ionic double layer is very small (sometime fraction of nanometer) leading to high value of capacitance. This forms the basis of electrochemical double layer capacitor (EDLC) [5]. Figure 1.8 schematically depicts the concept of double layer formation and the resulting variation of overall charge in the cell. During the charge/ discharge cycle of EDLCs, double layer appears and disappears repeatedly. As this is a simple mechanism requiring no bulk diffusion, the EDLC operates very fast (thus giving high-power) with long life-time.

Though double-layer (DL) is dominating in EDLC, the formation of space charge (SC) inside electrode also contributes to the overall capacity. When the electrode is charged, it develops different degree of space charge inside electrode, which helps forming more effective ionic double layers. So, the net electrochemical capacitance (C) is a series connection of two capacitor components owing to double layer and space charge as shown in figure 1.9.

$$C^{-1} = C^{-1}_{DL} + C^{-1}_{SC}$$

And the ratio of potential drops (ΔU) across two double-layer regions is:

$$\Delta U_{SC} / \Delta U_{DL} = C_{DL} / C_{SC}$$

Considering the EDLC electrodes to be semi-metallic-metallic layer, it is recently proposed that improvement in space charge can play key role in developing high specific capacity [16].



Figure 1.8: Schematic showing the formation of electrochemical ionic double layer at two electrodes. Regions I and 2 stand for Stern and diffused layer together known as electrochemical double layer. The diagram below shows overall charge (ϕ) in the whole configuration.

Several types of double-layer supercapacitors are commercially available (some major products shown in table 1.4). Carbon based materials occupy a predominant position in commercial EDLC market. Here, some commercially viable carbon materials are discussed below.



Figure 1.9: Schematic showing a negatively charged activated carbon electrodes with individual carbon particles developing negative space charge within electrode and subsequently forming positively charged ionic double layer outside carbon particles. The total capacitance (C) is parallel combination of space charge (C_{SC}) and double layer (C_{DL}) capacitance.

Manufacturer	Tradename	Capacitance (F)	Voltage (V) Type
A sala: slass	EDLC	500 2000	2	
Asani glass	EDLC	500-2000	3	carbon/ non-aqueous
AVX	Bestcap	0.022-0.56	3.5	carbon/polymer/aqueous
Cap-XX	Supercapacitor	0.09-2.8	2.3	carbon/ non-aqueous
Cooper	PowerStor	0.47-50	2.3	aerogel/non-aqueous
ELNA	Dynacap	0.33-100	2.5	carbon/ non-aqueous
Epcos	Ultracapacitor	5-5000	2.3	carbon/ non-aqueous
Evans	Capattery	0.01-1.5	5.5	carbon/ aqueous
Maxwell	Boostcap	1.8-2600	2.5	carbon/ non-aqueous
NEC	Supercapacitor	0.01-6.5	3.5	carbon aqueous/organic
Nippon Chemicon	n DLCAP	300-3000	2.5	carbon/ non-aqueous
Ness	NessCap	3-5000	2.7	carbon/organic
Matsushita	Gold capacitor	0.1-2500	2.3	carbon/organic
Tavrima/ECOND	Supercapacitor	0.13-160	14	carbon/aqueous
Ness Matsushita Tavrima/ECOND	NessCap Gold capacitor Supercapacitor	3-5000 0.1-2500 0.13-160	2.7 2.3 14	carbon/organ carbon/organ carbon/aqueou

Table 1.4: Some commercially available double layer supercapacitors (EDLC) [5]:

1.4.1.1 Activated carbons:

Various forms of carbon are used in electrochemical energy storage as: active electrodes, electro-conductive additives, electron transfer catalysts, supports for active materials, intercalation hosts (anodes), substrates for current leads and as controlling agents for heat transfer, porosity, surface area and capacitance [17]. This is particularly true in the field of electrochemical supercapacitors, where carbon occupy a dominating market share. Carbon exists in four crystalline (ordered) allotropes: diamond (sp³), graphite (sp²), lonsdaleite (sp³), carbyne (sp¹) and fullerenes (distorted/ curves sp²) (Figure 1.10, [18]). Depending on the relative content of these allotropes, various carbon electrodes deliver different physical/ electrochemical properties.



Figure 1.10: Some common allotropes of carbon: (a) diamond, (b) graphite, (c) lonsdaleite, (d-f) fullerenes (C_{60} , C_{540} , C_{70}), (g) amorphous carbon and (h) nanotubes.

Among all kinds of carbon, activated carbons dominate the commercial supercapacitor usages. They are also known as engineered carbons having amorphous structure with a disordered graphitic microstructure [19]. The activated carbons are fabricated using carbonization (heating in inert atmosphere) of carbon-rich organic

Carbon materials Carbon precursors		rs	Controlling production factors		Structural/textural feature	
Solid phase						
Activated carbons	: biomass, coals, c	oke,	carbonization/		nanosize pores	
	selected polymo	ers	activation			
Molecular sieve	selected biomas	ss,	selective pore		nanosize pores/	
Carbons:	coals, polymers	5	development		constrictions	
Glass-like carbons	s: thermosetting		slo	W	random crystallites	
	polymers		carbon	ization	and impervious	
Carbon fibres:	selected polymo	ers	slow		random crystallites	
			carbon	ization	and non-porous	
Highly-oriented	pyrolytic carb	on,	high-m	olecular	highly oriented	
graphites:	polyamide fil	ms	orien	tation	crystallites	
Liquid phase						
Cokes:	pitch, coke	shea	r stress	mesopha	se formation/ growth	
Graphite: p	etroleum coke	temp	perature	mesopha	se formation/ growth	
Carbon fibres:	coal pitch	spii	nning	mesopha	se formation/ growth	
Gas phase						
Carbon blacks:	hydrocarbon gas		prec	ursor	colloidal/nanosized	
			Concer	ntration		
Pyrolytic carbon:	hydrocarbon gas		deposi	tion on	preferred orientation	
			Subs	strate		
Fullerenes: graphite rods			condensation		nanosize molecule	
			of carbo	n vapour		
Nanotubes: hydrocarbon			condensation		single-wall, chiral,	
	Vapour		of carbo	n vapour	multi-wall	

Table 1.5: Some widely-used carbonaceous precursors and controlling production factors for various class of (activated) carbon materials [19]:

precursors. The final physical and electrochemical properties are directly related to activation process parameters like carbon precursors, aggregation state of precursors, carbonization conditions, structural/ textural feature of the products. Table 1.5 summarizes the effect of activation processing factors using common carbon precursors. The carbonization process involves thermal decomposition (pyrolysis) of existing volatile materials including heteroatoms. With higher temperature, condensation reactions are triggered forming localized evolution of microcrystallites (stacking of graphene sheets). The size and orientation of these localized graphitic

zones play pivotal roles in the resulting carbon texture and electrical conductivity. Some important parameters of activated carbons are presented below.

(a) Activation process:

Activated carbons are commercially prepared by using (a) thermal (physical) activation and (b) chemical activation [20]. Thermal or physical activation involves high temperature (700-1100 °C) controlled gasification of carbonaceous precursors in presence of oxidizing gases such as steam, carbon dioxide, air etc. The oxidizing ambience triggers a controlled burning of volatile materials and carbons to develop high surface area and porosity. The degree of activation is solely controlled by carbonization temperature and duration. Very aggressive activation is avoided as it incurs huge carbon burn-off, low carbon yield, low density and pore widening [21].

On the other hand, chemical activation is conducted at lower temperature (400-800 °C) involving chemical activating (dehydrating) agent e.g. potassium hydroxide, phosophoric acid, zinc chloride etc. The activating agent penetrates into the precursor and come out during activation creating huge porosity and surface area. The final morphology of carbon can be easily tuned by controlling the amount of activating agent, carbonization temperature/ duration, heating rate etc [22]. Chemical activation is widely used to produce exceptionally high surface area carbon (>2500 m²/g). Various forms of thermally/ chemically activated carbons (Figure 1.11) are commercially available for adsorption-based applications.



Fig 1.11: Commercially available thermally/ chemically activated carbons: SEM images of (a) platelet structured carbon, (b) spherical particulate carbon, and TEM images of (c) microporous and (d) mesoporous carbons.

(b) Carbon morphology (surface area and porosity):

Morphology is the most-important parameter for activated carbons. Activation process can yield high surface area (>3000 m²/g), which largely arises from a tortuous interconnected network of micro/mesopores. High surface area offers large number of pores, which are accessible to electrolyte ions. It favors more effective formation of interfacial ionic double layer leading to higher capacitance (110~140 F/g for activated carbons). Fig 1.12(a) shows a linear relation between surface area and electrochemical capacitance. However, the internal pore structure plays dominant role in effective double-layer formation. As per IUPAC [23], pores can be classified as micropores (0-2 nm), mesopores (2-50 nm) and macropores (>50 nm). The relatively larger mesopores (2-50 nm) not only contribute to large surface area but also encourage improved adsorbate accessibility and ionic diffusion. It can be easily accessible by organic electrolyte ions, hence actively takes part in surface layer formation.

On the other hand, micropores have high surface area to volume ratio, hence contributes to high surface area. However, micropores (0-2 nm) have restricted diffusion and molecular sieve effect. Due to its small size, micropores are mostly not accessible to electrolyte ions, specifically the solvent ions (specially non-aqueous organic electrolytes). Steady decrease in capacitance with smaller pore size is shown in figure 1.12(b). Further, microporous carbons have high electrolyte resistance and less electrolyte penetration, which limits their capacitance. Thus, mesoporous carbons are commercially favored (for organic electrolyte) for effective pore accessibility. However, recent studies have shown improved capacitance in microporous carbons [24,25], which argues that 'desolvation of organic electrolyte' and 'forced electro-adsorption' can facilitate organic electrolyte ions to access micropores.

Due to its influences on electrochemical performance, significant research effort is geared to obtain high surface area activated carbons with tailored pore size.



Fig 1.12: (a) A graph showing the near-linear relation between BET surface area of activated carbons with their specific capacitance and (b) The gradual decrease (shown by arrow mark) in specific capacitance of activated carbons with lower pore size [26].

(c) Carbon's electrical properties:

Apart from surface morphology, electrical properties are the most crucial properties for activated carbons. Electrical (electronic) resistivity depends on the intrinsic properties of carbon and aggregate properties (how fine particulates are bound). Carbonaceous precursors contain high proportion of sp³ (σ) bonded carbon, thus having low conductivity. During high-temperature carbonization, the electrical conductivity of activated carbons increases due to progressive formation of sp² (π) bonded carbon with delocalized π charge carriers [11]. So, depending upon carbonization condition, activated carbons with varying conductivity can be fabricated, higher temperature favoring more conductivity. The resistivity of some commercial carbons is shown in figure 1.13, showing carbons ranging from semi-conducting to semi-metallic nature [12].

In addition to intrinsic (intra-particle) resistivity of carbon, the electrical resistivity of packed bed (aggregate) of carbons depends on contact (inter-particle)

resistance. The combined effect of intrinsic electronic nature and agglomeration nature (particle packing/ effective percolation) leads to final electrical resistivity, which is preferred to be minimum in order to deliver high electrochemical performance.



Figure 1.13: Graph showing the electrical resistivity (ρ) vs. temperature for various forms of carbons:
(1) single-crystal graphite,
(2) highly oriented pyrolytic graphite (HOPG),
(3) graphite whisker,
(4) pyrolytic graphite,
(5) petroleum coke carbon,
(6) lampblack carbon,
(7) glassy carbon,
(8) electron beam evaporated carbon film.

1.4.1.2 Carbon materials for supercapacitor electrodes:

Carbons exist in myriad of forms and morphology. The structure, porosity and morphology of carbons can be manipulated greatly by controlling the processing routes and processing parameters. Thus, apart from meso/microporous activated carbons, many other types of carbons are being pursued for their possible usage in electrochemical supercapacitors. Some typical carbon materials with potential supercapacitor use are described in a nutshell here.

1.4.1.2.1 Carbon aerogels/ xerogels:

Carbon aerogels are monolithic 3-dimensional mesoporous network of carbon nanoparticles [Figure 1.14]. These gels can be manufactured via pyrolysis of organic aerogels or sol-gel synthesis. The structure and morphology of carbon aerogels can be easily controlled. The morphology (microtexture, particle size, pore distribution) is controlled by precursor gel composition and pyrolysis temperature [29]. Recently, aerogels are proposed to be used in Supercapacitors owing to their high surface area, low density, excellent electrical conductivity and possibility of avoiding any binders [30-32]. Aerogels have interconnected pores with homogeneous pore size and high pore volume, which strongly affects the electrochemical properties. These carbons can be further improved via surface functionalisation that improves overall capacity by pseudocapacitance. Carbon xerogels are aerogels produced by conventional drying. These aerogels/xerogels are capable of delivering around 60~180 F/g capacitance.



Figure 1.14: SEM images showing uniform and porous (a) carbon aerogels, (b) carbon xerogels (Merketech Inc).

1.4.1.2.2 Carbon nanotubes (CNTs):

From fundamental research to technical applications, carbon nanotubes (CNT) have attracted significant attention in last decade [33] with potential electrochemical usages such as catalyst membrane support [34], hydrogen storage [35], lithium battery anodes [36] and supercapacitors [37]. Pristine and surface-functionalized CNTs possess exciting structural and electronic properties along with pseudocapacitance. They can be thought of as rolled graphite sheets with different chirality. The structure of nanotubes is shown in Fig 1.15. The hollow tubes with large pore canals yield very high porosity and surface area ranging between 100~410 m²/g. Further, a group of

entangled CNTs form a porous structure. These porous CNTs favour higher electronic conductivity, easy formation and movement of electrolyte ions [38]. These CNTs can be further improved by chemical doping, composite formation etc. Recently, CNTs based thin films are demonstrated as shape-tunable capacitors [39]. CNTs fabrication/ purification is expensive, which limits their commercial application. Never the less, with further research on CNTs, they are promising to be commercially viable for high specific power applications.



Fig 1.15: High-resolution TEM images showing (a) porous, entangled multi wall nanotubes, (b) one purified MWNTs and (c) linear networked nanotubes (SWNT).

1.4.1.2.3 Carbon fibres:

Carbon fibres form another electrode candidate for supercapacitors. Carbon fibres are commercially fabricated by thermosetting organic precursors e.g. polyacrylonitrile (PAN), rayon, pitch and phenolic resins [40]. The carbonaceous precursors (in solution or melt form) are extruded through a die or spinnerette and are drawn to form fibre of different thickness. These fibres are stabilized (150-500 °C) and carbonized (700-1700 °C) and activated in controlled atmosphere to form carbon fibre electrodes. The quality of fibres can be controlled by precursor materials and

carbonization process parameters [41]. Generally, activated carbon fibres (ACFs) have very high surface area (200-2500 m²/g) with very narrow pore size distribution with predominant microporosity (0~2 nm). Due to the elongated structure of ACFs, the porosity and reaction sites are vastly located on fibre surface, giving good access to electrolyte ions. Thus, ACFs deliver high adsorption capacity and adsorption kinetics, making it suitable for supercapacitors with capacitance of 160-170 F/g [42].

Currently, ACFs are available in many forms like woven cloth, thread, carbon bundles, mat, felt etc (as shown in figure 1.16). ACFs (specially woven cloth) offer very high surface area, excellent electronic conductivity and ease of fabrication in comparison to activated carbon powders [43]. However, they are relatively more expensive that limits their commercial applications.



Figure 1.16: SEM images showing the activated carbon fibres (a) low magnification, (b) high magnification and (c) commercial woven activated carbon fibre cloth.

1.4.1.2.4 Glassy carbons:

Glassy carbons are synthesized by (partial) thermal degradation of polymeric resins such as furfuryl alchohol, phenolic resins etc. The resin precursors are processed through curing, slow carbonization and heating at high temperature (600-3000 °C). Due to their precursor nature, glassy carbons are also known as vitreous or polymeric carbons. Freshly produced glassy carbons possess high degree of closed pores of size 1~5 nm with little accessible surface area, low density and high electrical conductivity. The closed pores are created by randomly-oriented and intertwined graphene sheets. These glassy carbons can be fabricated in variety of forms like free-standing films, thin sheets or powder forms (Figure 1.17) [44, 45].



Fig 1.17: SEM images showing (a) fractured and (b) spherical version of glassy carbon materials produced via thermal activation.

With the help of thermal or electrochemical activation process, the isolated closed pores in glassy carbons can be opened up to give materials with high specific surface area (up to 1800 m²/g), which is desirable for supercapacitors [46, 47]. During the activation process of glassy carbons, a film with open pores is crated on the surface due to interconnection of closed pores. The growth and thickness of these active films (from surface to centre of carbon particles) can be controlled to form porous carbons. As glassy carbons contain inter-twinned graphene sheets, they have excellent electrical conductivity making it suitable for high power supercapacitors with the ability to deliver capacitance of ~120 F/g.

1.4.1.2.5 Templated carbons:

For supercapacitor application, the charge storage and rate capability are adversely affected if the existing pores are non-uniform and randomly oriented. Such effects are directly related to transport properties of the electrolyte solution through the material. High surface area carbons with regularly connected, uniform meso/micropores are ideal candidate for supercapacitors. This kind of carbon can be fabricated using templating methods. Here, carbonaceous precursors (e.g. sucrose solution, pitch, propylene etc) are deposited into pores of silica based templates (e.g. MCM41, SBA15 etc) [48-50]. Afterwards, carbonization treatment (600-900 °C) is carried out followed by removal of silica template by dissolution in hydrofluoric acid. The porosity of templated carbons can be easily engineering by using appropriate templates. Figure 1.18 shows some templated carbons with controlled porosity.



Figure 1.18: High-magnification microscopy images showing templated carbons with uniform mesoporosity and microporosity.

In templated carbons, micro and mesopores are well-connected, where mesopores results due to dissolution of silica walls and micropores due to carbonaceous walls. This feature is suitable for supercapacitor use. Although relatively high cost and fabrication difficulty limits the commercial use of templated carbons, it is widely used to study the pore-size effect in supercapacitors.

1.4.1.2.6 Carbons containing heteroatoms:

The precursor materials and processing conditions (atmosphere, temperature, activation procedure etc) invariably induce different degree of heteroatoms like nitrogen, oxygen, sulfur, hydrogen etc. The possibility of surface functional group can drastically modify the electrochemical properties via faradaic reaction induced

pseudocapacitance. Thus, introduction of surface functionalities is an alternative route to develop high performance carbon. The presence of different foreign atoms (heteroatoms e.g. oxygen, nitrogen) can modify the electronic properties of carbon that directly affects its capacity [51]. Any foreign atom, when substituted in graphitic layers, alters the electron donor/acceptor properties of graphene layers and consequently modifies both double layer formation and faradaic pseudocapacitance [52]. Some major type of oxygen surface functional groups is shown in figure 1.19.



Figure 1.19: Various possible surface oxygen functionalities on edge of graphene layer (a) carboxyl group, (b) carboxylic anhydride, (c) lactone, (d) lactol, (e) phenolic hydroxyl group, (f) carbonyl group, (g) 0-quinone-like structure, (h) ether-type oxygen [51].

The surface functionalities can be used to modify the space charge inside electrode and interfacial faradaic pseudocapacitance, thus improving the overall electrochemical performance of different types of pristine carbons. For example, in case of nitrogen enriched carbon prepared by thermal activation (from pitch blended with polyacrylonitrile, PAN), the specific capacitance linearly improves with nitrogen content. With 7 wt% nitrogen content, the capacitance improves by 80% and 40% for aqueous and organic electrolytes respectively [3]. Nitrogenation triggers electronic charge transfer and thereby improves the electronic conductivity and faradaic pseudocapacitance. Some properties of different kinds of commercially available carbons are summarized in table 1.6.

Carbonaceous materi	als Electrolyte	Capacitance (μ F/cm ²)	BET area (m ² /g)
Activated carbons	10% NaCl	19	~1200 m ² /g
Carbon black	$1MH_2SO_4$	8	$80 \sim 230 \text{ m}^2/\text{g}$
	31 wt% KOH	10	C
Carbon fibre cloth	0.51 M Et ₄ NBF ₄ :PC	C 7	$\sim 1630 \text{ m}^2/\text{g}$
Graphite			-
Basal plane	0.9 N NaF	3	Highly-oriented
Edge plane	0.9 N NaF	50-70	pyrolytic graphite
Graphite powders	10% NaCl	35	$\sim 4 \text{ m}^2/\text{g}$
Graphite cloth	0.17 N NaCl	10.7	$\sim 630 \text{ m}^2/\text{g}$
Glassy carbon	0.9 N NaF	~13	$\sim 900 \text{ m}^2/\text{g}$
Carbon aerogel	4 M KOH	23	$\sim 650 \text{ m}^2/\text{g}$

Table 1.6: Typical values of double layer capacitance of carbonaceous materials [1]:

1.4.2 Pseudocapacitors:

Double-layer capacitors are complemented by (redox) pseudocapacitors, which involve completely different charge storage mechanism. Ideally, double-layer capacitors store charge solely by non-faradaic process, with positive and negative charges residing on two electrode interfaces separated by a dielectric. It involves no electrode-electrolyte faradaic reaction and gives a voltage-independent capacitance (C = dQ/dV).

On the other hand, for (redox) pseudocapacitors, most of the charge is transferred at/ near the surface of solid electrodes. In this case, the interaction between solid electrode and liquid electrolyte involves faradaic charge transfer (CT) reaction. The interfacial charge transferred between electrode and electrolyte is directly related to applied voltage. Hence, the resulting CT pseudocapacitance (C = dQ/dV) is voltagedependent. Theoretically, pseudocapacitance appears when for some special thermodynamic reasons, the potential (V) at which charge transfer occurs is a function of integrated charge (Q) in the electrode. Here, the extent of reaction (Q) is a continuous function of reaction potential (V). The derivative at any point can be expressed as pseudocapacitance $C_{\Phi} = dQ/dV$. Pseudocapacitor involves reversible (faradaic) chemical change in the active electrode. Table 1.7 compares the effective electronic charge in pseudocapacitors with EDLC and batteries.

Table 1.7: Comparison of charge storage in EDLC, pseudocapacitors and battery:

Double-layer capacitor:0.17~0.20 electrons per atom of accessible surfacePseudocapacitor:1.5~2.5 electrons per electroactive atom of accessible surfaceBatteries:1~3 electrons per atom/ molecule of bulk phase

Broadly, three types of electrochemical processes are being used in developing pseudocapacitors. They are: (1) surface adsorption (chemisorption) of ions from the electrolyte, (2) redox reactions involving ions from electrolyte, and (3) doping/undoping of active conducting polymer electrodes. Among these, the first two processes is more surface dependent. The primary thermodynamic relations in these pseudocapacitors are given in table 1.8.

Table 1.8: Correlation of essential thermodynamic relations for different types of pseudocapacitance based supercapacitors:

System Types	Essential thermodynamic relations
(a) Redox system	$E = E_0 + \left(\frac{RT}{zF}\right) \ln\left(\frac{R}{1-R}\right)$
$Ox + Ze^ Red$	where, $R = \frac{[Ox]}{([Ox] + [\operatorname{Re} d])}$ $\frac{R}{1-R} = \frac{[Ox]}{[\operatorname{Re} d]}$
(b) Underpotential deposition	$E = E_0 + \left(\frac{RT}{2F}\right) \ln\left(\frac{\theta}{1-\theta}\right)$
$M^{z+} + S + ze^{-} - S \times M$ (S = surface lattice sites)	$(\theta = 2$ -dimensional site occupancy fraction)
(c) Intercalation system Li^+ into MA_2	$E = E_0 + \left(\frac{RT}{zF}\right) \ln\left(\frac{X}{1-X}\right)$ (X = occupancy fraction of layer-lattice sites)

Figure 1.20 compares the equivalent electrical circuit of double layer capacitor to that of a pseudocapacitor. In all these cases, ideal electrodes should have good electronic conductivity for effective distribution and collection of electronic current. Generally, pseudocapacitors have higher energy-density than activated carbon based electrodes. Some pseudocapacitor electrodes are briefly discussed in the following section.



Figure 1.20: Equivalent electrical circuit of (a) double layer capacitance (C) with series resistance (Rs) and potential dependent Faradaic leakage resistance (R_F), (b) pseudocapacitance (C_{ϕ}) in addition to double layer capacitance.

1.4.2.1 Metal oxide capacitors:

Metal oxides (MnO₂, V₂O₅, RuO₂, TaO₂ etc) are perhaps the most widely investigated pseudocapacitors till date. Among them, ruthenium oxide (RuO₂) has achieved most success, originally proposed by Trasatti etal [53]. Ru exists in different oxidation states (Ru⁺² ~ Ru⁺⁴), which supports multiple redox reaction at electrode interface. Mostly thin films structure of RuO₂ has been studied. Electroactive RuO₂ thin films can be easily generated by (a) electrochemical potential cycling of metallic ruthenium in H₂SO₄ aqueous solution [54, Fig 1.21] and (b) chemical oxidation of RuCl₃ via sol-gel route, pulsed-laser deposition, chemical vapour deposition etc [53].



Fig 1.21: (a-d) SEM images of electrochemically deposited RuO₂ surface layer on Ru. (e) Cyclic voltammogram showing the gradual development of multilayers of RuO₂.

Typically, a hydrous RuO₂.xH₂O based supercapacitor with H₂SO₄ electrolyte can yield ~8 Wh/kg energy-density with ~30 kW/kg power-density. During the electrochemical charging/ discharging of RuO₂, a coupled electron-proton transfer process occurs. RuO₂ is semi-metallic in nature allowing electron transfer through it. Further, the hydrous RuO₂.xH₂O triggers proton transfer reaction. Combining these electron and proton transfer reactions, the following electrochemical reaction occurs.

$$HRuO_{2} \longleftrightarrow H_{1-\sigma}RuO_{2} + \sigma H^{+} + \sigma e^{-}$$
$$HRuO_{2} + \sigma H^{+} + \sigma e^{-} \Longleftrightarrow H_{1+\sigma}RuO_{2}$$

the overall reaction being: $HRuO_2 + HRuO_2 \longrightarrow H_{1-\sigma}RuO_2 + H_{1+\sigma}RuO_2$

It is worth mentioning that even though these redox reactions generate most of the capacitance, RuO₂ also generates some double layer charge storage due to its relatively high surface area. The relatively higher cost of RuO₂ limits its wide-spread usages to only defense related applications.

Apart from RuO₂, research is geared towards several other metal oxides such as IrO_2 [55], CoO_x [56], MnO_2 [57] for pseudocapacitor use. These alternative metals oxides are less expensive and deliver promising pseudocapacitance with multiple redox reaction due to the presence of transition metals.

1.4.2.2 Metal nitride capacitors:



Fig 1.22: Physicochemical properties of vanadium nitrides (a) cyclic voltammograms showing multiple redox states, (b) Specific capacitance at different scan rate, (c and d) high-resolution TEM images of nanostructured vanadium nitrides [58].

As mentioned earlier, ruthenium oxide (RuO₂) is expensive that limits its commercial viability. The search for economic redox pseudocapacitor has led to the invention of metal nitride supercapacitors. RuO₂ based electrodes delivers 350~720 F/g capacitance due to interfacial redox activity of Ru, which supports variety of oxidation states (Ru⁺² ~ Ru⁺⁴) coupled with excellent electronic conductivity [59]. Vanadium also exhibits multiple oxidation states (V⁺²~V⁺⁵), but poor electronic conductivity of vanadium oxide (V₂O₅) hinders its application. However, vanadium nitride (VN) has been found to exhibit excellent electronic conductivity coupled with multiple oxidation states of vanadium. This unique combination makes VN ideal for pseudocapacitor use [58]. Nanoscale VN can be prepared using low-temperature (~400 °C) ammonolysis (NH₃) reaction of VCl₄. Figure 1.22 (a) shows the cyclic voltammograms of nanostructured VN electrodes, where multiple peaks appears pertaining to several reversible redox reactions. Consequently, VN delivers very high capacitance (~1340 F/g for scan rate of 2mV/s, Fig 1.22 b), well above that of RuO₂. The specific capacitance reduces logarithmically with scan rate. This electrochemical development is found to be due to the formation of thin surface layer of vanadium oxide (monolayer) on nanostructured, agglomerated VN as confirmed by TEM (Fig 1.21 c-d). It involves the following redox reaction:

$$VN_xO_y + OH^-$$
 $VN_xO_y || OH^- + VN_xO_y - OH$

VN has laid a foundation for future research on different metal nitrides (Mo [60], V, Ti, Nb) with conducting oxide layers as possible low cost candidates for next generation pseudocapacitors.

- **1.4.2.3 Conducting polymers capacitors:**

Figure 1.23: Structures of some commonly used conducting polymers delivering pseudocapacitance.

Conducting polymers were first discovered by MacDiarmid et al [61, Noble prize, Chemistry, 2001] and soon formed a new group of supercapacitor electrodes based on pseudocapacitance. Some commonly known pseudocapacitor conducting polymers are polyaniline, polypyrolle, polyacetylene and polythiophene (Figure 1.23). These polymers have large π -orbital conjugation, which leads to electronic conductivity. These π -orbitals support reversible insertion/ extraction of electrons i.e. reversible oxidation/ reduction reaction inducing faradaic pseudocapacitance. Unlike RuO₂, the charging/ discharging cycle in conducting polymers do not involve any change in chemical structure. It simply involves continuous movement of electrons in the π -orbitals. Thus, it has very fast charging cycle and is highly reversible in nature. Polymers are much cheaper than RuO₂ and give higher capacitance. The use of conducting polymers for pseudocapacitors has some distinct advantages over metal oxide systems. They are:

- The materials have good intrinsic autoconductivity, at least in the charge state, so it does not need a dispersed current-collecting matrix.
- (2) Conducting polymers are relatively cheaper, so is their preparation/ fabrication cost making it economically competitive.
- (3) These materials can be generated chemically or electrochemically *in-situ* at/ on cheap substrate materials such as metal foils, metal gauges, porous metal substrates or fibrous conducting carbon substrates.
- (4) They have very good specific capacitance values (per gram/ per cm³).
- (5) Good reversibility of the systems on cycling can be achieved, but some electrochemical degradation takes place over long periods of cycling.
- (6) The conducting polymer based electrochemical pseudocapacitors can be easily fabricated employing existing battery-type technology.

However, due to its low operating voltages and inherent chemical instability over a long period of time, it is yet to see any commercial applications.

1.4.3 Hybrid supercapacitors:

Apart from electrochemical double-layer capacitor and pseudocapacitors, as shown in figure 1.7, hybrid supercapacitors form a new class of supercapacitors. Broadly speaking, these hybrid capacitors combine two different types of electrodes, operating on same or different electrochemical mechanism. The hybrid capacitor concept is schematically shown in figure 1.24.



Figure 1.24: Schematic presentation of hybrid capacitors with (a) two supercapacitors/ battery type electrodes (A and A') and (b) combination of supercapacitor electrode (A) with battery electrode (B). The separator is designated as S.

Three main types of hybrid capacitors are:

- (a) Composite hybrid capacitors: It employs a double layer type electrode against a pseudocapacitance electrode e.g. carbon gel-MnO₂, RuO₂- graphites etc.
- (b) Battery-type hybrid capacitors: It uses two different kinds of intercalation/ conversion type battery electrodes e.g. LiCoO₂-Li₄Ti₅O₁₂, LiFePO₄ Li₄Ti₅O₁₂ etc.
- (c) Asymmetric hybrid capacitors: It uniquely combines a battery-type electrode (faradaic in nature) with a supercapacitor electrode (faradaic/ non-faradaic) (e.g. activated carbons-Li₄Ti₅O₁₂). They aim to constructively combine the high energy-density of battery electrode to the high power-density of supercapacitor electrode.

- High degree of reversibility of non-faradaic (supercapacitor) component is retained in one electrode.
- (2) High power-density at capacitor electrode is retained.
- (3) The low energy-density of capacitor is compensated by high energydensity of battery (faradaic) electrode.
- (4) The resultant voltage does not decrease very fast as faradaic component prefers flatter voltage profile during discharge.
- (5) Point 4 leads to overall higher energy-density, which is the area occupied by voltage profile.
- (6) The hybrid capacitor has lower self-discharge as it is confined to only one electrode (supercapacitor type).

One such asymmetric hybrid capacitor system was introduced by Amatucci et al [63-65] by combining nanostructured $Li_4Ti_5O_{12}$ (faradaic) with activated carbons (traditional non-faradaic supercapacitor electrode). Nanostructured $Li_4Ti_5O_{12}$ was specially chosen as it possesses low reduction potential, high specific capacity (~170 mAh/g), exceptional cycling life and rate capability. Most of the faradaic battery electrodes are ceramic materials with high Young's modulus. During electrochemical cycling, repeated isotropic and anisotropic expansion/ contraction triggers extensive amount of electromechanical grinding at incoherent grain/ grain boundaries. It leads to electromechanical and electrochemical degradation of battery electrodes. However, Li₄Ti₅O₁₂ shows almost zero expansion/ contraction during cycling, thus giving excellent cycling stability matching that of non-faradaic activated carbon electrodes.



Figure 1.25: (a) Schematic presentation of electrochemical reactions namely anions (PF_6) adsorption at activated carbon cathode and lithium intercalation at $Li_4Ti_5O_{12}$ anode, (b) voltage profiles of non-faradaic activated carbons, faradaic $Li_4Ti_5O_{12}$ and overall hybrid configuration [63,65].

Figure 1.25 (a) schematically shows the hybrid capacitors. While the activated carbon (AC) cathode involves adsorption/ desorption of electrolyte anions (PF_6), $Li_4Ti_5O_{12}$ (LTO) anode involves Li^+ ions movement. An important point during hybrid cell fabrication is that different amount of cathode and anode electrodes are used in order to match the specific capacity of both electrodes. This situation ensures complete lithiation/ delithiation of battery-type anode. Activated carbons have lower capacity wrt $Li_4Ti_5O_{12}$ so very high amount of carbons are used to make the optimized hybrid capacitor. In the AC/LTO hybrid cell, the electrochemical reactions involved are proposed as:

$$AC + PF_6^- - AC^+ PF_6^- + e^-$$
 (at cathode)
Li₄Ti₅O₁₂ + 3 Li⁺ + 3 e⁻ - Li₇Ti₅O₁₂ (at anode)

The corresponding individual and overall voltage profiles (non-faradaic and faradaic type) are shown in figure 1.25(b).



Figure 1.26: (a) Graph showing the excellent cycling stability of activated carbon- $Li_4Ti_5O_{12}$ hybrid capacitors comparable to that of carbon based EDLC capacitors, (b) a Rutgers TR-100 award-winning asymmetric hybrid capacitor prototype [64].

The resulting AC-LTO hybrid capacitor has been shown to deliver excellent cycling stability while retaining its high capacity (Fig 1.26 a). This kind of hybrid capacitor has been fabricated using plastic-ion technology (Bellcore) as shown in figure 1.26 b. Further, these AC-LTO hybrid capacitors surpass carbon EDLC on both energy-density and power-density (Ragone plot, Fig 1.27). Thus, asymmetric hybrid capacitors have attracted attention for possible use in hybrid vehicles.



Figure 1.27: Ragone plots comparing the double layer capacitors (EDLC) to hybrid capacitors. The high energy-density and power-density of hybrid capacitors makes it promising for hybrid electric vehicles [66].

1.5 Definition of some technical terms

Capacitance (C) is defined as the amount of electric charge (Q) stored for given amount of electric potential (V). It is expressed as: dC = dQ/dV = Idt/dV. Capacitance is expressed in Farad (Coulomb/ Volt). Normalised capacitance (F/g or F/cc) is employed for direct comparison of different electrodes. This can be either specific gravimetric capacitance (F/g) or volumetric capacitance (F/cc).

Capacity of supercapacitor electrode is defined as the amount of charge passing through outer circuit during charging/ discharging. It is expressed in Amp•hour (Ah). Capacity can also be normalized to present the specific capacity (Ah/g) or volumetric capacity (Ah/cc). Theoretical capacity of any electrode can be calculated as:

$$C = \frac{(x \bullet F)}{(M \bullet 3600)}$$

where, x = amount of electron inserted per mole of electroactive material

F = Faraday's constant (96486 Coulomb/ mol)

M = molar mass of electroactive material.

Capacitance and *Capacity* presents the electrochemical activity of any electrode for capacitor and battery applications respectively. The performance of electroactive materials can further be quantified combining energy-density and power-density. *Energy-density* quantifies the amount of energy stored in a given system per unit mass/ volume (expressed in Wh/kg or Wh/L). It can be calaulated as: E = C X V, where C is the capacity and V is the average voltage during cell discharge. *Power-density* presents the speed with which the available energy can be delivered (expressed in W/kg or W/L). It is expressed as P = V X I, where V and I are voltage and current respectively. Combining these two quantities, Ragone plot is obtained for overall performance of electroactive materials.

1.6 Electrolytes:

An electrolyte is defined as any substance containing free ions, which acts as electrically conductive medium via the diffusion of ionic charge. Apart from molten electrolytes and solid electrolytes, most of the electrolytes consist of ions in solution, thus known as ionic solutions. Electrolytes are prepared by adding electroactive salt to a solvent. Upon formation of electrolytes, the free ions form ion-dipoles to minimize total energy. The ion dipole energy is expressed as:

$$U_{ion-solvent} = -(Ze\mu\cos\theta)/(4\pi\varepsilon_0)r^2$$

where, Ze = total charge of ions, ε_0 = vacuum permittivity, μ = permeability,

 θ = dipole angle relative to the line joining the ions to the centre of dipole Ideally, an electrolyte for electrochemical cells requires following properties:

- (a) High ionic conductivity to minimize the overall cell resistance,
- (b) Low toxicity and safe handling
- (c) Low solubility of electrode materials, conductive additives and binder,
- (d) Economic feasibility (low cost and good availability).
- (e) Low melting and high boiling points to provide sufficient conductivity and safety, thus providing wide temperature range of operation.
- (f) High chemical stability against decomposition at electrode surfaces, which is acquired in non-aqueous electrolyte that tolerate very high voltage difference between anode and cathode (x > 4 V).

As any single electrolyte hardly meets the entire application requirements,

mixed organic salts (ethylene carbonate: EC, proplylene carbonate: PC, dimethyl carbonate: DMC etc) are often used. In case of supercapacitor application, the ionic double layer formation at electrodes is the key electrochemical reaction. In this context, the aqueous electrolytes with inherently smaller ions show fast ionic

movement and access to smaller pores of electrodes operating at low voltage. Thus, it gives lower energy density with higher power density. On the other hand, the nonaqueous electrolytes have larger ions operating at higher voltage, thus giving higher energy density with lower power density.

1.7 Research objectives

Activated carbons are most-widely used electrode materials commercial double layer capacitors as well as asymmetric hybrid capacitors. In case of asymmetric hybrid capacitor, activated carbon electrode is used with various other electrodes (e.g. MnO_2 , nanostructured Li₄Ti₅O₁₂ etc) as schematically shown in figure 1.28.



Figure 1.28. Schematic presentation of asymmetric hybrid capacitor configuration using activated carbon (C) as cathode and $Li_4Ti_5O_{12}$ (LTO) as anode. By developing a higher capacity modified carbon (C-X), the overall materials consumption can be reduced to form a compact, high energy-density capacitor.

To match with high capacity counter electrodes, a large amount of activated carbon is required due to comparatively lower specific capacity of carbon. However, the consumption of high amount of carbon (with inherently low density) decreases the volumetric energy density of hybrid capacitor. The objective of current research is to modify activated carbons by some physico-chemical route to improve its capacity. The higher capacity of carbon can drastically decrease the materials consumption to match the capacity of counter electrode, which in turn leads to compact hybrid capacitor with improved volumetric energy density. The modified carbons are targeted to have a unique combination of high power density with improved energy density (as shown in Fig 1.29). This modified carbon can also be employed for low voltage battery type usages.



Figure 1.29. Ragone plot showing the area of interest for next generation hybrid supercapacitors. These materials can serve battery as well as hybrid capacitor usages.

1.8 Scientific approach to produce advanced supercapacitors

Activated carbon based electrochemical supercapacitors operates on the basis of non-faradaic double layer formation (C_{DL}) at the interface of high surface area, mesoporous carbon electrodes. This has led to world-wide research on surface morphology engineering (controlling the surface area and porosity) to optimize nonfaradaic double layer formation. However, in addition to surface morphology, the space charge formation (C_{SC}) inside carbon electrodes can play crucial role to improve the overall electrochemical performance [16]. In addition to these mechanisms, any charge transfer reaction and complex formation at the carbon interface can lead to faradaic pseudocapacitance (C_{FP}). The faradaic reaction mechanism can augment overall electrochemical performance of carbon.

In the current work, rather than the traditional way of controlling the carbon morphology, we try to improve the overall electrochemical capacity by simultaneous development of space charge capacitance (C_{SC}) and faradaic pseudocapacitance (C_{FP}) in activated carbon by suitable mechano-chemical modification.

- A. In order to achieve high capacity, pristine activated carbon has been treated with gr-VII halides (iodine, bromine) via two processing techniques: namely (a) solid-state iodation process and (b) chemical vapor iodation route. Halides, being highly electronegative, may induce strong charge-transfer reaction with semi-metallic amorphous carbon. Consequently, this CT reaction can form charge-transfer complexes thus modifying the chemistry of carbon materials. This modified carbon can improve the overall capacity majorly by developing faradaic development. This concept is portrayed in figure 1.30.
- B. Comprehensive effort has been made to investigate the structural, physical and electrochemical modification in activated carbons resulting from chemical iodation process. Using these results, we have tried to evaluate and optimize the chemical iodation process to obtain iodated carbon electrodes with maximum energy density.

C. The concept of chemical halidation of carbon system has been extended to different types of carbon. Carbon exists in a various forms starting from crystalline graphites, nanotubes, fullerenes to amorphous activated carbons, carbon fibers, carbon foams etc. The degree and effect of chemical halidation process on these carbons have been studied to gain insight into optimum possible halidation of activated carbons. Further, bromination process is employed on selected carbons to gain insight into CT reaction process.

Overall, a modified carbon is obtained via chemical halidation process. The chemical iodation process and resulting carbon-iodine nanocomposites system has been studied and implemented in electrochemical supercapacitor.



Fig 1.30: Flow diagram delivering the key concept of chemical halidation concept to obtain carbon-halide nanocomposites with improved electrochemical capacity.

1.9 Structure and bonding in polyiodides:

Iodine is a highly electronegative and reactive element, which readily forms compounds with multiple iodine atoms, known as polyiodides [67]. The current work on carbon-iodine nanocomposites largely involves the formation of polyiodides. Polyiodides form an interesting family of compounds involving fascinating structural chemistry. They exist from linear one-dimensional chain to three-dimensional network structure with anion ranging from I_2^- to I_{29}^{3-} . This vast range of polyiodide structure is possible due to the ability of iodine to catenate through donor-acceptor interactions combined with the influence of counterions [68]. Many polyiodides are hypervalent and highly conducting, which cannot be explained by simple covalent bonding models. The formation of various polyiodides can occur with iodine (I_2 , Lewis acid acceptor) and I^- or I_3^- (Lewis base donor) as fundamental building blocks. These building blocks catenate easily to form linear chains $[I_2 \bullet \Gamma]^1_{\infty}$, quadratic networks $[I_2 \bullet \Gamma]^2_{\infty}$ and cubic 3D networks $[I_2 \bullet \Gamma]^3_{\infty}$ using the following general reaction:

 $m I_2 + n I^- \rightarrow I_{2m+n}^{n-}$ (*m* and *n* integers > 0, n = 1~4)

These hypervalent, octet-rule violating polyiodides involve very intriguing chemical bonding that involves electrostatic interaction, localized d-orbital covalent bonding, delocalized σ -bonding. The influence of cation environment is very important on final polyiodide structure. For example, previous study proves the formation of symmetric triiodide in flexible cations units and asymmetric triiodide in rigid cations units [67]. Another example showing the cation influence is that of gold. Gold (Au) is highly electronegative and leads to the formation of AuI₄⁻ polyiodides. The very presence of gold favors square planar structure, although higher-order polyiodides generally prefer V/L shaped structure.
Triiodides (I₃⁻) and pentaiodides (I₅⁻) are the most widely observed polyiodides. Triiodides are (nearly) linear and mostly symmetric (D_{ih}) as shown in figure 1. Generally, triiodide ions are stacked/ layered in T-shape or zigzag patterns, interlinked with weak I₃⁻...I₃⁻ interactions (distance ~ 3.6 Å) (Fig 1.31). The pentaiodides (I₅⁻) have mostly V/L shape structure. The V-shaped pentaiodide ions have two iodine molecules coordinated to an apical iodide [(I⁻)•2I₂], while the Lshaped structure has an iodine molecule coordinated with a triiodide ion [(I₃⁻)•I₂]. The pentaiodide units are linked by strong intermolecular interaction forming variety of structure (chain to 3D networks) as shown in figure 1.32.



Figure 1.31: (a) basic triiodide linear structure, (b-c) formation of 2D and 3D network structure by interlinking of many triiodide units [67].



Figure 1.32: (a) basic V/L shaped pentaiodide structure. Formation of 2D and 3D network structure by interlinking of many pentaiodide units forming (b) zigzag shaped chain, (c) meander-shaped chain, (d) cis-shaped chain, (e) twinned chain, (f) square-nets and (g) trans-shaped chain [67].

1.10 Carbon-iodine interaction:

The semi-metallic carbon (C) and highly electronegative iodine (I) form an interesting materials combination for fundamental study. The carbon-iodine interaction has been investigated for various graphitic carbon nanostructures [69-70]. Often, C-I interaction is studied using nanographite as basic building block. The interplanar structure of graphite is shown in figure 1.33a. When iodine is introduced, it can react with edge or basal carbon atoms. Iodine, being a weak acceptor, does not readily form charge transfer compounds with any carbon structures unlike low-dimension polymer like acetylene [71]. However, recent study has found slight degree of charge transfer in iodine doped single-walled carbon nanotubes [72] and carbon

fibre [73,74]. Prasad et al recently reported [69] about various intercalated nanographite structures. Iodine-incorporation was carried out by a standard two-zone vapour transport method, where the iodine side (hot evaporation zone) and carbon side (cold condensation zone) was maintained at 200 °C and 60 °C respectively for 24 h. The weight-uptake calculation hinted at a composition of $C_{65}I$. Upon iodation, the carbon x-ray diffraction peaks were below detection limit showing an increase in structural disorder. Raman spectroscopy of iodated nanographites proves the absence of any molecular iodine band and formation of polyiodide bands (mostly linear I_3^- and angular I_5^-). In addition, a slight change in E_{2g} mode (G band) of graphite was proposed to be due to possible charge transfer reaction induced C-C bond stiffening. As the local carbon-iodine structure is not clear till date, interplanar iodine intercalation is refused widely. However, recent study shows physisorbed accumulation of iodine (polyiodide) forming helical structure inside carbon nanotubes (Figure 1.33b-d).



Figure 1.33: (a) The schematic presentation of crystal structure of graphite, (b) Z-contrast TEM image showing double helical iodine chain formation inside SWNTs, schematically shown for a single-wall (10,10) nanotubes (c) side view and (d) top view [75].

Carbon nanostructures (can be thought of as nanographites) have very low free carrier concentration ($\sim 10^{-4}$ carriers/ atom), which drastically improves with electron transfer from iodine. Consequently, chemical iodation modifies carbon's electrical/ thermal/magnetic properties. One such example is the change in electronic properties of single wall carbon nanotubes (SWNT) as reported by Grigorian et al [72]. In this work, iodine was intercalated in laser-assisted/ arc-assisted grown SWNT by immersing SWNT mats in molten iodine in an evacuated quartz tubes at 140 °C for several hours. The excess (physisorbed) iodine was then removed by mild heating at 60~80 °C for 2~4 h. From energy-dispersive x-ray spectroscopy (EDXS) and thermal analysis, the average composition of saturated iodated SWNT was found to be IC_{12} . X-ray diffraction patterns (Figure 1.34a) revealed the destruction and reappearance of SWNT peaks upon iodine-saturation and iodine-removal. Interestingly, the (002) peak of SWNT was unshifted with doping, thus rejecting any possibility of iodineintercalation into nanoscale graphite. Iodine is proposed to act like a 'chemical wedge', entering the interstitial channel in nanotubes by breaking the weaker van der Walls attraction. The presence of iodine inside SWNT was observed for the first time using Z-contrast Scanning transmission electron microscopy (STEM) (Figure 1.34b). Linear polyiodide chains (as captured by Raman spectroscopy) were proposed to exist inside SWNT separated by ~ 21 Å. The formation of polyiodides led to slight charge transfer from SWNT to polyiodide, as notices by slight up shift of G band by 9 cm⁻¹.



Figure 1.34: (a) Low-angle XRD peaks of pristine, iodated and de-iodated SWNT showing iodation-induced structural disordering, (b) Z-contrast STEM image of iodine-dopes SWNT showing the presence of iodine (bright spot).



Figure 1.35: Iodine-induced modification of electrical properties of single-wall nanotubes (a) decrease in 4-probe resistance and (b) decrease in thermopower of pristine SWNT upon saturation iodation (as shown by arrow marks).

Subsequently, iodine-doping drastically reduced the electrical resistance of Single-wall nanotubes (SWNTs), (Figure 1.35a). A factor of ~40 reduction was observed in 4-probe measurement (at room temperature) [72]. Similarly, iodation significantly reduces the thermopower of SWNTs (Figure 1.35b), the lower values being consistent with the metallic system. It is proposed that iodine increases the charge carrier concentration in π -band of graphene layers, making it more metallic in nature. As a result, the Fermi level (E_F) of carbon decreases slightly, which is

originally at the meeting point of π - π * band (Figure 1.36) [70]. It leads to more conducting (metallic nature) carbon system. Though there has been fundamental research on carbon-halide interaction on various graphitic carbons (C₆₀, SWNTs, graphites etc), till date there has been no major report on halide-modified activated carbons.



Figure 1.36: Electronic structure (density-of-states) of (a) pristine graphite and (b) iodine doped graphite. Iodine-incorporation leads to lower Fermi level and higher conductivity.

1.11 Carbon-bromine interaction:

The carbon-halide interaction is more pronounced in carbon-bromine system due to the smaller ionic size, higher reactivity, large electronegativity and charge transfer ability of bromine. The effect of bromination on structural and functional properties of carbon nanostructures (nanographites, SWNTs, MWNTs, etc) has been widely reported [76-81]. In this series of papers reported by Smalley and co-workers, frozen bromine was taken in a glass vessel, with carbon sample suspended over bromine. With gradual heating, the bromine vapour impregnated the carbon structure (soaked for 3 h). While iodine does not readily form charge transfer compound with carbon, bromine-induced charge transfer reaction can be observed by Raman scattering [78]. Raman spectroscopy of these brominated carbons shows possible formation of polybromide and chemically bonded bromine [76, 77]. A distinct shift in G band and increase in amorphosity (higher I_D/I_G ratio) is observed along with charge transfer reaction. In these brominated carbons, the presence of bromine inside carbon was observed and confirmed by high-resolution transmission electron microscopy (HRTEM) (Figure 1.37) and energy-dispersive x-ray microanalysis (EDAX) [82].



Figure 1.37: High-resolution transmission electron micrographs showing the presence of bromine (seen as dark spots due to Z-contrast) along the wall of carbon nanotubes [82].

Carbon nanostructures exist from semi-metallic to insulating structure, with very low concentration of free charge carrier. Bromination-induced charge transfer reaction creates holes in carbon π -bands and extra electron in bromine. Following, the electrical resistivity of carbon (SWNTs) sharply drops by orders of magnitude (Fig 1.38) [79]. Similar to iodation, bromination seemingly increases the charge carrier concentration in π -band of graphene layers, showing a metallic nature. The strong charge transfer reaction due to bromine notably decreases the Fermi level (E_F) of carbon, which is the meeting point of π - π * band in pristine carbon (Fig 1.38) [70]. The bromine-induced modification in density-of-states in nanotubes has been simulated using first-principle calculation by Park et al [83], which states preferential outer-wall adsorption of bromine corresponds to lowest band gap (Figure 1.39). Like the electronic properties, bromination can alter many a structural and functional

properties of carbons. Unlike the crystalline carbons, the effect of bromination on amorphous activated carbons is difficult to observe and has never been reported.



Fig 1.38: Electronic structure (density-of-states) of (a) pristine graphite and (b) bromine doped graphite [70]. Bromination decreases the Fermi level. (c) The manyfold decrease in resistivity (vs temperature) of pristine SWNT with saturation bromination [79].



Figure 1.39: Band structures of pristine and brominated SWNT calculated from density functional theory (DFT) with local density approximation (LDA). The bandgap is shown for (a) pristine nanotubes, (b) molecular bromine Br_2 adsorbed on outer-wall of CNT, (c) Br adsorbed on inner wall of CNT and (d) Br adsorbed on outer wall of CNT [83].

1.12 Organization of thesis

The current thesis is a comprehensive effort to study the physical and electrochemical properties of carbon-iodine nanocomposites, a new class of carbon electrode materials proposed for next generation supercapacitors, or high power density batteries. The whole investigation focuses not only on the fabrication of highenergy density iodated carbons, but also a whole range of characterization to understand the underlying structure, morphology and electrochemical modifications. Towards this end, Chapter 2 briefly summarizes materials synthesis, formation of carbon-iodine nanocomposites and suites of structural, morphological and electrochemical characterization techniques used throughout the work. Chapter 3 introduces the first set of iodine-incorporated commercial activated carbons via solidstate mechanical milling. The iodine-induced modification of carbon is described and improvement of electrochemical capacity is demonstrated for three existing commercial carbons. Chapter 4 takes the iodation process a step forward with an effort to fine-scale incorporation of iodine into activated carbons via a chemical vapor iodation route. The resulting nanocomposites has been analysed and observed to deliver higher electrochemical capacity.

Activated carbons consist of different degree of graphitic domains embedded in amorphous carbon matrix. On a local scale, when iodine is introduced to carbon, it interacts with graphitic planes. In order to decipher the role of graphitic nature of carbon, Chapter 5 is dedicated to study of carbon-iodine nanocomposites based on graphite carbon precursor.

The morphology and porosity is arguably the most important parameter for interfacial charge storage in carbon electrodes. Carbon consists of micropores and mesopores, both playing different roles. With a hint of preferential iodine entrapment inside micropores, Chapter 6 analyzes the possibility of using micropore carbon precursor to form high energy-density electrodes. Fabrication of microporous carbon precursor, chemical iodation and study of resulting carbon-iodine nanocomposites has been described with critical comparison to that of mesoporous carbon electrodes.

The whole concept of carbon-halide nanocomposites can be extended to different type of halide (bromine) in Chapter 7. Halides are highly electronegative, which can trigger charge transfer reaction with carbons. The carbon-halide reaction in bulk of carbon significantly modifies its density-of-states (DOS) and electronic properties. This charge transfer effect is more acute in case of bromine. The effect of bromination on activated carbons has been studied.

Carbon-halide nanocomposites based electrode is a proposed new class of electrode materials, having potential for low voltage battery and asymmetric hybrid capacitor type applications. Chapter 8 reports major conclusions of investigation on mechano-chemically modified activated carbon-iodine nanocomposites electrodes. This interesting material paves way for much possible future research (Chapter 9).

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2.1. Introduction:

The current work on halide modified activated carbons involves a range experimental work, from in-house carbon fabrication, halide modification to various physical and electrochemical characterizations. This chapter summarizes all the experimental methods used during investigation. It starts with procurement/ fabrication of various precursor carbons followed by processing of carbon-halide nanocomposites system. There on, it describes a range of characterization methods employed to study the physical and electrochemical properties of this electrode system.

2.2. Fabrication of carbon-halide nanocomposites: 2.2.1 Precursor carbon materials:

In the present work, a wide variety of activated carbons was used. The carbon system encompasses different structure (crystalline and amorphous) and different morphology (microporous and mesoporous). The following sections describe various carbon systems employed in the current research.

2.2.1.1. Commercial activated carbons:

Various commercially available activated carbon materials, ASupra (from Norit Inc[1]) and ASP (from Timcal Inc[2]), were taken as precursor carbons. Also, a relatively low surface area ($60 \text{ m}^2/\text{g}$) carbon black with trade name SP (Timcal, [2]) was procured. SP has a networked structure to give extraordinary conductivity and is typically utilized as a carbon additive in Li-ion battery electrode materials. ASP is a high surface area ($762 \text{ m}^2/\text{g}$) version of SP that has been activated. ASupra is an ultra high purity activated carbon of very high surface area ($1743 \text{ m}^2/\text{g}$). Throughout the

report, these materials are mentioned as ASupra, ASP and SP respectively. These activated carbons are industrially produced by partial oil oxidation of different carbochemical and petrochemical materials [3]. This combustion/ oxidation are conducted at a controlled velocity with no additive to obtain high-pure carbons of uniform size. All these activated carbons are amorphous in nature with mesoporous particle morphology.

Coming to crystalline carbon materials, commercial graphite with trade name SFG-15 (from Timcal Inc [2]) was used as precursor graphitic carbon. SFG-15 is synthetic graphite produced from graphitization of natural graphites at 2800 °C. It has high carbon content (>99.5% C, ~0.1% ash), low surface area (~9.5 m²/g) and particle size of 15.5~20 μ m. Further, various fluorinated graphites (CF_{0.8}, CF_{1.0} from Alfa-Aesar Inc) was used as precursor carbon.

2.2.1.2. Fabrication of microporous carbons:

Following the work of mesoporous carbon, microporous activated carbon system was investigated for electrochemical efficiency. Microporous carbon with adequate homogeneous pore structure can be manufactured by two different methods, namely the physical activation and the chemical activation [4]. The physical activation process [5] is a rather simple approach of carbonization of some precursor carbonaceous materials is conducted by thermal annealing in the presence of gaseous activating agent (e.g. carbon dioxide, hot steam or both). The thermal activation (or gasification) reacts with highly reactive carbon atoms and eliminates them to create the porous structure inside carbon. In contrast, the chemical activation process [6] is little complex, which involves impregnating the precursor carbon with some reactive chemical agent (such as phosophoric acid, ZnCl₂, KOH, NaOH etc). This step is followed by pyrolysis (activation process) for carbonization. The pyrolysis drives the impregnated chemical agent out of carbon leaving behind very fine porosity. The chemical activation process is a quick route that yields very high surface area with uniform porosity and is usually accomplished at lower temperature. Thus, we have adopted chemical activation method as described by Castello et al [7] for the fabrication of microporous carbon.

Anthracite coal (Reading Anthracite Co, Pennsylvania) with very high carbon content was taken as precursor carbonaceous material. Coal was ground to an average size of 1-2 micron. Potassium hydroxide (assay~87.2% KOH) (Baker Chemicals, NJ) was used as the chemical activating agent [7-9]. In every batch, 4 g of anthracite coal was impregnated in a solution containing different amount of KOH in 10 cc of H_2O (coal/KOH ratio =1:1 \sim 1:5). The solution was heated at 70 °C for 2h with constant stirring. The final slurry was dried overnight at 110 °C in an air oven. The dried mixture was used for carbonization process employing a horizontal Lindberg/BlueM tube furnace (Thermoelectron Co). An alumina crucible containing the dried impregnated carbon was placed inside the tube furnace and it was carbonized at 500-800 °C (heating rate 20 °C/min) for 1-2 h under steady nitrogen flow to avoid any oxidation of carbon. Carbonization step is central to microporous carbon formation, as it evolves any active carbon as well as activating agent, thus creating huge porosity in carbon. Thus, the final surface area and microporosity is mainly controlled by carbonization process (annealing temperature and annealing time). Upon cooling, the carbonized powders were soaked in sufficient 1N HCl solution (Aldrich, USA) to neutralize remaining activating agent. Later, HCl solution was filtered out and washed carbon material was dried overnight at 110 °C in an oven to obtain phase-pure microporous carbon. The whole process is presented in a flow diagram in figure 2.1 and the chemical activation experimental set-up is schematically shown in figure 2.2.



Fig 2.1: Flow chart showing the chemical activating process to get microporous carbon from anthracite coal.



Fig 2.2: Schematic presentation of tube furnace set-up for chemical activation process. The different parts are: (1) alumina tube, (2) alumina boat containing coal:KOH mixture precursor, (3) base of furnace, (4) nitrogen (N_2) inlet supply, (5) exhaust gas removal.

2.2.2. Iodine-incorporation (iodation) procedure:

Pristine activated carbons are chemically modified to form carbon-iodine nanocomposites. Different amount of molecular iodine was incorporated into carbon structure by two specific routes: solid state high-energy milling and chemical vapour iodation process. These iodation procedures are described in the following sections.

2.2.2.1. High-energy milling solid state iodation:

In order to study the effect of surface area and structure of the precursor carbon, the carbons were used after high-energy milling for different time from 0-60 minutes using a SPEX 1000 high-energy shock type milling machine. Spherical steel milling media of two different sizes were used throughout. This high-energy milling is a simple and effective technique [10,11] to form nanocomposites based electrode materials (e.g. carbon-halide nanocomposites). Various amounts (0-45 weight % of carbon) of molecular iodine flakes (Aldrich) were mechanically mixed with activated carbon precursors in a mortar and pestle. This mixture was then high-energy milled

for different period to form carbon-iodine nanocomposites. All materials loading and collection of modified carbon from milling cells was performed inside a dry room to avoid any external contamination or hydrolysis. The impact energy during shock-type milling results in the development of local heat causing molecular iodine to sublimate and interact with carbon materials. Also, continuous and random impact during high-energy milling cause local fracture in carbon, thus exposing fresh surface for reaction with iodine. The continuous random impact also leads to a homogeneous chemical composition. As a result, in-situ high-energy milling proves to be an effective technique for solid state iodation process. A point to note that bromination of activated carbons (Chapter 7) was also performed using this route.



Fig 2.3: Schematic diagram showing the chemical vapor iodation process set-up. The whole chamber is made of stainless steel, which has a stainless steel mess sample holder. The steel-chamber is equipped with safety-valve and gas-outlet system.

2.2.2.2. Chemical vapor phase iodation process:

A more sophisticated procedure to insert iodine into carbon structure is via vapour phase iodation process. Activated carbons were doped with iodine by a vapor phase iodation route using a specially designed reaction chamber. The schematic representation of vapor iodation method is shown in figure 2.3 [12]. The pre-weighed carbons were suspended on a circular steel mesh. Various amounts of solid iodine powder were placed at the bottom of the chamber. The entire chamber was sealed and was heated inside a muffle furnace. Upon heating, iodine sublimes at ~112 °C and its vapor fills the entire reaction chamber. This iodine vapor results in atomic level iodine incorporation into the activated carbon. This vapor phase iodation was conducted at operating temperature in the range of 120-170 °C for a soaking time of 2-7 hours.

2.3. Physical characterisation methods:

2.3.1 X-ray Diffraction (XRD):

X-Ray powder diffraction (XRD) [13] was performed using a Scintag X2 powder diffractometer equipped with a copper target X-ray tube (operating conditions: 40 kV, 35 mA, Cu-k α radiation, λ =1.5405 Å). Various pristine and modified activated carbons were placed inside a square-shaped, well sample holder with dimension 25 mm X 25 mm X 2 mm. The samples were scanned between 10° to 60° at a rate varying from 0.8° min⁻¹. For small angle x-ray studies in microporous carbon, a slower scan rate of 0.3 min⁻¹ was applied in a longer range of 5°~ 80°. Subsequently, the (002) and (100) peaks of diffractograms were analysed for calculating the crystalline graphene dimension 'L_a' and graphite layer thickness 'L_c'. The L_a and L_c parameters were calculated by using the FWHM data and peak angle of the (100) and (002) peaks respectively, using the Debye-Scherrer equation:

$$t = \frac{\lambda}{B\cos\theta_{B}}$$

where, t = graphitic crystalline dimension, λ = the X-ray wavelength, θ = the scattering angle (in radians) and B = the FWHM (in radians of θ).

2.3.2 X-ray Fluorescence (XRF) spectroscopy:

For a semi-quantitative elemental analysis, energy dispersive X-ray fluorescence spectroscopy (XRF) [14] was performed implementing a Philips MiniPal X-ray fluorescence unit with Rh anode. Pristine and iodine-modified carbon powders were manually mixed with silicon (Si) powder in 1:1 ratio for 15 minutes. A pinch of sample was put into the XRF sample holder having a thin polythene base coated with vacuum silicon grease. Silicon was used as a reference material to gauge the relative amount of different elements and to detect any external contamination in carbons. Before any XRF test, the instrument was thoroughly purged with Helium gas for 300 seconds to obtain a clean ambience. XRF tests were conducted for all samples by applying 10 kV and 100 mA with an X-ray exposure time of 100 seconds. The data were collected and analysed using Philips MiniPal software v1.0A.

2.3.3 Thermal analyses (TGA, DSC study):

Thermal analysis [15] of different carbon materials was conducted by differential scanning calorimetry (DSC) and thermo gravimetric analysis (TGA) techniques. For these thermal analyses, DSC Q10 and Hi-Res TGA-2950 units (Thermal Advantage Inc) were employed with nitrogen gas purging for atmospheric control. For the DSC experiments, ~50 mg of carbon samples were sealed in aluminium pans inside a He-filled glove box. DSC and TGA analyses were conducted

in the temperature range of (30-500) °C and (30-1000) °C (heating rate of 10°Cmin⁻¹) using Platinum (Pt) and aluminium (Al) pan respectively.

2.3.4 Raman spectroscopy:

Raman spectroscopy [16] was performed with a Renishaw inVia Raman spectrometer having 2 cm⁻¹ instrumental resolutions. For each test, ~20 mg of carbon sample was used. Only 0.05% (=0.15 mW) of the laser power at (785 nm wavelength) with exposure time of 900 s was used to avoid possible laser-induced damage. Raman spectroscopy is a widely used tool to detect polyiodide compounds in various organic and inorganic compounds, as most of the polyiodide units are centrosymmetric in nature. The molecular iodine (I₂) gives a sharp Raman peak at 181.15 cm⁻¹ due to the vibrational mode of linear iodine dimer. However, the formation of various polyiodide units gives rise to near-linear/ non-linear structural units, having distinct peak positions. For example, triiodide (I₃) give three Raman peaks around 107, 112 and 145 cm⁻¹. Often, the previous two peaks merge together forming a broader peak around 112-115 cm⁻¹, while the 145 cm⁻¹ peak has relatively low intensity. For pentaiodide (I_5) structure, the linear units (L-shaped) have Raman peak at 154-162 cm⁻¹, while the bent units (V-shaped) give sharp peak at 157-164 cm⁻¹. Collectively, pentaiodides often lead to a broad peak around 165 cm⁻¹. The formation and detection of higher order polyiodides (heptaiodide, nonaiodide etc) is quite rare in nature. Thus, Raman spectroscopy is widely employed to study iodation process.

2.3.5 Brunauer, Emmett and Teller (BET) surface area analysis:

The surface morphology and pore structure analysis was conducted with the help of a Brunauer–Emmett–Teller (BET) [17] Micromeritics ASAP 2000 surface area analyzer [18]. The BET theory is an extension of Langmuir theory for monolayer

adsorption and is based on the theory of multilayer adsorption of an analysis gas on test samples. It is assumed (i) analysis gas molecules physically adsorb on a solid in layers infinitely; (ii) absence of any interaction between each adsorption layer; and (iii) the Langmuir monolayer adsorption theory can be applied to each layer. The BET

equation can be expressed as:
$$\frac{1}{\nu[(P_0/P)-1]} = \frac{c-1}{\nu_m c} \left(\frac{P}{P_0}\right) + \frac{1}{\nu_m c}$$

where, P and P_0 are the equilibrium and saturation pressure of adsorbents at the temperature of adsorption, v is the adsorbed gas quantity (volume units), and v_m is the monolayer adsorbed gas quantity. The term c is the BET constant expressed as:

$$c = \exp\left(\frac{E_1 - E_L}{RT}\right)$$

where, E_1 is the heat of adsorption for the first layer, and E_L is heat of adsorption for the second/ higher layers (also known as heat of liquefaction).

The powder samples were evacuated at 383 K and 10^{-4} Pa for 4 h, prior to the BET analysis using surface adsorption of N₂ (at 77 K). Multipoint BET analysis was performed using a total of 55 data points between pressure range of 7 to 760 mmHg. The BET surface area and micropore area were calculated using BET equation and t-plot method [19] respectively. The BET area (S_{BET}) is calculated with the formula:

$$S_{BET} = \left(\frac{\upsilon_m Ns}{aV}\right)$$

where, v_m is the monolayer adsorbed gas quantity, N is Avogadro's number, s is adsorption gas cross section, a is molar weight of adsorbed gas and V is the molar volume of adsorbed gas.

The total pore volume was calculated from the nitrogen adsorption value at relative pressure (P/P₀) of 0.95[20]. Micropore volume (<2 nm) was calculated from the N₂ adsorption isotherm by using the Dubinin-Radushkevich (DR) equation. The

balance of total pore volume and micropore volume (at $P/P_0=0.95$) was reported as the mesopore volume (2-50 nm). Assuming the slit shape nature of micropores inside carbon, DR theory [21-23] was implemented to estimate the characteristic energy (E_o) of present microporosity. The micropore average size (L_o) and micropore surface area (S_{micro}) values were calculated as per the following equations.

$$L_o (nm) = 10.6/ E_o (kJmol^{-1}) - 11.4$$

 $S_{micro} (m^2/g) = 2000 V_{micro} (cm^3 g^{-1})/ L_o (nm)$

The external surface area and mesopore size distribution was estimated by using Barrett-Joyner-Halenda (BJH) method on N₂ isotherm [19].

2.3.6 Transmission electron microscopy (TEM):

The material microstructure was analyzed by transmission electron microscopy (TEM) utilizing a JEOL 2010F microscope operating at 197 kV. The TEM samples were prepared by dispersing the powder in DMC and by releasing a few drops of the suspension on a lacey carbon film supported on a copper grid. In order to increase contrast, defocus phase imaging technique was used to observe the pores and material microstructure [24]. Over and under-focus images were taken in this study with defocus value of +250 nm or - 250 nm.

2.3.7 Electrical resistivity analysis:

The resistivity of mechanochemically modified activated carbon samples were measured a custom-made cylinder/ piston copper cell design [25]. A schematic diagram showing the set-up is presented in figure 2.4. The carbon samples were gradually compressed between two copper electrodes until the maximum compression limit, while measuring the volume and electrical resistance (R) intermittently at

Resistivity =
$$\rho = \left(\frac{RXA}{x}\right)$$

where, A= surface area of copper cylinder base,



x = height of pressed carbon pellets.

Fig 2.4: Schematic presentation of the home-built instrument used for resistivity measurement.

2.3.8 X-ray photoelectron spectroscopy (XPS) analysis:

X-ray photoelectron spectroscopy (XPS) [26] is a very powerful tool to study the concentration and chemical state of different species present near surface region of carbon materials. XPS analysis of pristine and halidated (iodine and bromine doping) was carried out using an upgraded Kratos XSAM 800 system (at Laboratory for Surface Modification, LSM of Rutgers University). Powder samples were analysed after a short cycle of Ar ion sputtering to remove any residual contaminants. For the analysis, Mg K α radiation (1254 eV) was used at pass energy of 40 eV. During the XPS analysis, the base pressure inside analysis chamber was maintained at ~10⁻⁹ Torr. The binding energies were measured with a precision of ~0.1 eV. In order to avoid the specimen charging, the film was mounted on the sample probe using carbon tape. As carbon is inherently conducting, no charging effect was observed during the measurement.

2.3.9 Small-angle X-ray scattering (SAXS) analysis:

Small angle X-ray scattering (SAXS) [27] focuses on diffraction/ scattering at lower scattering angles. SAXS measurements were performed using a custom-built small-to-wide angle X-ray spectrometer with a large Huber 4-circle goniometer capable of accommodating large sample chambers (at MRL, UC, Santa Barbara). The 4-circle diffractometer was equipped with an OSMIC double focusing multiplayer monochromator and a MAR 345 mm diameter image plate detector. It can be used to study polymeric/ biological materials, liquid crystals, polycrystalline and microporous materials.

The incident Cu-*K* α radiation ($\lambda = 1.54$ Å) from a 18 kW Rigaku rotatinganode generator was monochromatized and focused using Osmic confocal multilayer optics. About 0.1 g of carbon sample was mounted in a motorized X-Y-Z stage. The X-ray beam size was adjusted 1 mm X 1 mm cross-section at the sample with a flux of ~10⁸ photons/s inside an evacuated flight tube. This particular setting is suitable for probing structural features from 0.2~20 nm (micropores, 0~2 nm). The scattered radiation was collected using a MAR 345 plate detector. For all samples, the experimental data collection and data analysis was performed using SPEC and CPLOT/Fit2D software respectively [28].

2.4. Electrochemical characterisation methods:

2.4.1. Fabrication of positive electrodes and electrochemical cells:

Pristine and iodine-incorporated activated carbons were used to formulate cathode (positive electrode) materials. Cathode was fabricated in an acetone-based slurry using the Bellcore process composed of 57 wt % active carbons, 6 wt % SuperP carbon black (MMM), 15 wt % poly(vinylidene diflouride-cohexafluoropropylene) (Kynar-2801, Elf Atochem) copolymer binder dispersed in 23% dibutyl phthalate (DBP) (Aldrich) plasticizer. The slurry was then cast and dried at room temperature in air. Following, the DBP plasticizer was removed by successive extractions in 99.8% anhydrous ether (Aldrich). These electrode tapes were then dried at 120 °C for 1 h under vacuum. Disks of about 1cm² punched from these electrode tapes were used as cathodes in 2025 type coin cells (NRC or Hohsen) with Li metal (Johnson Matthey) as anode using Whatman GF/D glass fibre separators soaked with 1 M LiBF₄ dissolved in a mixture of propylene carbonate (PC) as electrolyte solution (<20 ppm H₂O). The cathode loading was $6.1-10.5 \text{ mg/cm}^2$ with an overall loading of 78% active material relative to conductive black and binder. The cells were assembled in a He-filled glove box (Dew point: -80 °C) to avoid any contamination.

2.4.2 Electrochemical cycling of carbon based cells:

The cells were galvanostatically cycled in voltage range of 2.8–4V (current rate 15 mA/g) using an Arbin galvanostat cycler. The capacitance of cells was calculated in the linear section of discharge voltage profile using the equation:

$$C = \frac{I}{\left(\frac{dV}{dt}\right)}$$

where C = capacitance (F/g), I = discharge current (A) and dV/dt being the slope in volt per second (Vs⁻¹). Volumetric density of some modified carbon samples were

measured by forming pellets at a pressure of 7000 psi. Specific capacity was calculated using the galvanostatic capacity, BET area and volumetric density as:

Specific capacity (per area)
$$\left(\frac{mAh}{m^2}\right) = \text{Capacity} \left(\frac{mAh}{g}\right) / \text{BET area} \left(\frac{m^2}{g}\right)$$

Specific volumetric capacity
$$\left(\frac{mAh}{cm^3}\right) = \text{Capacity}\left(\frac{mAh}{g}\right) \text{X Density}\left(\frac{g}{cm^3}\right)$$

Potentiodynamic cyclic voltammetry testing was conducted using coin cells of some key sample in the voltage range of 2.5 to 4.2 V at a scanning rate of 5 mV/100 s. A Macpile (Biologic, France) unit was used for cyclic voltammetry.

In order to compare the energy-density and power-density of materials, Ragone plots of some key samples were obtained using coin cells. The cells were cycled in a voltage range of 2.8 to 4 V varying the current rate at 2, 4, 8, 16, 32, 64, 128, 256, 512 and 1024 times the initial current rate of 15 mA/g. Ragone plot data were collected using a MacPile unit. Similarly, the cycle life of some key carbon materials were cycled between 2.8 to 4 V (at a current rate of 100mA/g) using a MacPile for testing the cyclic stability.

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III: INVESTIGATION OF PHYSICAL AND ELECTROCHEMICAL PROPERTIES OF MESOPOROUS ACTIVATED CARBON MODIFIED VIA SOLID-STATE MECHANICAL MILLING

3.1 Introduction:

Commercially available activated carbons vastly rely on the formation of ionic double layer at the electrode interface, which delivers non-faradaic electrochemical capacity [1-3]. Hence, it attracts significant research to formulate high-performance carbons with engineered morphology (high surface area and tunable porosity). However, as outlined in chapter 1 (section 1.8), our approach is to improve the electrochemical capacity of carbons by developing faradaic pseudocapacitance with suitable mechanochemical halide modification. The current chapter is the first step to study and prove the concept of 'chemical halidation of carbon'. In this initial work, we tried to examine the effect of iodine-incorporation on commercially available activated carbons. To this end, we studied the iodation-induced modification on the structure, morphology, chemical bonding and electrical resistivity of different carbons by using XRD, XRF, DSC, BET analysis and Raman spectroscopy. Following, we investigated the effect of iodation on electrochemical properties of commercial activated carbons. Using commercial carbons as benchmark, effect of iodation on physical and electrochemical properties of activated carbons were probed to verify the usefulness of chemical halidation process.

3.2 Synthesis of mesoporous carbon-iodine nanocomposites via solid state high-energy milling route:

Different commercially available activated carbon materials, ASupra (from Norit Inc [4]), ASP and SP (from Timcal Inc [5]), were taken as precursor carbons. Some materials properties of these carbons are enlisted in table 3.1. ASupra is an ultra high purity activated carbon of very high surface area (1743 m^2/g). ASP is a high

surface area (762 m^2/g) version of SP that has been activated. SP is a relatively low surface area (60 m^2/g) carbon black, which is networked to give extraordinary conductivity and is typically utilized as a carbon additive in Li-ion battery electrode materials. Here onwards, these materials are mentioned as ASupra, ASP and SP respectively. These carbon materials were high energy milled for time ranging from 0-80 minutes using a SPEX 1000 high-energy shock type milling machine. Spherical steel milling media of different sizes were used throughout. Further, these activated carbon precursors were mechano-chemically modified [6-8] by with the addition of 0-25 weight % of iodine during high-energy milling. All materials loading and collecting modified carbon from milling cells were performed inside a He-gas filled glove box with better than -80° C dew point to ensure no external contamination or hydrolysis. The resulting carbon-iodine nanocomposites was studied in detail focusing on its structure, morphology, double layer formation and electrochemical development using a suites of characterization techniques, the details of which are summarized in chapter 2.

Table 3.1. Physico-chemical properties of various activated carbon precursors.							
Manufacturer	Morphology 1	Resistivity (Ω cm) Capacitance (F/g)	surface			
				area (m^2/g)			
Norit-ASupra	Spherical	2	105	1743			
Timcal-ASP	Porous-Interconnect	ted 1	70	762			
Timcal-SP	Interconnected	0.5	40	61			

3.3 Structural analysis of carbon-iodine nanocomposites: 3.3.1 X-ray diffraction analysis:

Normally, electrochemical capacitors employ high surface area, mesoporous carbon materials which are usually considered to be X-ray amorphous in nature. The X-ray diffractograms of three families of precursor and modified carbon materials, namely ASupra, ASP and SP, are shown in figure 3.1. The corresponding X-ray analysis data are summarized in table 3.2.

The broad spectra in all cases confirm the existence of amorphous carbon. However, a careful study reveals the evolution and variation of (002) and (100) broad peaks around 25° and 44°. These peaks indicate the presence of localized regions of graphitic order in either an amorphous carbon matrix or nanographene domains interconnected in a disordered fashion. The broad peak around 18° is a system peak originating from the sample holder. In all materials, longer milling of carbon leads to a narrowing and increase in intensity of the Bragg reflections, especially those originating from (100). Also the d spacing of all carbons gradually decreases with longer milling time. The d (002) is shown to decrease from approximately 3.6A for the precursor carbons to the 3.5A range for the milled carbons. This is consistent with the trend towards graphitic like domain formation (3.35A for d(002)). As discussed in

Materials	d spaci	ng (A°)	La	L _c	Capacity	
	(002)	(100)	(A°)	(A°)	(mAh/g)	
ASupra Raw	3.647	2.075	29.8980	23.4078	22.7950	
ASupra BM 20	3.613	2.052	42.8897	21.1638	13.7488	
ASupra BM 40	3.492	2.041	89.6929	30.0765	7.1061	
ASupra BM 60	3.459	2.040	110.9125	44.8350	3.9986	
ASupra 15%I BM20	3.522	2.077			13.3580	
ASupra 25%I BM20	3.602	2.052			18.0570	
ASP Raw	3.647	2.096	30.5649	37.2138	10.8966	
ASP BM 20	3.631	2.068	50.0615	25.2020	8.6054	
ASP BM 40	3.543	2.036	80.2150	29.3878	6.4324	
ASP BM 60	3.529	2.040	96.1957	34.4616	6.4580	
ASP 15%I BM20	3.522	2.077			11.2000	
ASP 25%I BM20	3.670	2.049			12.7441	
SP Raw	3.579	2.096	37.2475	30.8275	1.0500	
SP BM 20	3.557	2.063	48.8768	25.0100	3.9241	
SP BM 40	3.550	2.036	89.1214	26.9988	4.0295	
SP BM 60	3.507	2.036	104.6667	41.8715	3.4076	
SP 15%I BM20	3.544	2.055			5.3126	
SP 25%I BM20	3.647	2.072			6.1868	

Table 3.2: Crystallographic parameters of pristine and modified activated carbons as obtained from X-ray diffraction analysis.





Fig 3.1: X-ray diffractograms showing the amorphous nature of activated carbons along with (002) and and (100) broad peaks in iodated, high energy milled carbons (A) ASupra, (B) ASP and (C) SP materials. The word BM stands for ball milling (high-energy milling) and the subsequent numbers present the duration of milling process in minutes.

previous literature [7,8], longer shock-type milling of amorphous carbon leads to the formation of graphite nano-platelets, which grow both longitudinally and laterally. In sharp contrast, when these carbons are doped with iodine, it completely destroys any localized crystallinity present inside carbon for all the carbons investigated. From figure 3.1, it is clearly seen that higher amount of iodine doping to pristine carbon leads to destruction of any crystallinity, hence decreasing the (002) and (100) peaks compared to both the milled and unmilled pure carbon standards.

The FWHM values for (002) and (100) peaks were used to measure the crystallite size (L_a) and crystallite thickness (L_c) of graphitic regions inside carbon. The (100) peaks for milled samples can be deconvoluted to a broad peak around 43° followed by a sharp peak. In the current investigation, the sharp peak arising due to milling was used to calculate the crystallite size. The variation of L_a and L_c parameters of carbon with milling time and iodine doping are summarised in table 3.2. As these carbon samples are quite amorphous in nature, the L_a and L_c parameters were calculated to an approximate value. It indicates the longer milling time leads to graphitic crystallites growth, especially with respect to L_a . This is in agreement with the X-ray diffraction on carbon powders showing evolution of (002) and (100) peaks with longer milling time. In sharp contrast, the doping of iodine decreases the crystallinity of carbons to a state of X-ray amorphosity.

3.3.2 X-ray fluorescence analysis:

Solid-state milling may have lead to sublimation of iodine during processing. XRF was utilized as a qualitative technique to characterize the iodine content as function of milling time. The XRF analysis data of carbon samples are summarised in table 3.3. A powder mixture of modified carbon with a silicon internal standard was used in 1:1 weight ratio. XRF data confirms the presence of iodine in all iodine-doped, high-energy milled carbon samples. Further, the ratio of intensities of K- α peaks of iodine (at 3.938 keV) and silicon (at 1.739 keV) affirms the increasing amount of iodine in the iodated sample with higher starting iodine content. Also, the iodine content is almost unaffected by longer milling time. This holds good for all three classes of carbons tried in the current investigation. Moreover, the XRF data shows no metallic contamination in iodated carbons due to high-energy milling.

Materials system —	→ ASupra	ASP	SP
BM 20	0.0000	0.0000	0.0000
5% I BM 20	1.0307	0.9162	1.0360
15% I BM 20	2.4688	1.8335	2.2800
25% I BM 20	3.4837	2.8750	2.9600
25% I BM 40	3.4837	4.1493	4.0000
25% I BM 60	3.4837	3.7195	3.3800

Table 3.3: The X-ray fluorescence data (I/Si ratio) of carbon materials.
3.3.3 Raman spectroscopy analysis:

The Raman spectra of mechano-chemically modified carbons are given in figure 3.2. All carbon materials show two distinct peaks around 1300 cm⁻¹ (D peak, A_{1g} symmetry) and 1600 cm⁻¹ (G peak, E_{2g} symmetry). These D and G peaks correspond to the presence of breathing mode of the A_{1g} symmetry and the individual carbons involved in the sp² (planar) hybridization states in the carbon structure, respectively. Thus, the occurrence and change in these D and G peaks can be utilized to know any internal structural modification that is quite difficult to notice by techniques like X-ray diffraction.

Overall, the D peak (~1300 cm⁻¹) of SP based materials shows higher intensity relative to the G peak than the corresponding ASupra materials. For amorphous materials the increase of the D peak vs. G peak is consistent with an increase in ordering as it relates more to the probability of finding a six-fold carbon ring in a cluster of carbon as opposed to much longer range La development which would enhance the G band over the D band. The latter phenomena due to the confinement of the breathing mode of the 6 carbon as crystallinity progresses that is characteristic of the D peak [9]. The maximum in D/G ratio has been suggested to occur at approximately $L_a = 20$ Å. XRD revealed that upon milling the L_a is much greater than 20 Å, in this region the D/G ratio should therefore increase with crystallinity. The Raman analysis data of carbon materials are summarized in table 3.4. From table 3.4, it is indicated that the I_D/I_G ratio decreases with milling of pristine carbons. This indicates the formation of much more crystalline (graphitic) region in milled consistent with the XRD characterization. In sharp contrast, the presence of iodine in pristine carbon leads to higher I_D/I_G ratio indicating the destruction of any crystalline graphitic regions for $L_a \sim 20$ Å. However, the XRD results indicate complete X-ray

amorphosity, therefore in this region ($L_a < 20$ Å) the D/G should actually decrease with decrease in crystallite size. This paradox may indicate the survival of a significant number of six-membered rings which are isolated from crystal development due to the presence of $I_n^{(-)}$. This interesting possibility will be investigated in more detail in following chapters.

Materials	I_D/I_G ratio	D Peak (cm ⁻¹)	G Peak (cm ⁻¹)	D-FWHM (cm ⁻¹)	G-FWHM (cm ⁻¹)
ASupra	1.9950	1299.18	1591.24	108.60	59.68
ASupra BM 20	1.9434	1304.08	1587.34	120.34	62.12
ASupra 25% I BM 20	2.1160	1307.99	1584.40	122.30	68.97
SP	2.8182	1322.72	1581.69	124.25	83.16
SP BM 20	2.4892	1316.13	1580.75	110.05	90.01
SP 25% I BM 20	2.5366	1328.37	1593.93	113.00	90.01

Table 3.4: Summary of Raman spectroscopy data of ASupra and SP materials.



Fig 3.2 Raman spectra of (A) ASupra and (B) SP based materials showing the D and G bands of amorphous activated carbons.

3.4 Thermal analysis of carbon-iodine nanocomposites

Thermal analysis of various iodinated high-energy milled carbon powders was conducted. The DSC curves are shown in Fig 3.3. As shown in the figure, free iodine gives rise to an endothermic peak around 110 °C owing to the sublimation of iodine.



Fig 3.3 DSC graph showing the absence of free molecular iodine in iodated carbons and the possible formation of strong chemical bonding to deliver exothermic peaks at higher temperature. The chemical nature holds true for all three carbons tried here.

The exothermic peak immediately following it (marked with an asterisk) may be due the reaction of the sublimated iodine with aluminium pan or the failure of the pan itself under the pressure of sublimed I₂. All pristine carbon materials show negligible reaction. Upon doping these carbons with iodine, the DSC does not show any endothermic peak in the range 100-120 °C, indicating the absence of any free iodine. The iodinated carbon shows a sharp exothermic peak around 270-420 °C. It suggests that the high energy milling leads to some degree of chemical bonding between carbon and iodine thereby leaving no free iodine.

3.5 Electrical resistivity study of iodated carbons:

Figure 3.4 shows the variation of resistivity as a function of density of different carbons, indicating the effect of compression on resistivity. It clearly shows a marked increase in density for the milled and especially the iodine reacted samples. The high energy milling leads to breaking of the interconnected morphology and large macropores of carbon raw materials, which leads to a closer packing of carbon particles hence resulting in higher density. Iodated sample shows the highest density due to the combine effect of high-energy milling and inclusion of highly dense iodine in carbon. The milling significantly destroys the spherical particle morphology of ASupra and the interconnected morphology of ASP and SP based materials. This in turn enhances the resistivity for the ASP and SP samples vs. the non-iodated milled, and is similar to the non iodated milled ASupra sample. However, there is very little increase in resistivity with high-energy milling and iodine doping. Upon complete densification, the resistivity of all samples narrows down to almost same value.





Fig 3.4 The variation of resistivity of pristine and iodated carbon samples with increase in density of pressed pellets. The resistivity data are shown for (A) ASupra, (B) ASP and (C) SP carbon systems.

3.6 Morphological development in carbon-iodine nanocomposites

The non-faradaic capacitance of any capacitor is directly proportional to its mesoporous surface area of the carbon. In the current work, the surface area and morphology of activated carbon precursors was modified in two ways: by high energy milling of carbon for different time and by the chemical treatment of this milled carbon with different amount of iodine doping. The morphological development of carbon upon solid-state iodation is discussed below.

3.6.1 Variation of surface area (BET area and micropore area)

Figure 3.5 (A-C) shows the variation of surface area of carbon materials. The high-energy milling leads to smaller surface area in case of ASupra and ASP carbons, where as the surface area increases for SP carbon. The (shock-type) high-energy milling transfers appreciable amount of impact energy to the carbon particles resulting in continuous local fracture of carbon materials. As these high surface area carbon precursors contain small particles even before any treatment, the application of milling reduces the particles size below a limit where they become thermodynamically unstable due to very high surface energy. As a result, these particles tend to agglomerate together forming larger particles [10]. In this case, even if there are many small particles, the overall surface area decreases due to the agglomeration of fine particles making them inactive. Further, it is marked the addition of iodine into carbon leads to even smaller surface area (Fig 3.5). The possible formation of nanocomposites due to iodine doping may envelop the mesoporosity in the carbon making part of their surface area inactive. Also, the inherently high density of iodine leads to lower specific surface area. Thus, the surface area decreases both by high-energy milling and iodine doping.



Fig 3.5: Histograms showing the effect of high-energy milling and iodation on BET surface area [(A) ASupra, (B) ASP and (C) SP system] and average pore size [(D) ASupra, (E) ASP and (F) SP systems].

The mechano-chemical treatment of carbon not only changes the overall surface area but also affects the internal pore size and porosity distribution. Figure 3.5 (D-F) shows the change in overall pore size of carbon materials. While for ASupra, pore size increases with longer milling time and decreases with iodine doping, the reverse phenomena occur with ASP and SP. The initial pore size is relatively larger for ASP and SP carbons. The high-energy milling destroys the interconnected particle morphology of the intrinsically mesoporous ASP and SP carbons. This in turn leads to lower mesoporosity and smaller pore size. In contrast, it leads to higher mesoporosity and increased pore size in the initially smaller pore size ASupra materials.

3.6.2 Variation of pore size distribution

Although the overall surface area is responsible for the electrode performance, on a microscale, the pore size distribution is an equally important factor. Even with the same surface area, the relative degree of mesoporosity leads to better electrochemical performance as microporosity (<1.2 nm) sterically inhibits the adsorption of the required electrolyte, specifically the solvated salt. The porosity distribution in the modified carbon based samples is presented in figure 3.6. In case of ASupra materials, the initial ASupra possesses little mesoporosity. But, high-energy milling of ASupra leads to smaller particles with larger pores, hence inducing some degree of mesoporosity especially around 2.5nm. However, this mesoporosity is destroyed upon addition of iodine. In case of ASP and SP, the precursor itself possesses high mesoporosity for 10-50nm. This mesoporosity is destroyed by high energy milling and more so by iodine doping. From figure 3.6, it is inferred that high-energy milling may lead to favourable pore structure, while the iodine doping often negates these modified pore structure.



Fig 3.6: Pore size distribution of (A) ASupra, (B) ASP and (C) SP based materials. It shows the effect of high-energy milling and iodine doping to the relative porosity (microporosity and mesoporosity) in activated carbons.

3.7.1 Galvanostatic analysis (Electrochemical capacity):

The specific capacity of the initial precursor as well as modified carbon electrodes are summarized in figure 3.7 (a), (b), (c) for ASupra, ASP and SP materials respectively for cells cycled between 3.2 and 4. V. Capacity was calculated in the non-faradaic reaction region between 3.2 and 4V for all the materials. Here, capacity is utilized as opposed to capacitance as if one looks closely, most activated carbons have discharge curves that are not completely linear and resulting in skewed data if given in F/cc based on a narrow range. As we will see this is a region of the electrochemical activity that is defined by non-faradaic behaviour. It is clearly marked that for untreated carbon materials, the capacity decreases with longer milling time. This can be solely assigned to the previously noted decrease in surface area with longer milling. However, upon doping the carbons with iodine via high energy milling, the capacity systematically increases for all three systems even though a significant portion of the weight of the electrode is iodine and not carbon.

Of particular interest is the fact that there is a very large disparity in surface area normalized capacitance between the iodine doped and undoped carbon samples (Figure 3.8 A-C). This specific capacitance values were normalized per surface area by dividing the specific capacitance (μ F/g) of carbon materials to their corresponding BET surface area (m²/g) values. Theoretically all materials should give approximately the same value, however a tremendous increases in surface area normalized capacitance is developed for the iodine doped samples, where normalized capacitance is in excess of 200-400% of the raw materials. The surface area normalised capacitance data for carbon electrodes were obtained using the slope of linear portion of corresponding voltage discharge profiles. Upon halide introduction, the normalised



Figure 3.7: Discharge capacity of 2^{nd} cycle of (A) Asupra, (B) ASP and (C) SP based materials cycled between 4 to 3.2 V. Gradual increase in electrochemical capacity with higher degree of iodation is observed for all three types of carbon tested here.

capacitance increased from 5.9 μ F/cm² to 15.7 μ F/cm² in case of ASupra (~150 % increase) and from 6.8 μ F/cm² to 32.8 μ F/cm² in case of ASP (~380 % increase). From the BET tests, the relative amount of micropore area of ASupra materials was seen to increase from 24.9 % to 60.4 % upon halide doping. Even though the amount of inaccessible micropores increases significantly upon high-energy milling of iodinated carbon, the resultant capacitance increases instead of decreasing. The very large increase in surface specific capacitance, among the highest reported, suggests a possible internal electronic modification to the carbon or access of the electrolyte to the newly developed micropore area.

Figure 3.8 (D, E, F) plots the volumetric capacity of the modified carbons vs. the raw carbons. The density of the carbons was based on the density of carbon pellets pressed at 7000 psi. Although we have previously shown that the specific capacity of the doped activated carbons is less in the non faradaic region (3.2-4V), the volumetric capacity is superior to the raw material by almost 100%. For the best raw materials, ASupra, the volumetric capacity raises from 12 mAh/cc to 24 mAh/cc with mechanochemically induced iodine addition.

The comparative discharge voltage profiles to lower voltages (from 4 to 2.8 V) of pristine and modified carbons are shown in figure 3.9. In case of ASupra and ASP based materials, the voltage profiles indicate a decrease in capacity with milling, which can be correlated to the decreasing surface area. But, an incremental increase in capacity occurs in SP materials as high-energy milling leads to higher surface area. Further, the addition of iodine results in a significant modification of the voltage profile in all three classes of carbon. The incorporation of iodine gives rise to a large plateau around 3.1 V, making the voltage profiles non-linear. This voltage is well



above the traditional Li + I_2 reaction potential of 2.7V and preliminary evidence points to a faradaic reduction reaction of lithium with a CI_x complex. The nature and

Figure 3.8: Summary of normalized electrochemical performance of modified carbons. Specific capacitance (4-3.2 V) of (A) ASupra, (B) ASP and (C) SP materials. Volumetric capacity (4-2.8 V) of (D) ASupra, (E) ASP (F) SP materials.



Figure 3.9: The comparison of discharge voltage profile showing the effect of iodine addition (A) ASupra, (B) ASP and (C) SP carbon materials.

degree of covalency of this bond will be discussed in a future paper. This C-I reduction increases the capacity of the carbon materials significantly. Figure 3.8 (D-F) shows that the incorporation of this faradaic reaction increases the volumetric capacity of the iodine reacted samples vs. the doped samples by 500%. For example, the volumetric capacity of ASupra materials increases from 11 to 56 mAh/cc upon iodine doping. This increase in volumetric capacity is even more significant in case of ASP and SP based materials. Figure 3.10 summarises the effect of milling time and iodine doping on volumetric capacity of modified carbons. In all cases, the incorporation of iodine into carbon leads to higher volumetric efficiency, the maximum increase being in case of SP materials.

From practical application point of view, unlike batteries, the electrochemical capacitors are often limited by volume rather than by weight. Thus, these iodine-doped carbons showing high volumetric capacity can be useful candidates for electrode materials. Also, the higher volumetric energy density makes the electrodes thinner with less propous electrode diffusion required resulting in higher performance.

3.7.2 Potentiodynamic analysis (Cyclic voltammetry):

In order to closely follow the change in electronic properties of carbon upon modification, the potentiodynamic cycling was conducted on undoped and doped samples. The potentiodynamic cycling curves of ASupra, ASP and SP based materials are presented in figures 3.11. They clearly illustrate the change in the specific current profiles of active carbon materials upon iodine doping. While the undoped carbons show a smooth curve, indicative of a non-faradaic reaction through most of the voltage region, the doping of iodine leads to peaks in current around 3.1~3.5 V. These spikes are reversible in nature indicating no permanent formation of any particular



Figure 3.10: Volumetric capacity of (A) ASupra, (B) ASP and (C) SP materials cycled between 3 to 4.2 V.

compound and also are strong indication of a faradaic process. Also, over the non-Faradaic region, the specific current is higher for iodinated carbons consistent with the galvanostatic results.



Figure 3.11: Cyclic voltammograms showing the effect of iodation on the voltage profile of ball milled carbons (A) ASupra, (B) ASP and (C) SP materials. Two sets of figures are shown in each case corresponding to milling duration of 20 and 60 minute.

To get a better understanding of the underlying electrochemistry, a sample voltage discharging profile of an iodinated carbon cycled between 4-3 V is shown in figure 3.12. It shows three distinct regions (marked I, II, III) corresponding to three electrochemical reactions. The region I involves the movement of adsorbed BF_4^- ions (of electrolyte) from the mesoporous carbon. The change in slope at about 3.5 V is due to the p to n type transition (point of zero charge, PZC). After PZC, the adsorption of Li⁺ ions within the Helmholtz double layer occurs. Further, a large plateau is marked around 3.1 V, starting region III, which is likely due to the cathodic reaction of C-I compound. The transition from I to II and II to III regions yields corresponding reversible peaks in the CV curves of iodinated sample.



Fig 3.12: A typical discharge voltage profile on iodine-modified activated carbons showing three distinct zones marked as I, II and III. The change in slope in the non-faradaic region occurs at point-of-zero-charge (PZC, 3.5 V). The faradaic pseudocapacitance arises around 3.1 V.

3.7.3 Initial cycle life stability study:

The volumetric discharge capacities of six key carbon based samples are shown as a function of cycle number in Fig. 3.13. The charge/discharge cycle is shown for more than 200 cycles from 3 to 4.2 volts cycling at 15 mA/g (figure 3.13 a) and from 2.8 to 4.2 volts cycling at 100 mA/g (figure 3.13 b). The high capacity of carbon modified with iodine is fairly retained even after long cycling. The capacity profile is marked to be completely flat in case of SP and ASP materials and there is a slight decrease in case of ASupra materials. Even though the 2.8-4 samples are cycling through the faradaic region (Fig 3.13 b), the cycling on this plateau is very reversible as evidenced by the flat cycling profile. The retention of this faradaic region indicates the chemical stability of iodinated carbon upon cycling. The very efficient cycling of the iodine doped ASP in both the non-faradaic region and faradaic regions make it a superior choice in volumetric energy density (20 mAh/cc) relative to ASupra (12 mAh/cc) by almost 100%. Figure 3.14 compares the voltage discharge profiles of iodinated ASP at different cycles (from 1 to 600, cycled at 100 mA/g from 4 to 2.8 V). It shows an excellent cyclic stability after the drop in initial cycles.





Figure 3.13: Cycle life stability of iodinated cells cycled between (A) 4 to 3.2 V, (B) 4 to 2.8 V. The number is parenthesis marks the specific capacity (mAh/g) values.



Figure 3.14: The comparative discharge voltage profiles of iodinated ASP sample at different Cycles, cycled between 4 to 2.8 V at 100 mA/g. The numbers in the figure indicate the cycle index numbers.

3.8. Summary and Conclusions:

The effect of iodation on physical and electrochemical properties of carbons was examined by mechanochemical iodine incorporation into three commercial carbons. In all cases, distinct evidence was obtained to support significant structural and electrochemical modification of iodine-modified carbon nanostructures vs pristine carbon nanostructures. The resulting materials show the formation of polyiodide structures and an interesting combination of lower surface area coupled with markedly higher volumetric and gravimetric electrochemical capacity. In particular, iodation led to a 200–400% increase in volumetric capacitance of carbon materials.

After showing the proof-of-concept on chemical iodation, we attempted to optimize the iodation process to further improve the electrochemical capacity of carbon. A more intimate chemical interaction between host carbon and guest iodine may hold the key for effective utilization of iodine, which can subsequently lead to higher faradaic pseudocapacitance and electrochemical improvement. With this idea in mind, we attempt a fine-scale introduction of iodine into activated carbon and study its effect on modified carbon in the following chapter.

3.9 References:

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IV: FINE-SCALE IODINE INCORPORATION INTO MESOPOROUS ACTIVATED CARBONS VIA A CHEMICAL VAPOR IODATION ROUTE: STRUCTURAL, MORPHOLOGICAL AND ELECTROCHEMICAL INVESTIGATION

4.1. Introduction:

In Chapter 3, the incorporation of iodine was found to result in the formation of polyiodides, shift the PZC, and alter the electrochemical properties of the carbon electrodes resulting in the improvement in non-faradaic capacity, and the development of a psuedocapacitive reaction that is not related to free molecular iodine. A more intimate interaction between carbon and iodine may further improve the electrochemical properties of resultant nanocomposites. In the current chapter, we go one step further to introduce iodine into carbon structure at very fine scale with a vapor phase iodine impregnation technique. In addition to improve the electrochemical performance of iodated carbons, our goal is to separate the effects of high energy milling and iodine doping on the material modification. The effect of iodine modification of activated carbons and their resultant physical, electronic and electrochemical properties have been examined through a combination of techniques including XRD, XRF, XPS, TGA, DSC, BET analysis, Raman spectroscopy and electrochemical characterization.

4.2 Production of mesoporous carbon based activated carbon-iodine nanocomposites via chemical vapor iodation route:

Commercially available activated carbon material trade named E350 and identified as ASP from this point forward (from Timcal Inc) was used as precursor carbon. The ASP material is industrially produced by partial oil oxidation of carbochemical and petrochemical materials. This combustion/ oxidation is conducted at a low velocity with no additive to obtain high-pure carbon of uniform size [1].

The ASP carbons were doped with iodine by a vapor phase iodation route using a specially designed reaction chamber as described in chapter 2. This vapor phase iodation results in atomic level iodine incorporation into the activated carbon. In order to study the effect of surface area and structure of the precursor carbon, the carbons were used after high-energy milling for different time from 0-60 minutes using a SPEX 1000 high-energy shock type milling machine. Also, the amount of initial iodine content utilized during the vapor treatment was varied from 0-45 weight % of carbon. All materials handling was performed inside a dry room to avoid any external contamination or hydrolysis.

4.3. Optimization of chemical vapor iodation process:

The iodine vapor deposition on activated carbon was performed inside a closed steel chamber. The degree of carbon-iodine interaction depends on two main parameters: the operating temperature and the soaking duration. As the melting, sublimation and boiling point of iodine are 113.7 °C, 120 °C and 184.4 °C respectively, iodine incorporation was tested at two extreme temperatures 120 °C and 170 °C for time ranging from 2 hr to 8 hr. In all initial cases, 25 weight percentage of iodine relative to carbon was evaporated. The resultant weight uptake for different processing conditions is summarized in figure 4.1. Surprisingly, almost all the iodine added (approximately 23%) was incorporated into the carbon by the vapor reaction leading to a molar composition of C-I_{0.03}. There is a very minor increase in iodine uptake with the higher soaking temperature of 170 °C, possibly due to an increase in the activity of the carbon at higher temperatures. Maximum iodine uptake occurred early in the process. Increasing annealing times from 2h to 8h resulted in a 1.5-3.5% decrease in iodine uptake for the 120°C and 170°C samples, respectively. In light of this, the 2h processing condition was utilized for all subsequent iodation experiments.



Fig 4.1: The relative iodine uptake ability of activated carbon at two extreme temperatures tried (120 and 170 °C) for soaking time ranging from 2 to 8 hour.



Fig 4.2: Graph showing the percentage weight of iodine uptake by activated carbons which are pre-milled from 0 to 60 minutes with initial iodine charge varying from 15 to 45 weight percent. All iodation experiments were performed at a reaction temperature of 170 $^{\circ}$ C with a soaking time of 2 hours.

The relative effect of surface area and structural modification of carbon and initial iodine charge (amount added to cell) on the resultant carbon-iodine adsorption was studied. In this case, the as-received activated carbon as well as carbon highenergy milled for different period of time (20 min, 40 min and 60 min) were utilized as reactants. In addition, the iodine charge was varied from 15 to 45 weight percentage of activated carbons. All iodine sublimation reactions were performed at the optimized reaction condition of 170 °C annealing for 2 hours identified above. The amount of iodine weight uptake is presented in figure 4.2 as a function of carbon reactant milling time and iodine wt%. In all cases, higher iodine amounts lead to higher iodine weight uptake into the carbon structure. The observed values agree very well with the theoretical weight uptake for the 15% (C- $I_{0.017}$), 25% (C- $I_{0.032}$) and 35% $(C-I_{0.051})$ I samples. Though longer milling time aggressively decreases the effective surface area (as discussed in detail later), the relative degree of iodine adsorption remains almost same for all cases until a high iodine charge of 45%. At this iodine charge, the effects of saturation are reached. The highest surface area material (762.07 m^2/g (0 min mill) gained iodine at a value of 88% of theoretical value, while the lowest surface area (297.35 m²/g) (60 min mill) revealed only 68% efficiency. So although, as will be shown below, the iodine seems to induce a bulk effect, the uptake of iodine is limited by the surface area and controls the ultimate saturation values at a 2h exposure time.

4.4 X-ray diffraction structural study of carbon-iodine nanocomposites:

The X-ray diffractograms of precursor and modified carbon materials for three separate milling times (20 min, 40 min, and 60 min.) are shown in figure 4.3 (a, b, and c respectively). The corresponding X-ray analysis data are given in table 4.1. The appearance of broad spectra in all carbons corroborates the amorphous nature of

carbon. However, a close look depicts the evolution and variation of two broad peaks around 25° and 44° . These peaks correspond to (002) and (100) Bragg reflections, suggesting the presence of localized graphitic ordering in amorphous carbon matrix or localized interconnected nano-graphene domains arranged in a random order. The broad peak around 18° is a system peak originating from the sample holder. As seen in comparisons of figure 4.3 (a, b, c), longer milling of the precursor carbon gives rise to narrow and intense Bragg reflection, especially those originating from (100). Additionally, d (002) decreases from approximately 3.6 Å for the precursor carbon to the 3.5 Å upon modification, consistent with the trend towards graphitic like domain formation which would occur at 3.35 Å. This observation is consistent with previous literature [2] where longer shock-type milling of amorphous carbon leads to the formation of graphite nano-platelets with longitudinal and lateral growth. The FWHM values for (002) and (100) peaks were used to determine the graphene crystallite size (L_a) and graphitic crystallite thickness (L_c) of nanographitic regions inside the modified carbons. The broad (100) peaks for milled samples can be deconvoluted to a broad peak around 43° two-theta followed by a well developed sharp peak. In the present study, the sharp peak of the milled samples was used to calculate the crystallite size. The variation of La and Lc parameters of precursor and modified carbons are summarized in table 4.1. These L_a and L_c parameters were calculated to an approximate value due to the amorphous nature of carbons. The data indicates very little change with respect to L_c but a distinct increase of L_a from 30 to 96 Å is observed. This is in agreement with the X-ray diffraction on carbon powders showing evolution of the (100) peak with longer milling time.

When iodine is introduced into these carbons via vapor phase deposition, it destroys all localized XRD identifiable crystalline ordering inside carbon, regardless

of the milling induced crystallization. This is represented by the drastic decrease in the (002) and (100) peaks compared to pristine carbons. Special care was taken in sample preparation and analysis such that such relative comparisons can be made accurately. In our previous study involving solid-state iodation via high-energy milling of carbon, we found a very similar effect. As opposed to the milling technique [3, 4], we have started with a pre-milled carbon that has demonstrated ordering and then eliminated this structure through the incorporation of iodine. Therefore, we can now conclude that the amorphization was not related in any way to the milling process in our former study (Chapter 3), it was due to the iodine. In the previous section, we noted that the degree of iodine uptake is limited by the surface area of the material. However, based on the drastic changes to the core structure, it seems that the iodine uptake leads to C-I chemical effect within the bulk of the structure.





Fig 4.3: The X-ray diffractograms of pristine and iodated activated carbons initially milled for (A) 20 min, (B) 40 min and (C) 60 min. The initial iodine feed during iodation of carbon was varied from 0 to 35 weight percentage. The synonym BM refers to high-energy milling.

Materials	d space	ing (A°)	La	L _c
	(002)	(100)	(Å)	(Å)
ASP Raw	3.647	2.096	30.5	37.2
ASP BM 20	3.631	2.068	50.0	25.2
ASP BM 40	3.543	2.036	80.2	29.3
ASP BM 60	3.529	2.040	96.1	34.4
ASP 15% I BM 20	3.643	2.072		
ASP 25% I BM 20	3.620	2.065		
ASP 35% I BM 20	3.578	2.037		

Table 4.1: Summary of X-ray diffraction data of iodated activated carbons.

4.5 X-ray fluorescence spectroscopy of iodated carbons:

Upon iodine incorporation into carbon, one possibility may be that the iodine completely covers all the surface of mesoporous carbon. In this hypothetical case, the absorption of the X-ray radiation will be dominated by the iodine as it has very high X-ray absorption factor (XAF) relative to that of carbon. In such a case, XRD data can be illusive to comment on the relative ordering of bulk carbon structure. However, as the iodine amount is minor i.e. $15 (C-I_{0.017})$ to $35 (C-I_{0.051})$ weight %, the amounts are not theoretically sufficient to form a monolayer on entire carbon surface area. Therefore we can reasonable conclude that (i) the incorporation of iodine destroys ordering in the carbon structure and (ii) the carbon-iodine interaction occurs within the bulk of the structure.

4.6 Investigation of localized chemistry of iodated activated carbons:

4.6.1 Raman spectroscopy analysis:

Following the X-ray diffraction analysis, Raman spectroscopy was conducted to further investigate the localized structural development of iodated carbons. Carbon materials usually exist of two distinct hybridization states: graphitic sp² (planar) structure and diamond like sp³ (tetrahedral) structure. Subsequently, carbon materials show two distinct peaks around 1300 cm⁻¹ (D peak, A_{1g} symmetry) and 1600 cm⁻¹ (G peak, E_{2g} symmetry) [5]. The evolution and variation of these D and G peaks is often used to study the internal structural changes in carbons. The Raman spectra of all vapor phase iodated activated carbons are shown in figure 4.4 (a) (high wave number window) and (b) (low wave number window). The corresponding Raman analysis data are summarized in table 4.2.

Table 4.2: Raman spectroscopy data of iodated activated carbons.

High wave number window			Low wave number window			Capacity	
Materials	I _D /I _G ratio	D peak (cm ⁻¹)	G peak (cm ⁻¹)	I ₅ /I ₃ ratio	I ₅ peak (cm ⁻¹)	I ₃ peak (cm ⁻¹)	(mAh/g)
ASP	1.8245	1303.0	1592.5	0.0			10.9
ASP 15%	I 1.8009	1312.4	1602.0	1.0	164.1	107.7	30.0
ASP 25%	I 1.8267	1309.9	1599.6	1.6	164.1	108.4	34.6
ASP 35%	I 1.8122	1307.6	1599.6	1.8	163.0	108.4	38.3





Fig 4.4: Raman spectra of activated carbons with 0 to 35 weight percent iodine incorporation (A) High wave number window showing the D and G bands pertaining to carbons, (B) Low wave number window showing the polyiodides (I_3^- and I_5^-) peaks related to iodine, (C) XPS spectra showing iodine peaks (not molecular iodine).

Figure 4.4 (a) shows the D and G band of pristine as well as iodated carbons. From table 4.2, it is evident the D/G ratio of activated carbons remains almost constant independent of iodation process. The relatively high D/G ratio is indicative of a large number of six-membered carbon rings, which are poorly interconnected. In addition, a minor shift in the D and G bands towards higher wave number is noted upon iodation. Usually, this shift towards higher wave number indicates the localized clustering of graphene rings in the amorphous carbon matrix [5]. Although the XRD result shows the complete destruction of any long range ordering inside carbon, a more sensitive technique like Raman spectroscopy reveals the development of significant number of localized disconnected graphene nanoclusters, possibly of varying size. These may be inhibited from larger crystal formation due to the presence of different polyiodides (I_n ⁻). The relative intensity of these G bands remains almost constant for different degree of iodation.

The Raman spectra revealed the presence of peaks characteristic of polyiodide species in low wave number regions in figure 4.4 (b). This strongly suggests a degree of charge transfer from the carbon host. Iodine has a strong tendency to form different charge transfer complexes even with weak donor like the π -electron cloud of carbon [6]. These complexes often result in I₃⁻ and I₅⁻ compounds [7], giving rise to characteristic Raman vibration modes below 200 cm⁻¹. Figure 4.4 (b) shows the iodine related peaks in activated carbons. While the pristine ASP carbon shows no peak, pure iodine (I₂) gives a sharp peak around 180 cm⁻¹, in good agreement with the recognized value of 186cm⁻¹. All iodine containing samples contain no peak associated to free iodine but rather peaks associated to polyiodides. In all iodated carbons, a broad peak assigned to I₃⁻ appears at approximately 120 cm⁻¹. This is a resultant peak due to merging of three I₃⁻ peaks at 107, 112 and 145 cm⁻¹ [8]. This

peak suggests the presence of I_3^- as a component of charge transfer carbon-iodine complexes. In addition to the I_3^- peak, a relatively sharper peak around 165 cm⁻¹ is present in all cases. This peak is assigned to I_5^- complexes [9]. With increasing iodine in the cell charge, the peak intensity of I_3^- in the C-I complex remains same, the intensity of I_5^- peak increases with higher iodine content. This higher order I_5^- can be thought of as a summation of I_3^- and I_2 iodides. The relative amount of I_5^- over I_3^- can be estimated to be equal to the relative intensities of 165 over 120 cm⁻¹ peaks [10]. It is noted that with increase in iodine content from 15 to 35 %, the relative amount of I_5^- complex increases and the corresponding electrochemical capacity increases as will be shown later. Figure 4.5 depicts the almost linear relation between higher order polyiodides and electrochemical capacity. Higher order polyiodides (I_5^-) resembles close to molecular iodine and involves weaker bond than triiodides (I_3^-), which facilitates smoother electrochemical faradaic reaction giving higher capacity.



Fig 4.5: The direct relation between higher order polyiodide present in carbon and corresponding electrochemical capacity.

4.6.2 Thermal analysis (Differential scanning calorimetry):

In order to shed light on the bonding of iodine within the graphite structure, thermal analysis of various iodated, high-energy milled carbon samples was conducted. The resulting DSC curves are shown in figure 4.6. As per our previous report [3, 4], free iodine gives rise to a sharp endothermic peak (onset point = 114.4 °C) owing to the melting of iodine. The pristine activated carbon is almost featureless, showing a very shallow endothermic peak. However, the doping of iodine via vapor deposition route yield a uniform carbon-iodine compound, which does not show any endothermic peak in the range 100-120 °C confirming the absence of free iodine (I₂). All iodated carbons show sharp exothermic peaks around 300-450 °C. This suggests the formation of chemical bonding between carbon and iodine.

The thermal analysis data of all iodated carbons are shown in table 4.3. It is marked that the onset point of exothermic peak decreases with increasing amount of iodine present in carbons. In addition, the corresponding heat of reaction (Δ H) increases with higher iodine content. Upon incorporating higher amount of iodine into carbon structure, the bonding is weaker, consistent with the formation of a sequential longer chain of different polyiodides (I₃⁻ or I₅⁻) as confirmed by Raman spectroscopy. These higher order polyiodides resembles closely to molecular iodine (I₂). Thus, upon heating, these polyiodides decompose at lower temperature. For all milling time (from 0 to 60 minutes), the higher amount of iodine leads to larger heat of reaction. Further, it is marked that the heat of reaction and exothermic peak intensity decreases with carbon milled for longer milling time (table 4.3).

Figure 4.7 shows the TGA weight loss curves for iodated carbons. There is no severe weight loss around 100-120 °C, indicating the absence of any free iodine (I_2) [11].



Fig 4.6: The DSC curves of activated carbons with different amount of iodine uptake (15 to 35 weight %), heated from room temperature to 500 °C. The carbons were initially milled for (A) 20 min, (B) 40 min and (C) 60 min.
	Exothermic reaction involving carbon-iodine							
Materials	Onset	Peak	Heat of	Specific heat				
	point (°C)	maximum	reaction	capacity (c_p)				
		point (°C)	$(\Delta H) (J/g)$	(J/g-C)				
ASP 15% I								
ASP 25% I	365	370	159.30	5.32				
ASP 35% I	336	339	143.10	3.98				
ASP 45% I	306	313	299.30	11.84				
ASP 15% I BM 20	456	461	139.80	4.68				
ASP 25% I BM 20	418	425	204.78	7.05				
ASP 35% I BM 20	317	310	303.40	4.84				
ASP 45% I BM 20	284	291	345.40	7.86				
ASP 15% I BM 40	435	439	80.71	1.62				
ASP 25% I BM 40	411	415	128.80	3.21				
ASP 35% I BM 40	345	350	209.27	5.87				
ASP 45% I BM 40	204	213	320.50	3.45				
ASP 15% I BM 60	462	476	18.07	0.54				
ASP 25% I BM 60	396	399	121.10	2.55				
ASP 35% I BM 60	319	325	155.40	3.48				
ASP 45% I BM 60	386	391	153.00	4.02				

Table 4.3: The thermal analysis (DSC) data of iodated activated carbons.



Fig 4.7: Weight loss curves (TGA) of iodated activated carbons showing two distinct zones of weight loss.

However, with gradual heating, the weight decreases sharply in two distinct zones. The first zone appears around 200-250 °C (marked as P) and the second zone around 750-850 °C (marked as C). As will be discussed below, the reaction of the amorphous carbon with iodine results in the formation of polyiodide complexes. The loss in zone P can be ascribed to the destruction of these compounds. Indeed the loss realized is similar to the amount of iodine that was charged into the cell and measured in uptake relative to the pristine carbon. The reaction in zone C is most likely small amounts of simple carbon oxidation with residual surface groups.

4.7 Surface morphological modification post iodation process:

Activated carbons give very high non-faradaic capacitance owing to high mesoporous surface area. Figure 4.8 shows the large mesopores (>10 nm) in precursor carbon. The variation of surface area with high energy milling and various post milling iodization treatments are shown in figure 4.9 (a). Generally, the longer highenergy milling leads to smaller surface area of the ASP carbons. The continuous local fracture of carbon particles with (shock-type) high-energy milling results in the destruction of the carbon's mesoporosity and the possibility of the formation of very fine particles which are thermodynamically unstable due to very high surface energy. Subsequently, these particles may agglomerate together to form larger stable particles. The agglomerated particles give rise to a smaller effective surface area. Initial amounts of iodine reduce the surface area and does to a greater percentage as the surface area of the precursor carbon decreases. In most cases, further increasing the amount of iodine incorporated into structure decreases the surface area only slightly (Fig 4.9 a). This data suggests that after an initial surface reaction with minimal amount of iodine, the porosity does not fill with increasing amount of iodine. If indeed true, this would support a bulk reaction.



Figure 4.8: High resolution transmission electron microscopy images showing uniformly distributed large mesopores (size, d > 10 nm) in activated carbons. These images were taken at different defocus value of -250 nm and +250 nm.



Fig 4.9 (a): The histogram summarizing the BET surface area of mechanochemically modified activated carbons pre-milled from 0 to 60 minutes with iodine uptake ranging from 0 to 45 weight percent.



Fig 4.9 (b): The histogram showing only the micropore area (0~2 nm) as analyzed by BET investigation of pre-milled (0 to 60 minutes) activated carbons with iodine uptake ranging from 0 to 45 weight percent.

Apart from the surface area, the relative amount of microporosity (<2nm) vs. mesoporosity is a key factor for EDLC applications. Figure 4.9 (b) presents the variation of microporosity in iodated carbons. The non-iodated carbons possess very high microporosity irrespective of the milling time. Upon iodation, the microporosity decreases drastically by more than 150%. With longer milling time and higher iodine intake, the microporosity gradually decreases. The surface area decrease was observed, especially for the pre-milled sample is almost equal to the overall decrease in micropore area. This decrease in microporosity with iodine modification leads to a higher relative degree of mesoporosity in modified carbons. Iodine incorporation into the finer micropores in carbon structure may enhance a bulk-like reaction with carbon especially as the inter-micropore distance is expected to be low.

Figure 4.10 summarizes the average pore size of activated carbons with varying degree of iodation. Overall, all these carbons are mesoporous in nature (mesopores: 2-50 nm). High-energy milling decreases the inherently high pore size by destroying the initial interconnected particle morphology of the mesoporous ASP carbon precursor. In all cases, increasing amount of iodine induces an increase in the average pore size consistent with the destruction of micropores as discussed above. On the whole, the incorporation of iodine leads to a slight increase in average mesopores diameter with the decrease in initial surface area (trend from 20min to 60 min high-energy milling). Pore size can be calculated using t-plots, where the intersection point between two slopes indicates the average pore size. As shown in figure 4.11, for ASP carbons pre-milled for 20 minutes, the average pore size increases with increase in degree of iodation. Figure 4.12 summarizes pore size distribution of pristine and modified mesoporous carbons, which confirms gradual development of mesoporosity in iodine-modified carbons.



Fig 4.10: The graph showing the variation of average pore size of activated carbons as a result of pre-milling (0 to 60 minutes) and iodine incorporation (0 to 45 wt %).



Fig 4.11: Comparison of t-plots showing the development of larger pores with increase in iodine content in activated carbons. It hints at micropore filling by iodine. Points a, b, c, d are projection of intersection of slopes at point A, B, C and D respectively. These points denote average pore size.



Fig 4.12: Graphs showing the development of mesoporosity in iodated carbons upon increasing degree of iodine incorporation into ASP carbon pre-milled for (A) 20 minutes, (B) 40 minutes, and (C) 60 minutes.

4.8 Electrochemical study of carbon-iodine nanocomposites:

4.8.1 Galvanostatic analysis (Electrochemical capacity)

The iodine-incorporated activated carbons show non-linear discharge voltage profile (Figure 4.13 a) having three distinct regions (marked I, II, III) corresponding to three proposed electrochemical reactions. As proposed in our previous paper, region I involves the desorption of adsorbed BF_4^- ions (of electrolyte) from the mesoporous carbon. The change in slope at about 3.5 V is due to the "p" to "n" type transition (region II) (point of zero charge, PZC). After PZC, the adsorption of Li⁺ ions within the Helmholtz double layer occurs possibly combined with a small Faradaic reaction. Further, a large plateau is marked around 3.1 V, starting region III, which is likely due to the main cathodic reaction of the C-I_n⁻ compound. These underlying electrochemical mechanisms lead to modification in the electrochemical capacity of iodated carbons.





Fig 4.13: (A) A sample voltage discharge profile showing the deviation from linearity with three distinct zones marked as I, II, III related to non-Faradaic and Faradaic regions. This voltage profile corresponds to the ASP carbon pre-milled for 20 minutes followed by 15 wt% iodation. (B) The comparative voltage profiles of pristine and iodine-modified activated carbons.

A comparative voltage discharge profile of pristine and iodated carbon is shown in figure 4.13(b). The evolution of faradaic plateau at 3.1 V is seen upon iodation, which leads to higher capacity. The voltage deviation from the 2.7 V observed for the traditional $2\text{Li} + \text{I}_2 \rightarrow 2$ LiI reaction can be explained assuming a faradaic reaction of C-I_n⁻ with lithium as Li⁺ + C-I_n⁻ $\leftarrow \rightarrow$ C + LiI. In addition to the large 3.1 V plateau for region III, in region II and in parallel with an increase in the non-faradaic component, a small faradaic plateau appears around 3.4 V for carbons with higher iodine content (C-I_{0.032} to C-I_{0.077}).

The galvanostatic capacity of the iodated and non iodated carbons is shown in figure 4.14 for cells cycled between 2.8 to 4 V. In the present context, capacity is utilized instead of capacitance as most activated carbons have discharge curves that

are not completely linear. The voltage range can be thought of as the summation of two distinct ranges; a linear non-Faradaic region (4 to 3.1 V) and a non-linear Faradaic region (3.1 to 2.8 V). For pristine carbon materials, the capacity gradually decreases with longer milling time. This effect is exclusively due to corresponding decrease in mesoporous surface area with longer premilling duration. However, when these carbons are iodine modified, the capacity systematically increases for all milling time even with the relative decrease in carbon amount. The increase in overall capacity is a combination of increased capacity (and capacitance) in the non-faradaic and the development of a faradaic region. In the current work, during the iodine incorporation process, the loading and collection of carbon was performed inside a dry room to avoid any external contamination. In order to ensure oxygen did not play a role in the reaction, some iodation experiments were conducted with an environment of He gas, these resulted in similar electrochemical results.



Fig 4.14: Histogram showing the capacity values (mAh/g) of various pre-milled activated carbons, with iodation ranging from 0 to 45 weight percent. The capacity values were calculated from the second voltage discharge profile between 2.8 to 4 V.

The specific capacitance (Figure 4.15 a) values were obtained by dividing the non-faradaic capacitance (μ F/g) to respective BET surface area (m^2/g) of carbons. There is a large increase (100-450 %) in the normalized capacitance upon iodine doping. Upon iodine doping, the normalized capacitance increases from 10 μ F/cm² to 36 μ F/cm² (for 20 min milling) and to 57 μ F/cm² (for 40 and 60 min milling). Even though the surface area decreases with high-energy milling, the increase in normalized capacitance in iodated carbons indicates possible modification of intrinsic electronic properties (such as shift in PZC) of carbon owing to iodine doping. As opposed to the materials identified in our initial paper [3] which have a distinctly clear non faradaic region II, a few of the materials analyzed here may have a slight faradaic reaction in parallel with the non faradaic reaction in this region. Details regarding this contrast will be discussed in a future paper devoted to the faradaic reactions.

The volumetric capacity of pristine and iodated carbon was calculated by multiplying the density of carbon pellets (g/cc) pressed at 7000 psi and corresponding specific capacity (mAh/g) (between 4 to 2.8 V) (Figure 4.15 b). The incorporation of dense iodine and high-energy milling leads to higher density hence higher volumetric capacity. For the best material (ASP milled for 20 min followed by 35% iodine doping), the volumetric capacity improved from 13 mAh/cc to 57 mAh/cc (340% increase). From practical application point of view, a number of EDLC/ NAH applications are often limited by volume rather than by weight. Further, the higher volumetric energy density makes the electrodes thinner with less porous electrode diffusion required resulting in higher electrochemical performance.



Fig 4.15: The graphs showing the normalized electrochemical capacity values of iodated activated carbons. (A) Surface area normalized specific capacitance of iodated carbons (μ F/cm²) cycled between 3.2 to 4 V and (B) Volumetric capacity of iodated carbons (mAh/cc) cycled between 2.8 to 4 V.

As mentioned earlier, the introduction of iodine triggers significant modification of the voltage profile of carbons. The iodated carbons show a large plateau around 3.1 V, making the voltage profiles non-linear. This voltage is well above the traditional Li + I₂ reaction potential of 2.7 V and preliminary evidence points to a faradaic reduction reaction of lithium with a CI_x complex. The C-I reduction increases the capacity of the carbon materials significantly. As a result of the Raman characterization, we can consider this compound to be a carbon-polyiodide compound, C-I_n⁻. The Faradaic reaction can be associated with a reaction with lithium as follows (Eq 1):

$$nLi^{+} + ne^{-} + C - I_{n}^{-} \leftrightarrow C + nLiI \quad (1)$$

Preliminary experiments show that this reaction retains significant capacity well above a 25C rate.

4.8.2 Cyclic voltammetry and cycling stability:

To complement the galvanostatic study of these modified carbons, the potentiodynamic cycling was conducted on pristine and iodated carbons. Figure 4.16 shows a comparison between the potentiodynamic cycling curves of pristine and iodated ASP carbons. It shows a clear change in the specific current profiles of active carbon materials upon iodine doping. The undoped activated carbon gives a smooth curve indicating non-faradaic reaction throughout the voltage range of 2.8 to 4.2 V. Upon incorporation of iodine into carbon, a sharp peak around 3.1 V appears due to the inception of faradaic reaction, which was found to be very reversible with longer cycling suggesting a reversible reaction as proposed in equation 1. With higher iodine content (25 to 45 wt %), a small peak appears at 3.4 V in congruence with the voltage profile shown in figure 4.13 a. Additionally, the vapour iodated carbons were found to transmit higher specific current in agreement with their higher non-faradaic

capacitance over the pristine carbons. There is a shift in baseline current suggesting higher degrees of oxidation and reduction current at the voltage extremes of the current. These may be related to a degree of corrosion current, this is presently being investigated as a function of time and fabrication parameters.



Fig 4.16: The comparative potentiostatic cycling curves of pristine and iodated activated carbons cycled between 2.8 to 4.2 V.

The discharge volumetric capacity of some key iodated carbons is summarized as a function of cycle number in figure 4.17 a. These cells are cycled at 100 mA/g current between 2.8 to 4 V (including both non-faradaic and faradaic regions). The significant increase in capacity with iodine doping into the precursor carbon is clearly seen. When the precursor carbon is iodine treated without prior mechanical milling, though it shows initial high capacity, it decreases continually with cycling. Initially, ASP materials have a number of surface groups (oxides, nitrides, sulphates etc) as a result of the activation process. These oxygen-containing groups may be detrimental to the efficiency of the initial reaction and the long-term stability of the reaction. However, when the carbon is pre-milled before iodine vapour deposition, the milling process develops a large amount of fractured surfaces which react well with the iodine vapor and may act as sites which will allow polyiodide diffusion within the bulk of the samples. These types of iodated carbons not only show high capacity but also retain the high capacity even after long cycling. The capacity decreases in the early stage of cycling due to some possible leaching of iodine. After this, the capacity retention improves considerably. Even though these iodated carbons cycle through the faradaic plateau region involving various carbon polyiodide species, the cycling on this plateau is very reversible as evidenced by the flat cycling profile. This suggests the chemical stability of iodinated carbon during long run in spite of the proposed reversible conversion of carbon polyiodides to lithium iodide (Eq 2).

Figure 4.17 b shows the cycling stability of some iodated carbons in the voltage range 3.2 to 4 V, involving only the non-faradaic reaction. The incorporation of iodine steers higher volumetric capacity with respect to pristine carbons. As non-faradaic reaction does not involve any change in the chemistry of iodated carbons unlike the faradaic reaction process, these iodated samples retain their high capacity upon long cycling. From figure 4.17 (a and b), it is quite relevant that the faradaic process is less favorable to cycling stability. However, the degree of reversibility of the faradaic region is impressive compared with other types of faradaic reactions and offers hope to offer stable cycling for thousands of cycles. Further research on possible failure modes in these iodated activated carbons and improving their cycling stability will be presented later.



Fig 4.17: Cycle life of some key iodated carbon materials; cycled between (A) 2.8 to 4 V (non-faradaic and faradaic reaction) and (B) 3.2 to 4 V (only non-faradaic electrochemical reaction).

4.9 Summary and Conclusions:

The physical and electrochemical properties of vapor phase iodated carbons clearly link the mechanochemical modification of the mesoporous activated carbons (as discussed in chapter 3) to a chemical iodine interaction with the carbon to form polyiodides. Indeed, the localized impact energy and temperature rise may induce a localized sublimation of the I₂ mimicking the more macro chemical vapor iodations technique discussed in this chapter. The existence of a C-I_n⁻ compound cannot be specifically proved at this point, however, the (1) confirmed existence of polyiodide species I_n⁻ by Raman spectroscopy, (2) lack of I₂ and formation of a stronger bonded entity by DSC, (3) the high 3.1V reaction potential, (4) and a systematic shift in OCV suggests strongly the presence of a C-I_n⁻ complex.

In general, surface area decreased upon iodine incorporation. Almost all of the reduction in surface area occurred in the micropore area vs mesopores area, therefore suggesting the preferential segregation of the iodine within the micropores. Based on this finding, chapter 6 will specially focus on the fabrication of microporous activated carbons to study its iodation behaviour and resulting structural and electrochemical modification.

Activated carbons contain randomly-oriented graphitic zones surrounded by amorphous carbon matrix. So, a fine-scale iodation can involve localized chemical interaction between iodine and graphitic carbon. Secondly, previous literature reports about a small reversible faradaic reaction around 3.1 V observed in ionic graphite fluorides [12], which was related to a reversible reaction of Li + CF_x \rightarrow LiF + C. This reaction has never been proven. However, our current work raises the possibility that such a reaction may consist of a reaction of lithium with residual iodine (possibly polyiodide) as IF₅ is commonly utilized to form the highly ionic graphite fluoride. In chapter 5, we make an attempt to resolve these two issues by studying the effect of

chemical iodation on crystalline carbons namely graphite and fluorographites.

4.10 REFERENCES:

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5.1. Introduction:

In the previous chapters, the effect of chemical iodation on physical and electrochemical properties of activated carbons has been presented and is related to carbon-iodine interaction and polyiodide formation. All activated (amorphous) carbons can be thought of as a random mixture of localized graphitic domains of different dimensions, embedded inside amorphous matrix. Thus, at a microscopic level, the carbon-iodine interaction boils down to the reaction between iodine guest species with nanographite. To further our understanding of the halidated activated carbons, the current investigation focuses on pristine graphite system as a foundation. In this chapter, (structural) graphite has been taken as carbon precursor and is iodinemodified. The resultant physical, electronic and electrochemical properties have been examined in details. The morphological and electrochemical modification of graphite is investigated to gain some more insight on carbon-iodine nanocomposites system.

5.2. Production of graphite (or nano graphite)-iodine nanocomposites via Solid-state mechanical milling using graphitic carbon precursor:

In the current investigation, commercial graphite with trade name SFG (from Timcal Inc [1]) was used as carbon precursor. In addition, some fluorinated graphites ($CF_{0.8}$ and CF_1) were obtained (from Aldrich Inc, USA). The morphology and chemistry of SFG carbon was mechanochemically modified by combining the high-energy shock type milling and by iodine doping as described in chapter 2. The high-energy milling duration was varied from 0-4 hours, with iodine content ranging from 0 to 30 weight percentage of carbon. Details of all physical and electrochemical experiments are described in chapter 2.

5.3.1. X-Ray Diffraction analysis:

X-ray diffractograms of the graphites as a function of milling time (milling duration = $0 \sim 4$ h, iodine wt% = $0 \sim 20$) and corresponding X-ray data are presented in figure 5.1 and table 5.1, respectively. Figure 5.1(a) shows the X-ray diffractograms of precursor graphite milled from 0 to 4 hours. The broad peak around 18° is a system peak originating from the sample holder. The precursor graphite shows sharp crystalline peaks around 26° , 44° and 54° corresponding to (002), (101) and (004) planes respectively (Fig. 1a). The precursor graphite shows a mixed graphitic nature with multiple peaks around 44°, particularly located at 42.3°, 43.3°, 44.5° and 46° related to (100), (101), (101) and (012) planes respectively along with other Bragg reflections expected for P63/mmc [ICDD# 23-0064, 25-0284] and R3 [ICDD# 26-1079] space groups of graphite [2]. A dramatic and systematic decrease in graphitic ordering is revealed by the destruction and broadening of (002), (101) and (004) peaks. Specifically, the (00L) peaks corresponding to (002) and (004) planes almost disappear with longer milling. The FWHM values for (002) and (100) peaks were employed to calculate the longitudinal graphene crystallite size (L_a) and lateral graphitic crystallite thickness (L_c) of existing graphitic regions in all sample. The amorphous-like nature in the samples which were milled for longer periods makes these L_a and L_c parameters approximate. Due to the decrease in crystallite size, mechanical milling leads to coalescence of a number of the peaks around 44° and formation of a single broad peak with lower intensity. The longer milling reduces the L_a from 405 to 60 Å. The L_c value initially decreases from 421 to 70 Å (1 h milling) but later increases to 227 Å (4 h milling) consistent with earlier findings [3-5]. From table 1, the d spacing (for (002), (101) and (004) planes) initially increases (from 0 to



60 minute). This slight exfoliation may possibly be induced by mechanochemical oxidation.



Figure 5.1: X-ray diffraction showing (a) the effect of mechanical milling on pristine graphite, (b) the effect of mechanical milling on iodated (10 wt%) graphite, and (c) the effect of iodine content on milled graphite (milling time = 1 h). In all cases, the inset figures show the variation of less intense (101) and (004) peaks. The peak around 44° results due to the merger of four small peaks at 42.3°, 43.3°, 44.5° and 46° related to (100), (101), (101) and (012) planes. The 42.3° (100) and 44.5° (101) peaks have P63/mmc space groups; where as the 43.3° (101) and 46° (012) peaks belong to R3 space groups.

When iodine is introduced during mechanical milling, a similar crystallite size reduction/destruction as function of milling time is observed. Figure 5.1(b) shows the X-ray diffractograms of mechanically milled graphite with a fixed iodine content of 10 weight%. As with the precursor graphite, longer milling leads to the destruction of graphitic ordering. However, upon iodation the (002) peaks have smaller FWHM (more crystallinity) relative to the non-iodated graphite. While the longitudinal ordering is eventually destroyed upon milling, it still retains some lateral ordering as shown by sharp (101) peak in the inset diagram. The L_a value decreases gradually from 658 to 44 Å with mechanical milling.

Materials	peak position		d spacing (Å)			La	L _c	
	(002)	(100)	(004)	(002)	(100)	(004)	(Å)	(Å)
Pristine	26.48	44.46	54.58	3.36	2.04	1.70	405.0	421.4
MM 20	26.32	43.84	54.42	3.38	2.06	1.69	263.7	76.1
MM 40	26.15	43.15	54.23	3.40	2.10	1.69	125.7	78.0
MM 60	26.05	43.28	54.15	3.42	2.09	1.69	68.1	70.6
MM 120	26.10	44.42		3.41	2.04		54.0	123.2
MM 240	26.29	44.53		3.39	2.03		60.3	227.4
1% I								
MM 20	26.16	43.76	54.35	3.40	2.07	1.69	316.3	75.8
MM 40	26.17	43.50	54.16	3.40	2.08	1.69	148.2	79.3
MM 60	25.99	43.30	53.63	3.43	2.09	1.71	65.4	79.6
MM 120	25.39	44.52		3.51	2.03		39.7	129.8
MM 240	25.88	44.53		3.44	2.03		51.2	219.5
5% I								
MM 20	26.32	44.03	54.43	3.38	2.06	1.68	525.3	110.6
MM 40	26.26	43.46	54.40	3.39	2.08	1.69	242.7	85.9
MM 60	26.20	43.18	54.62	3.40	2.09	1.68	80.0	81.0
MM 120	26.03	44.64		3.42	2.03		34.0	92.9
MM 240	26.36	44.53		3.38	2.03		58.4	270.1
10% I								
MM 20	26.22	44.42	54.37	3.40	2.04	1.69	658.2	81.8
MM 40	26.36	44.20	54.40	3.38	2.05	1.69	346.3	77.4
MM 60	26.36	43.78	54.30	3.38	2.07	1.69	131.1	80.5
MM 120	25.31	44.38		3.52	2.04		43.2	85.8
MM 240	25.05	44.65		3.55	2.03		44.0	274.8
20% I								
MM 20	26.56	44.76	54.67	3.35	2.02	1.68	680.7	
MM 40	26.34	44.79	54.44	3.38	2.02	1.68	600.6	
MM 60	26.46	44.53	54.62	3.37	2.03	1.68	416.1	110.4
MM 120	26.34	44.17		3.38	2.05		117.8	96.4
MM 240	25.63	44.64		3.47	2.03		63.4	229.5

Table 5.1: The summary of X-ray diffraction of carbon materials.

In order to show the effect of iodine content on graphite crystallography, figure 1(c) shows the XRD graphs of graphites milled for fixed duration of 20 minutes with increasing amounts of iodine (0~20 weight%). It is evident, while increasing amount of iodine gradually destroy the (101) peak, it retains the (002) and (004) peaks representative of the basal planes. However, the lack of change in the lattice parameter and detectable shift in (002) peak position with iodine content suggests that the iodine or iodine species are not intercalating between the basal planes.

5.3.2 XRF analysis:

Shock-type mechanical milling can lead to the generation of considerable amount of very localized heat, which may result in the sublimation of iodine during processing. In light of this, x-ray fluorescence (XRF) spectroscopy was used as a qualitative technique to identify the iodine content in the final iodated graphites as a function of mechanical milling time and initial iodine feed. A powder mixture of modified graphitic carbons with a silicon internal standard was used in 1:1 weight ratio. The XRF analysis data of carbon samples are summarized in table 5.2. The XRF data confirms the presence of iodine in all iodine-doped, high-energy milled graphite products. Further, the ratio of intensities of the K- α peaks of iodine (at 3.938 keV) and silicon (at 1.739 keV) verifies the increasing amount of iodine content in the iodinated carbons with higher initial iodine feed. The iodine content remains fairly unaffected by longer milling time. High-energy milling using steel media may lead to some external metallic contamination. The XRF confirms the presence of a small amount of iron (Fe) metallic contamination in the iodated graphites, which increases with longer milling time.

Materials)			
Milling time (min)	1%	5%	10%	20%	
MM 0	0.31	0.41	0.47	0.63	
MM 20	0.30	0.77	1.23	1.79	
MM 40	0.39	0.86	1.59	3.23	
MM 60	0.35	0.84	1.47	2.39	
MM 120	0.42	0.91	1.25	2.19	
MM 240	0.37	0.96	1.80	3.43	

Table 5.2: The X-ray fluorescence data (I/Si ratio) of iodated graphitic carbons.

5.3.3 Raman spectroscopy:

Carbonaceous materials usually consist of planar sp² graphitic structure and tetrahedral sp³ diamond structure with a little amount of linear sp¹ structure. Singlecrystalline graphite possesses D_{6h} symmetry having $2E_{2g}$, $2B_{2g}$, E_{1u} , A_{2u} vibrational modes [6]. Thus, the Raman spectra of carbon materials show two distinct peaks; the A_{1g} symmetry D peak (~1300 cm⁻¹) and the E_{2g} symmetry G peak (~1580 cm⁻¹) [7]. For disordered graphitic materials, a first order D' peak (~1620 cm⁻¹) and a G' peak (~2660 cm⁻¹) can arise [8, 9]. Raman spectra results of the milled and iodine doped samples are shown in figure 5.2 and table 5.3. Three specific regions are shown in each case related to (i) polyiodides peaks (low wave number window, 0-300 cm⁻¹), (ii) carbon D and G peaks (medium wave number window, 800-1800 cm⁻¹) and (iii) higher order G' peak (high wave number window, 2400-2800 cm⁻¹).

The Raman peaks related to iodine are shown in the low wave number regions featured in Fig 5.2a and b. Figure 5.2(a) shows that pristine and pre-milled graphite show no Raman activity in this range. However, when different amount of iodine is incorporated (Figure 5.2b), activity develops but none can be attributed to that of molecular I_2 around 181 cm⁻¹, proving the absence of free iodine. Instead, there arise two peaks around 120 and 160 cm⁻¹, which are assigned to polyiodides. The first broad peak, assigned to I_3^- is a convolution of three individual I_3^- peaks at 107, 112

and 145 cm⁻¹ [10]. Additionally, a very sharp peak around 160 cm⁻¹ arises in iodated graphites, which is assigned to I_5^- complexes [11]. The higher order I_5^- peak can be thought of as a summation of I_3^- and I_2 peaks. These polyiodide peaks become stronger, when iodine content is more than 5 weight %. The increase in iodine content in C-I compound makes the C- I_5^- more intense than C- I_3^- peaks. The area under I_5^- and I_3^- can be used to determine the relative amount of I_5^- over I_3^- [12]. From table 5.3, it is observed the increase in iodine content leads to higher degree of I_5^- compounds.

In the medium wave number region, in figure 5.2(c) and (d), the Raman peaks related to carbon structure are shown. In Fig 5.2(b), the effect of mechanical milling on pristine carbon is illustrated. The pristine carbon shows sharp D and G peaks, with a D' shoulder peak appearing around 1620 cm⁻¹. Over longer milling, the continuous destruction of graphene structure results in the gradual decrease of G band, consistent with the XRD results. The D' shoulder peak arises due to the defect structure in graphite, which later merges with the G band. However, while the XRD result shows the complete destruction of any crystalline ordering inside carbon, the Raman spectroscopy reveals the G band, stating the possibility of localized disconnected graphene nanoclusters of varying size inside the overall amorphous carbon.

When iodine is incorporated into pristine graphite, the Raman spectra show a slight increase in the G peak intensity relative to the D for samples milled for 1h (figure 5.2d). The overall amorphous nature (broad D peak) is retained with different degree of iodation. With a higher degree of iodation both a decrease in FWHM and a slight red shift of the G-band occurs from 1586 cm⁻¹ (5% I) to 1578 cm⁻¹ (20 %I) (table 5.3) . The combination of the two is usually attributed to an increase in local crystallinity. The red shift can also be attributed to a small degree of charge transfer [13].



Fig 5.2: The Raman spectra of pristine graphite modified by mechanochemical iodation. Low wave number window showing (a) the absence of polyiodide bands in mechanically milled pristine and (b) development of polyiodide bands in iodine-doped graphite. Medium wave number window showing the variation of D and G bands in (c) pristine graphites and (d) iodine-doped graphites. High wave number window showing the evolution and variation of G' band in (e) pristine graphite and (f) iodated. graphites. For iodine-incorporation in graphite (b,d,f), the mechanical milling duration was fixed at 1h.

Low shift window			indow	Medium shift window High shift window					
Materials	I ₅ /I ₃ ratio	I ₅ peak (cm ⁻¹)	I ₃ peak (cm ⁻¹)	I _D /I _G ratio	D peak (cm ⁻¹)	G peak (cm ⁻¹)	G' peak (cm ⁻¹)	La (Å)	
Pristine				1.184	1307.85	1581.50	2644.37	96.61	
MM20				1.100	1309.06	1577.55	2639.62	105.82	
MM60				2.245	1305.11	1581.50		58.76	
MM120				2.447	1309.06	1583.94		61.13	
MM60 5%I	0.25	115.96	155.87	1.869	1312.64	1586.39	2615.48	60.14	
MM60 10%	I 1.20	116.87	156.44	1.673	1312.64	1581.01	2619.48	67.02	
MM60 20%	I 1.50	117.33	161.88	0.735	1315.03	1578.02	2645.13	160.32	

Table 5.3: The Raman spectroscopy data of iodated graphites

In the high wave number region, in Fig 5.2(e) and 5.2(f), the Raman peaks related to G' carbon peaks are shown. For the pristine graphite, the G' peak red shift as a function of milling time suggests a gradual increase disorder. This is consistent with the D:G discussion and the XRD diffraction. As a function of iodine content the G' band blue shifts, this is consistent with an increase in graphite character as was demonstrated by the modulated of the G band.

5.4 Thermal analysis:

Thermal analysis of all modified graphites was conducted to qualitatively decipher the local mixing nature between carbon and iodine. The differential scanning calorimetry results of some iodated graphites are shown in figure 5.3. The molecular iodine (I₂) sublimates early upon heating, thus showing a sharp endothermic peak (onset point = $114.4 \,^{\circ}$ C). The immediate exothermic peak (marked by an asterisk) is a system peak due to possible reaction of vapor iodine with the aluminum sample pan. The pristine as well as pre-milled graphites are entirely featureless, showing a very shallow endothermic peak. When different amounts of iodine are being introduced to the graphites through high-energy milling, the DSC spectra shows no peak in 100-120

°C temperature range, but rather exotherms developing in the temperature range of 300-450 °C. This indicates the absence of any free molecular iodine (I₂) inside graphite, agreeing with the aforementioned Raman characterization. The higher evolution temperatures are consistent with the polyiodides forming a charge transfer complex with the carbon (C-I₃⁻, C-I₅⁻, C-I₇⁻ etc). The exothermic peaks tend to shift to lower onset temperature with gradual increase in iodine content. As reported in our previous study [14], the higher amount of iodine induces the formation of higher order polyiodides i.e. longer iodide chain structure making the C-I bonding weaker (i.e. decomposition at lower temperature).



Fig 5.3: The DSC curves of graphites with different amount of iodine uptake (0 to 10 weight %), heated from room temperature to 500 °C at a heating rate of 10 °C/min. The graphites are mechanically milled for 20 min.

Figure 5.4 presents the comparative TGA curves for graphites (milled for 1 h) with varying amount of iodine. The weight loss systematically increases and evolution occurs at lower temperatures as the addition of iodine increases. Most importantly, the loss relative to the 0% iodine sample is consistent with the quantity of iodine added.



Figure 5.4: The thermo gravimetric analysis (TGA) curves of graphites premilled for 60 minutes with different amount of iodine content (from $0 \sim 20$ weight %).

The graphitic carbon-iodine forms an interesting system for fundamental study. The anisotropic graphene (host) sheets can form two kinds of host-guest reaction with iodine (guest). Iodine can be incorporated into graphite by two ways. First, although never proven experimentally, iodine can intercalate between graphene planes forming weak Vander wall bonds via charge transfer reaction (ionic bonding). In this case, iodine serves as π -electron acceptor with carbon as electron donor species. Alternately, iodine may form strong covalent bonds with the C atoms at the edges of broken graphitic basal planes. While the first reaction can be thought of as iodine intercalated into graphite basal planes, the later is a chemically adsorbed C-I bonds. It has been shown that macro graphite particles do not readily react with iodine but nanographite has a preferential reaction with iodine at the edges [15]. The increase in exposed graphene basal planes favors iodine-intercalation process, whereas the availability of broken carbon edges prefers covalent C-I bonding. Figure 5.5 presents a schematic diagram showing these two kinds of carbon-iodine interaction. As

discussed later, the high-energy milling develops morphology by breaking and later agglomerating nanographene platelets. This in turn favors different degree of C-I bonding.



Figure 5.5: Schematic diagram showing the formation of iodine-intercalation and covalent C-I bonding in mechanically milled graphite matrix. The longer milling duration of mechanical milling forms more fractured surfaces, which increases the possibility of covalent C-I bonding.

5.5 Surface area and morphological analysis (BET):

Solid-state iodation via shock-type mechanical milling sharply disrupts the carbon morphology [14, 16, 17]. The effect of mechanical milling and iodine doping on overall BET surface area is shown in figure 5.6. It shows an inverse 'V' type variation. Upon milling the pristine graphites, the strong covalent planar sp² (C-C) bonds and the weak Vander Waal interplanar bonds are disrupted in a three-stage mechanism (namely division, fracture and agglomeration stages) [3-5] resulting in a final crumpled card-house type arrangement. A schematic diagram showing these three stages of mechanical milling of graphitic carbon is shown in figure 5.7. When the mechanical milling continues with iodine-incorporated graphite, polyiodide species develop and seem to preferentially react inside available porosity among individual graphene units. Thus, the incorporation of higher amount of iodine further

decreases the surface area of modified graphite (figure 5.6). For prolonged milling, the individual nano-graphene units are so random and closely-packed that it entraps many inaccessible pores for gas analysis. With iodation, these pores are filled by



Figure 5.6: The histogram showing the BET surface area of pristine as well as modified graphites as a function of the mechanical milling time and the amount of iodine incorporated into the system.



Figure 5.7: A schematic diagram showing the three stages of morphology modification of pristine [3-5] and iodated graphites during the mechanical milling process (I) division stage, (II) fracturing stage and (III) agglomeration stage.

iodine that reaches a steady state after a certain milling time. To illustrate the effect of mechanical milling and chemical iodation comparative adsorption isotherms are shown in figure 5.8. The mesoporous nature of modified graphites are reflected in IUPAC type-IV isotherms with distinct hysteresis in the relative pressure range 0.5~1. The degree of hysteresis decreases with longer milling time and higher iodine content. The variation of microporosity as determined by BET analysis is shown in figure 5.9, which follows the same trend as that of BET surface area, which has also been observed for various activated carbons (Chapters 3 and 4).

For energy storage applications, along with the effective surface area of carbon electrodes, the pore structure plays a very key role in the interfacial electrodeelectrolyte interaction. The iodine doping via milling changes the internal pore structure as shown in figure 5.10. Here, the pore volume distribution has been presented for two distinct pore sizes; the small mesopores $(2 \sim 10 \text{ nm})$ and large mesopores (10 \sim 50 nm). Due to instrumental limitation, the micropore (0 \sim 2 nm) volume could not be determined. Never the less, the smaller mesopore zone, which acts as the tail of micropore zone, can give useful information about existing micropore volume. The pristine graphite gives a broad peak in small mesopore range (Fig 5.10). When increasing amount of iodine is introduced into graphite, the pore volume related to small mesoporosity (2~4 nm) sharply decreases. Iodine seems to preferentially occupies smaller mesopores/ micropores present in graphite. Thus, iodated graphites have open large mesopores, which increases the average pore size from 4 nm to 7 nm. This preferential trapping of guest iodine species into smaller pores has also been observed in variety of activated mesoporous carbons [14, 16]. The percentage contribution to overall pore volume from pores of different size range in mechanochemically modified graphitic carbons is listed in table 5.4.



Figure 5.8: Comparative BET Nitrogen adsorption isotherms showing (a) the effect of milling duration and (b) the effect of degree of iodation on pristine graphite. The hysteresis at high pressure range shows the IUPAC-type IV mesoporous nature in all mechanically milled graphites.



Figure 5.9: The histogram showing the variation of micropore area (as determined by BET analysis) in the modified graphites as a function of their milling duration and iodine content.



Figure 5.10: The graph showing the preferential filling of smaller mesopores ($2\sim5$ nm) by iodine. The increasing amount of iodine content (from 0 to 20 weight %) inside graphite (pre-milled for 1 h) leads to the destruction of any existing small mesopores.

Sample	Micropore 0-3 nm	Percentage Por Small mesopor 3-10 nm	osity Contributio e Large mesopo 10-50 nm	on re Macropore 50-300 nm
Pristine Graphite	3	6	35	54
MM 20 0% I	18	34	34	12
MM 20 5% I	17	33	37	12
MM 20 10% I	11	26	42	19
MM 20 20% I	10	22	42	25
MM 40 0% I	18	22	22	15
MM 40 5% I	10	32	33	13
MM 40 10% I	19	33	33	13
MM 40 20% I	10	25	41	21
MM 60 0% I	20	33	30	15
MM 60 5% I	18	30	34	16
MM 60 10% I	19	32	28	20
MM 60 20% I	12	28	40	18
MM 120 0% I	17	26	33	23
MM 120 5% I	15	24	32	27
MM 120 10% I	17	26	32	24
MM 120 20% I	20	32	30	17
MM 240 0% I	9	19	37	33
MM 240 5% I	9	18	36	36
MM 240 10% I	11	21	36	30
MM 240 20% I	10	22	42	25

Table 5.4: The percentage porosity distribution in modified graphites

5.6 Resistivity of modified graphitic carbons:

Mechanochemical iodine-modification results in significant change in the electrical resistivity of pristine graphite. In the current investigation, graphites have been modified by two ways (a) changing morphology by mechanical milling and (b) modifying the materials chemistry via iodation. The effect of both modifications on electrical resistivity of pristine graphite is shown in figure 5.11. As discussed in previous section, high-energy milling gradually increases the BET surface area of graphite (from 0-60 min) by separating graphitic platelets and forming a planar, interconnected structure. The higher degree of exposed graphite basal planes leads to
decrease in electrical resistivity from 0-60 minutes. However, after 60 minutes, the high-energy milling gradually destroys the planar, interconnected morphology of graphites, hence the resistivity increases.

The incorporation of guest atoms (e.g. iodine) into graphite has been reported to significantly change the electrical resistivity (or conductivity) [15, 18]. The guest species like iodine may be intercalated in between graphene planes forming ionic bonds (charge transfer type reaction), which can suppress the electrical resistivity of graphite by adding electrons to the conduction band and holes to the valence band. Another possibility is that iodine may form covalent bonds with broken edge of graphites [15]. The covalent bonding suppresses the carrier concentration and disrupts the planar structure of pristine graphite by displacing some C atoms, which in turn increases resistivity. Depending on the nature of graphite-iodine interaction (ionic charge transfer intercalation or covalent C-I bonding), the electrical resistivity may decrease or increase. As these two mechanisms (charge transfer and covalency) are opposite in nature, the net electrical resistivity of iodated graphite is determined by the relative degree of ionic/ covalent bond formation.



Figure 5.11: The variation of electrical resistivity of mechanochemically modified graphitic carbons showing the effect of mechanical milling duration and degree of iodine-incorporation on pristine graphite.

Figure 5.11 presents the variation in overall electrical resistivity in milling and iodine-modified graphites. At a microscopic scale, iodine involves very weak host-guest reactivity leading to weak charge-transfer reaction. This can slightly reduce the resistivity. However, on a macroscale, the net electrical resistivity can be controlled by various parameters like conductivity of polyiodide chains, percolation network in carbon and graphitic particulate orientation. The iodine-induced development in electrical properties (e.g. metal-insulator transition) can be conducted using He cryostat measurements [19, 20], which is beyond our scope of project.

5.7 Electrochemical characterization:

5.7.1 Galvanostatic:

A graph comparing the discharge voltage profiles of precursor graphite with different milling time is shown in figure 5.12 As mechanical milling significantly modifies the surface area, which dictates the degree of non-faradaic interfacial double layer formation, the slope of the discharge curve changes sharply in comparison to that of pristine carbon. Indeed, the normalized capacitance (F/m^2) is similar for all materials. When iodine is introduced, a slight voltage modulation is induced at 3.1V (Fig. 5.13). The voltage profiles can be divided into two distinct regions, namely the linear non-Faradaic region (from 4 to 3.15 V) and the non-linear Faradaic region (3.15 to 2.8 V). It is observed that iodation induces (i) a slight decrease in slope in the non-faradaic region and (ii) the evolution of a small faradaic plateau around 3.15 V in the faradaic region. While the non-Faradaic zone is associated with the interfacial desorption of BF₄⁻ ions (from the electrolyte) from the existing mesopores in carbon, the Faradaic zone may involve the simultaneous interfacial adsorption of Li⁺ ions and the formation of Li-I or I_n compounds (conversion reaction) around 3.1 V.



Fig 5.12: The galvanostatic voltage discharge profiles (cycled between 2.8 to 4 V) showing the effect of milling duration on pristine graphites.



Figure 5.13: The graph showing the comparative galvanostatic voltage discharge profiles of graphites pre-milled for 1 h with different amount of iodine content. Two distinct zones (non-Faradaic and Faradaic) are shown in the figure.

As shown by Raman study (section 5.3.3), higher amount of iodation favors higher order polyiodides (I_5^-). Consequently, the higher order polyiodides leads to prolonged faradaic conversion reaction. It is similar to the significant increase of the faradaic plateau observed in amorphous activated carbons containing polyiodides [14, 15].

The effect of mechanical milling and iodine doping on the electrochemical capacity of graphitic carbon is shown in figure 5.14. In case of pristine graphite materials, the mechanical milling triggers an initial increase in capacity following by a gradual decrease. This effect can be solely correlated to the corresponding surface area variation as described in section 5.3.5. The surface area of pristine graphite improves from 139 m²/g (milling time = 20 min) to 312 m²/g (milling time = 60 min). This increase in BET surface area favors more effective ionic double layer formation and improves the capacity. But, with milling longer than 60 minutes, the surface area decreases from 312 m²/g to 112 m²/g (milling time = 240 min). Consequently, the electrochemical capacity decreases with lesser degree of double layer formation. This surface area effect is quite common in case of electrochemical double layer capacitors. However, when increasing amount of iodine is introduced to the graphitic system, although the capacity shows a similar decrease as a function of surface area, the corresponding electrochemical capacity is higher all milling duration. The capacity increases systematically as a function of iodine content (figure 5.14). This unique combination of lower surface area proving higher electrochemical capacity has been shown for various polyiodide-activated carbons by our group [14-16]. The volumetric density of the modified graphites was measured by pressing iodated graphite pellets at 7000 psi. When the capacity is normalized with respect to the volumetric density, the resultant volumetric capacity shows as high as 200% increase upon iodation (Figure 5.15) although the absolute capacity is relatively small.



Figure 5.14: The electrochemical capacity (mAh/g) of all graphitic carbons modified by mechanical milling (0-2 h) and iodine doping (0-20 weight%). The capacity values were calculated with the cells cycling between 2.8 to 4 V.



Figure 5.15: Volumetric capacity of modified graphites (mAh/cc) cycled between 2.8 to 4 V.

5.7.2 Potentiodynamic:

Following the galvanostatic study, the potentiodynamic cycling was conducted on pristine and some key iodated graphites as shown in figure 5.16. In case of pristine graphite (milled and non-milled), it shows a smooth curve in congruence with the linear non-Faradaic type double layer reaction throughout the voltage range tested (4~2.8 V). However, when iodine is introduced into the system, the cyclic voltammograms show a small peak around 3.15 V. This peak can be related to the transition between non-Faradaic to faradaic zones in the galvanostatic voltage discharge profiles. This 3.15 V peak is in agreement with the evolution of Faradaic plateau in galvanostatic cycling. Additionally, the increase in iodine content in modified graphites lead to slightly higher specific current carrying ability in the electrodes.



Figure 5.16: Cyclic voltammograms showing the evolution of Faradaic peaks upon with iodation of graphite carbons cycled between 2.5 to 4.2 V.

5.7.3 Iodation study of fluorographites:

Owing to its electronegativity, iodine has been reported to bring about chargetransfer (CT) reaction, thus oxidizing the carbon entity [21, 22]. This CT reaction is proposed to be a key factor in increasing the electrochemical performance of iodated carbons [18]. For further investigation, we examined the iodation process on two preoxidized graphitic materials (fluorographites CF_x , x= 0.8, 1). The potentiodynamic voltage profile (cycled between 2.5~4 V, scan rate = 5 mV/s) of an iodated CF_x is compared with pristine CF_x in figure 5.17. Surprisingly, the 3.1 V peak related to the presence of polyiodides appears even for these pre-oxidised carbons. It indicates the possibility of polyiodide formation at unreacted edge carbon atoms in fluorographites [15]. These iodated fluorographites were galvanostatically cycled between 2.8 to 4 V (current rate = 15 mA/g). The resulting change in capacity is presented in figure 5.18 for different milling duration. Even with polyiodide formation (at 3.1 V), iodations hardly improves the electrochemical capacity. This lack of capacity improvement is attributed to the higher polarization in iodated CF_x , even though iodation increases the specific current values over entire voltage range (Figure 5.17).

On another note, the small 3.1 V peak in iodated CF_x (Figure 5.17) is proposed to be due to the reaction between Li and carbon-polyiodide complex, as observed in activated carbons [14, 16]. Coincidentally, a similar 3.1 V peak has been observed earlier in CF_x compounds [21, 22], which was synthesized by the chemical reaction between carbon and iodofluoride:

$$C + IF_x \longrightarrow CF_x + CI_y$$
 (residue).

Though never proved, this 3.1 V peak was associated with the reaction between CF_x and Li to form LiF, which generally occur at 2.7 V.

$$CF_x + x Li \longrightarrow C + x LiF$$
 (occurs at 2.7 V)

On the basis of our work, it is proposed:

$$CI_x + x Li \longrightarrow C + x LiI$$
 (occurs at 3.1 V).

Thus, we believe the 3.1 V peak in the earlier work [21, 22] was due to the reaction between Li and residual iodine/ CI_x and not due to LiF formation.



Figure 5.17: Cyclic voltammograms of iodated $CF_{0.8}$ compounds revealing a small reaction peak around 3.1 V related to LiI formation.



Figure 5.18: The electrochemical capacity of (pre-oxidized) fluorinated graphite upon iodation (a) $CF_{0.8}$ compound and (b) CF_1 compound.

5.7.4 Cycle life study:

Following, the cycling stability of some iodated graphites, cycled at 15 mA/g in the voltage range of 4~2.8 V (combining both non-faradaic and faradaic segments, are shown in figure 5.19. The gradual improvement in volumetric capacity with iodation is observed. These iodated graphites retain the high capacity over long cycling, though some capacity fading occurs at early stage of cycling. This is proposed to occur by possible leaching of iodine. The flat cycling in long run proves the chemical stability of polyiodide species inside graphite, which retains the faradaic reaction.



Figure 5.19: Cycling life for iodated graphites with different degree of iodation.

5.8 Summary and Conclusions:

Graphitic carbons were chemically modified by means of iodine-incorporation via high-energy milling. A suite of physical, morphological and electrochemical properties of iodated graphites was studied in details. The mechanical milling destroys the pristine graphene morphology making it amorphous. When iodine is incorporated, polyiodide species (C- I_n) are formed through an interaction with the carbon surface. The iodation leads to change in electrochemical properties, namely a well defined non Faradaic reaction at 3.15V. Although of little practical impact, the physico-chemical and electrochemical analysis of iodated graphite was useful in establishing theories to support the more practically important iodated activated carbons.

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VI: MICROPOROUS CARBON BASED CARBON-IODINE NANOCOMPOSITES: THE ROLE OF MICROPORES AND IODINE ON ELECTROCHEMICAL PROPERTIES OF ACTIVATED CARBONS

6.1. Introduction:

The electrochemical capacity of activated carbon improves with higher surface area, as it favors more effective interfacial double layer development. Never the less, the underlying pore structure (microporosity/ mesoporosity) plays a significant role in case of high voltage supercapacitors that employs non-aqueous organic electrolytes [1,2]. In contrast to aqueous electrolytes, organic electrolytes have relatively large solvated salt ions. Although micropores (0~2 nm) delivers higher specific surface area, they are quite inaccessible and offer restricted diffusion towards the solvated ions. On the contrary, the larger mesopores (2~50 nm) easily accommodate organic solvated ions, promote faster ionic movement and deliver high power density. Very recently, Simon et al have claimed anomalous increase in capacity in microporous carbons possibly due to partial desolvation of organic electrolytes and forced electroadsorption [3,4]. Even then, mesoporous carbons still dominate the commercial arena of non-aqueous high-power supercapacitor. Therefore, we have focused our research to various mesoporous carbons (Chapters 3-5) for chemical iodation and resulting electrochemical development.

Interestingly, we observed iodine is preferentially captured by inherent micropores in all kinds of carbon without exception (Chapter 3-5) [5-7]. Taking advantage of this phenomenon, the current chapter extends the chemical iodation process to microporous carbon precursor. Microporous carbon (here onwards referred as MPC) can accommodate higher amount of iodine, which can improve the 3.1 V faradaic pseudocapacitance reaction and overall energy-density. To examine the role of internal pore on chemical iodation process and final electrochemical properties,

highly microporous carbon of varied morphology has been fabricated (by chemical activation process) and utilized to produce microporous carbon-polyiodide nanocomposites. The physical and electrochemical properties of these electrodes have been examined and compared to corresponding mesoporous carbons.

6.2. Fabrication of microporous carbon by chemical activation route and carbon-iodine nanocomposites via solid-state mechanical milling:

Microporous carbon was fabricated using chemical activation method [8]. We used anthracite coal as carbon precursor and KOH as activating agent. The detail of chemical activation process is explained in chapter 2. Various activation process parameters were optimized to produce MPC with controlled morphology. Later, these carbons were mechanochemically modified through high-energy shock type milling as described in chapter 2. The degree of iodation was varied from 0 to 60 weight percentage of pristine MPC carbon. Later, different standard laboratory techniques were employed (as described in chapter 2) to investigate the physicochemical and electrochemical development in these microporous carbon-iodine nanocomposites.

6.3 Optimization of microporous carbon production:

Chemical activation process, as described in chapter 2, is widely used to manufacture microporous carbons. It involves many parameters controlling the final morphology of product carbon. Further, different carbon precursors have marked effect on final carbon morphology. Here, we present the effect of some major processing parameters on the morphological development of final carbons. Further, the development of mesoporosity and carbon yield has been studied to optimize the activation processing conditions for the whole study. Some morphological properties of microporous carbons are listed in table 6.1 as was achieved for different processing conditions.

Sample density * % yield * BET area * Micropore area * % Micro porosity * % Meso porosity * pore size porosity * Effect of activating agent (KOH) Effect of activating agent (KOH) Effect of activating agent (KOH) 191.4 91.1 8.9 1.852 C-KOH 1:2 1.143 88.4 507.4 425.3 84.0 16.0 1.943 C-KOH 1:3 1.115 63.0 703.1 586.0 83.3 16.7 1.943 C-KOH 1:5 0.950 48.2 1235.0 977.8 79.2 20.8 1.956 Effect of carbonization temp (°C) 250 °C 1.407 83.4 254.0 190.2 74.9 25.1 2.102 400 °C 1.305 72.0 564.0 466.3 82.7 17.3 1.944 50 °C 1.316 63.4 703.1 586.0 83.3 16.7 1.943 700 °C 0.870 56.8 1259.0 1029.5 81.8 18.2 1.927 80 °C 0.806	Summary of microporous carbon fabrication process parameters.								
(g/cc)area‡area‡MicroMesosizeporosity‡porosity‡(nm)#Effect of activating agent (KOH)C-KOH 1:11.23889.3210.0191.491.18.91.852C-KOH 1:21.14388.4507.4425.384.016.01.945C-KOH 1:31.11563.0703.1586.083.316.71.943C-KOH 1:41.11453.9869.8708.881.518.51.951C-KOH 1:50.95048.21235.0977.879.220.81.956Effect of carbonization temp (°C)250 °C1.40783.4254.0190.274.925.12.102400 °C1.30572.0564.0466.382.717.31.94450 °C1.31663.4703.1586.083.316.71.943700 °C0.87056.81259.01029.581.818.21.927850 °C0.86137.01656.51156.870.030.01.973Effect of carbonization time (h)0.25 h1.48788.0318.0256.080.519.51.9960.50 h1.07278.0469.0378.083.416.61.9432.00 h0.98061.0750.0593.079.021.01.9503.00 h0.9	Sample	density *	% yield†	BET	Micropore	e %	%	pore	
Effect of activating agent (KOH) C-KOH 1:1 1.238 89.3 210.0 191.4 91.1 8.9 1.852 C-KOH 1:2 1.143 88.4 507.4 425.3 84.0 16.0 1.945 C-KOH 1:3 1.115 63.0 703.1 586.0 83.3 16.7 1.943 C-KOH 1:4 1.114 53.9 869.8 708.8 81.5 18.5 1.951 C-KOH 1:5 0.950 48.2 1235.0 977.8 79.2 20.8 1.956 Effect of carbonization temp (°C) 250 °C 1.407 83.4 254.0 190.2 74.9 25.1 2.102 400 °C 1.305 72.0 564.0 466.3 82.7 17.3 1.944 50 °C 0.870 56.8 1259.0 102.5 81.8 18.2 1.927 850 °C 0.861 37.0 1656.5 1156.8 70.0 30.0 1.973 Effect of carbonization time (h) 0 25.0 <td></td> <td>(g/cc)</td> <td></td> <td>area‡</td> <td>area‡</td> <td>Micro</td> <td>Meso</td> <td>size</td>		(g/cc)		area‡	area‡	Micro	Meso	size	
Effect of activating agent (KOH)C-KOH 1:11.23889.3210.0191.491.18.91.852C-KOH 1:21.14388.4507.4425.384.016.01.943C-KOH 1:31.11563.0703.1586.083.316.71.943C-KOH 1:41.11453.9869.8708.881.518.51.951C-KOH 1:50.95048.21235.0977.879.220.81.956Effect of carbonization temp (°C)250 °C1.40783.4254.0190.274.925.12.102400 °C1.30572.0564.0466.382.717.31.94450 °C1.31663.4703.1586.083.316.71.943700 °C0.87056.81259.01029.581.818.21.927850 °C0.86137.01656.51156.870.030.01.973Effect of carbonization time (h)0.25 h1.48788.0318.0256.080.519.51.9960.50 h1.07278.0469.0378.080.619.41.9701.00 h1.11063.0703.1586.083.416.61.9432.00 h0.98061.0750.0593.079.021.01.9503.00 h0.94043.9885.0733.983.017.01.948Effect of heating rate (°C/						porosity‡	porosity‡	(nm)#	
C-KOH 1:1 1.238 89.3 210.0 191.4 91.1 8.9 1.852 C-KOH 1:2 1.143 88.4 507.4 425.3 84.0 16.0 1.945 C-KOH 1:3 1.115 63.0 703.1 586.0 83.3 16.7 1.943 C-KOH 1:4 1.114 53.9 869.8 708.8 81.5 18.5 1.951 C-KOH 1:5 0.950 48.2 1235.0 977.8 79.2 20.8 1.956 <i>Effect of carbonization temp (°C)</i> 250 °C 1.407 83.4 254.0 190.2 74.9 25.1 2.102 400 °C 1.305 72.0 564.0 466.3 82.7 17.3 1.944 550 °C 1.316 63.4 703.1 586.0 83.3 16.7 1.943 700 °C 0.870 56.8 1259.0 1029.5 81.8 18.2 1.927 850 °C 0.861 37.0 1656.5 1156.8 70.0 30.0 1.973 <i>Effect of carbonization time (h)</i> 0.25 h 1.487 88.0 318.0 256.0 80.5 19.5 1.996 0.50 h 1.072 78.0 469.0 378.0 80.6 19.4 1.970 1.00 h 1.110 63.0 703.1 586.0 83.4 16.6 1.943 2.00 h 0.980 61.0 750.0 593.0 79.0 21.0 1.950 3.00 h 0.940 43.9 885.0 733.9 83.0 17.0 1.948 <i>Effect of heating rate (°C/min)</i> 5 °C/min 1.510 48.8 750.0 633.2 84.4 15.6 1.931 10 °C/min 1.290 63.0 708.0 599.0 84.6 15.4 1.926 20 °C/min 1.150 51.8 688.0 577.0 83.9 16.1 1.944 <i>Effect of nitrogen flow rate</i> 1X 1.030 38.0 590.0 490.5 83.1 16.9 1.949 2X 1.010 59.4 642.5 540.4 84.1 15.9 1.943 3X 1.050 72.3 703.1 586.0 83.3 16.7 1.943	Effect of act	ivating agent	(KOH)						
C-KOH 1:1 1.238 89.3 210.0 191.4 91.1 8.9 1.852 C-KOH 1:2 1.143 88.4 507.4 425.3 84.0 16.0 1.945 C-KOH 1:3 1.115 63.0 703.1 586.0 83.3 16.7 1.943 C-KOH 1:4 1.114 53.9 869.8 708.8 81.5 18.5 1.956 <i>Effect of carbonization temp (°C)</i> 20.8 1.956 72.0 564.0 466.3 82.7 17.3 1.944 550 °C 1.305 72.0 564.0 466.3 82.7 17.3 1.944 50 °C 1.316 63.4 703.1 586.0 83.3 16.7 1.943 700 °C 0.870 56.8 1259.0 1029.5 81.8 18.2 1.927 850 °C 0.861 37.0 1656.5 1156.8 70.0 30.0 1.973 <i>Effect of carbonization time (h)</i> 0.25 h 1.487 88.0 318.0 256.0 80.5 19.5 1.996 0.50 h 1.072 78.0 <td></td> <td></td> <td></td> <td></td> <td></td> <td></td> <td></td> <td></td>									
C-KOH 1:2 1.143 88.4 507.4 425.3 84.0 16.0 1.945 C-KOH 1:3 1.115 63.0 703.1 586.0 83.3 16.7 1.943 C-KOH 1:4 1.114 53.9 869.8 708.8 81.5 18.5 1.951 C-KOH 1:5 0.950 48.2 1235.0 977.8 79.2 20.8 1.956 Effect of carbonization temp (°C) 250 °C 1.407 83.4 254.0 190.2 74.9 25.1 2.102 400 °C 1.305 72.0 564.0 466.3 82.7 17.3 1.944 550 °C 1.316 63.4 703.1 586.0 83.3 16.7 1.943 700 °C 0.870 56.8 1259.0 1029.5 81.8 18.2 1.927 850 °C 0.861 37.0 1656.5 1156.8 70.0 30.0 1.973 Effect of carbonization time (h) 0.25 h 1.487 88.0 318.0 256.0 80.5 19.5 1.996 0.50 h 1.072 78.0 469.0 378.0 80.6 19.4 1.970 1.00 h 1.110 63.0 703.1 586.0 83.4 16.6 1.943 2.00 h 0.980 61.0 750.0 593.0 79.0 21.0 1.950 3.00 h 0.940 43.9 885.0 733.9 83.0 17.0 1.948 Effect of heating rate (°C/min) 5 °C/min 1.510 48.8 750.0 633.2 84.4 15.6 1.931 10 °C/min 1.290 63.0 708.0 599.0 84.6 15.4 1.926 20 °C/min 1.150 51.8 688.0 577.0 83.9 16.1 1.944 Effect of nitrogen flow rate 1X 1.030 38.0 590.0 490.5 83.1 16.9 1.949 2X 1.010 59.4 642.5 540.4 84.1 15.9 1.943 3X 1.050 72.3 703.1 586.0 83.3 16.7 1.943	C-KOH 1:1	1.238	89.3	210.0	191.4	91.1	8.9	1.852	
C-KOH 1:3 1.115 63.0 703.1 586.0 83.3 16.7 1.943 C-KOH 1:4 1.114 53.9 869.8 708.8 81.5 18.5 1.951 C-KOH 1:5 0.950 48.2 1235.0 977.8 79.2 20.8 1.956 Effect of carbonization temp (°C) 250 °C 1.407 83.4 254.0 190.2 74.9 25.1 2.102 400 °C 1.305 72.0 564.0 466.3 82.7 17.3 1.944 550 °C 1.316 63.4 703.1 586.0 83.3 16.7 1.943 700 °C 0.870 56.8 1259.0 1029.5 81.8 18.2 1.927 850 °C 0.861 37.0 1656.5 1156.8 70.0 30.0 1.973 Effect of carbonization time (h) 0.25 h 1.487 88.0 318.0 256.0 80.5 19.5 1.996 0.50 h 1.072 78.0 469.0 378.0 80.6 19.4 1.970 1.00 h 1.110 63.0 703.1 586.0 83.4 16.6 1.943 2.00 h 0.980 61.0 750.0 593.0 79.0 21.0 1.950 3.00 h 0.940 43.9 885.0 733.9 83.0 17.0 1.948 Effect of heating rate (°C/min) 5 °C/min 1.510 48.8 750.0 633.2 84.4 15.6 1.931 10 °C/min 1.290 63.0 708.0 599.0 84.6 15.4 1.926 20 °C/min 1.150 51.8 688.0 577.0 83.9 16.1 1.944 Effect of nitrogen flow rate 1X 1.030 38.0 590.0 490.5 83.1 16.9 1.949 2X 1.010 59.4 642.5 540.4 84.1 15.9 1.943 3X 1.050 72.3 703.1 586.0 83.3 16.7 1.943	C-KOH 1:2	1.143	88.4	507.4	425.3	84.0	16.0	1.945	
C-KOH 1:41.11453.9869.8708.881.518.51.951C-KOH 1:50.95048.21235.0977.879.220.81.956Effect of carbonization temp (°C)250 °C1.40783.4254.0190.274.925.12.102400 °C1.30572.0564.0466.382.717.31.944550 °C1.31663.4703.1586.083.316.71.943700 °C0.87056.81259.01029.581.818.21.927850 °C0.86137.01656.51156.870.030.01.973Effect of carbonization time (h)0.25 h1.48788.0318.0256.080.519.51.9960.50 h1.07278.0469.0378.080.619.41.9701.00 h1.11063.0703.1586.083.416.61.9432.00 h0.98061.0750.0593.079.021.01.9503.00 h0.94043.9885.0733.983.017.01.948Effect of heating rate (°C/min)1.5051.8688.0577.083.916.11.944Effect of nitrogen flow rate11.03038.0590.0490.583.116.91.9492X1.01059.4642.5540.484.115.91.9433X1.05072.3703.1586.083.316.7<	C-KOH 1:3	1.115	63.0	703.1	586.0	83.3	16.7	1.943	
C-KOH 1:5 0.950 48.2 1235.0 977.8 79.2 20.8 1.956 Effect of carbonization temp (°C) $250 \ ^{\circ}C$ 1.407 83.4 254.0 190.2 74.9 25.1 2.102 $400 \ ^{\circ}C$ 1.305 72.0 564.0 466.3 82.7 17.3 1.944 $550 \ ^{\circ}C$ 1.316 63.4 703.1 586.0 83.3 16.7 1.943 $50 \ ^{\circ}C$ 0.870 56.8 1259.0 1029.5 81.8 18.2 1.927 $850 \ ^{\circ}C$ 0.861 37.0 1656.5 1156.8 70.0 30.0 1.973 Effect of carbonization time (h) $0.255 \ h$ 1.487 88.0 318.0 256.0 80.5 19.5 1.996 $0.50 \ h$ 1.072 78.0 469.0 378.0 80.6 19.4 1.970 $1.00 \ h$ 1.110 63.0 703.1 586.0 83.4 16.6 1.943 $2.00 \ h$ 0.940 43.9 885.0 733.9 83.0 17.0 1.948 Effect of heating rate (°C/min) $5 \ ^{\circ}C/min$ 1.510 48.8 750.0 633.2 84.4 15.6 1.931 $10 \ ^{\circ}C/min$ 1.290 63.0 708.0 599.0 84.6 15.4 1.926 $20 \ ^{\circ}C/min$ 1.150 51.8 688.0 577.0 83.1 16.9 1.949 $2X$ 1.010 59.4 642.5 5	C-KOH 1:4	1.114	53.9	869.8	708.8	81.5	18.5	1.951	
Effect of carbonization temp (°C) $250 ^{\circ}C$ 1.40783.4254.0190.274.925.12.102 $400 ^{\circ}C$ 1.30572.0564.0466.382.717.31.944 $550 ^{\circ}C$ 1.31663.4703.1586.083.316.71.943 $700 ^{\circ}C$ 0.87056.81259.01029.581.818.21.927 $850 ^{\circ}C$ 0.86137.01656.51156.870.030.01.973Effect of carbonization time (h) $0.25 ^{h}$ 1.48788.0318.0256.080.519.51.996 $0.50 ^{h}$ 1.07278.0469.0378.080.619.41.970 $1.00 ^{h}$ 1.11063.0703.1586.083.416.61.943 $2.00 ^{h}$ 0.98061.0750.0593.079.021.01.950 $3.00 ^{h}$ 0.94043.9885.0733.983.017.01.948Effect of heating rate (°C/min)S °C/min1.51048.8750.0633.284.415.61.931 $10 ^{\circ}C/min$ 1.29063.0708.0599.084.615.41.926 $20 ^{\circ}C/min$ 1.15051.8688.0577.083.916.11.944Effect of nitrogen flow rate1X1.03038.0590.0490.583.116.91.9492X1.01059	C-KOH 1:5	0.950	48.2	1235.0	977.8	79.2	20.8	1.956	
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	Effect of car	bonization ter	mp (°C)						
$200 \ ^{\circ}C$ 1.305 72.0 564.0 466.3 82.7 17.3 1.944 $550 \ ^{\circ}C$ 1.316 63.4 703.1 586.0 83.3 16.7 1.943 $700 \ ^{\circ}C$ 0.870 56.8 1259.0 1029.5 81.8 18.2 1.927 $850 \ ^{\circ}C$ 0.861 37.0 1656.5 1156.8 70.0 30.0 1.973 Effect of carbonization time (h) $0.25 \ h$ 1.487 88.0 318.0 256.0 80.5 19.5 1.996 $0.50 \ h$ 1.072 78.0 469.0 378.0 80.6 19.4 1.970 $1.00 \ h$ 1.110 63.0 703.1 586.0 83.4 16.6 1.943 $2.00 \ h$ 0.980 61.0 750.0 593.0 79.0 21.0 1.950 $3.00 \ h$ 0.940 43.9 885.0 733.9 83.0 17.0 1.948 Effect of heating rate ($^{\circ}C/min$) $5 \ ^{\circ}C/min$ 1.510 48.8 750.0 633.2 84.4 15.6 1.931 $10\ ^{\circ}C/min$ 1.290 63.0 708.0 599.0 84.6 15.4 1.926 $20\ ^{\circ}C/min$ 1.150 51.8 688.0 577.0 83.9 16.1 1.944 Effect of nitrogen flow rate1X 1.030 38.0 590.0 490.5 83.1 16.9 1.949 2X 1.010 59.4 642.5 540.4	250 °C	1 407	83.4	254.0	190.2	74 9	25.1	2 102	
550 °C1.31663.4703.1586.083.316.71.943700 °C0.87056.81259.01029.581.818.21.927850 °C0.86137.01656.51156.870.030.01.973Effect of carbonization time (h)0.25 h1.48788.0318.0256.080.519.51.9960.50 h1.07278.0469.0378.080.619.41.9701.00 h1.11063.0703.1586.083.416.61.9432.00 h0.98061.0750.0593.079.021.01.9503.00 h0.94043.9885.0733.983.017.01.948Effect of heating rate (°C/min)5 °C/min1.51048.8750.0633.284.415.61.93110 °C/min1.29063.0708.0599.084.615.41.92620 °C/min1.15051.8688.0577.083.916.11.944Effect of nitrogen flow rate1X1.03038.0590.0490.583.116.91.9492X1.01059.4642.5540.484.115.91.9433X1.05072.3703.1586.083.316.71.943	400 °C	1.305	72.0	564.0	466.3	82.7	17.3	1.944	
$700 \ ^{\circ}C$ 0.870 56.8 1259.0 1029.5 81.8 18.2 1.927 $850 \ ^{\circ}C$ 0.861 37.0 1656.5 1156.8 70.0 30.0 1.973 <i>Effect of carbonization time (h)</i> $0.25 \ h$ 1.487 88.0 318.0 256.0 80.5 19.5 1.996 $0.50 \ h$ 1.072 78.0 469.0 378.0 80.6 19.4 1.970 $1.00 \ h$ 1.110 63.0 703.1 586.0 83.4 16.6 1.943 $2.00 \ h$ 0.980 61.0 750.0 593.0 79.0 21.0 1.950 $3.00 \ h$ 0.940 43.9 885.0 733.9 83.0 17.0 1.948 <i>Effect of heating rate (°C/min)</i> $5 \ ^{\circ}C/min$ 1.510 48.8 750.0 633.2 84.4 15.6 1.931 $10 \ ^{\circ}C/min$ 1.290 63.0 708.0 599.0 84.6 15.4 1.926 $20 \ ^{\circ}C/min$ 1.150 51.8 688.0 577.0 83.9 16.1 1.944 <i>Effect of nitrogen flow rate</i> 10.30 38.0 590.0 490.5 83.1 16.9 1.943 $3X$ 1.050 72.3 703.1 586.0 83.3 16.7 1.943	550 °C	1.316	63.4	703.1	586.0	83.3	16.7	1.943	
850 °C 0.861 37.0 1656.5 1156.8 70.0 30.0 1.973 Effect of carbonization time (h) 0.25 h 1.487 88.0 318.0 256.0 80.5 19.5 1.996 0.50 h 1.072 78.0 469.0 378.0 80.6 19.4 1.970 1.00 h 1.110 63.0 703.1 586.0 83.4 16.6 1.943 2.00 h 0.980 61.0 750.0 593.0 79.0 21.0 1.950 3.00 h 0.940 43.9 885.0 733.9 83.0 17.0 1.948 Effect of heating rate (°C/min) 5 °C/min 1.510 48.8 750.0 633.2 84.4 15.6 1.931 10 °C/min 1.290 63.0 708.0 599.0 84.6 15.4 1.926 20 °C/min 1.150 51.8 688.0 577.0 83.9 16.1 1.944 Effect of nitrogen flow rate 1 1.030 38.0 590.0 490.5 83.1 16.9 1.949 <t< td=""><td>700 °C</td><td>0.870</td><td>56.8</td><td>1259.0</td><td>1029.5</td><td>81.8</td><td>18.2</td><td>1.927</td></t<>	700 °C	0.870	56.8	1259.0	1029.5	81.8	18.2	1.927	
Effect of carbonization time (h) $0.25 h$ 1.487 88.0 318.0 256.0 80.5 19.5 1.996 $0.50 h$ 1.072 78.0 469.0 378.0 80.6 19.4 1.970 $1.00 h$ 1.110 63.0 703.1 586.0 83.4 16.6 1.943 $2.00 h$ 0.980 61.0 750.0 593.0 79.0 21.0 1.950 $3.00 h$ 0.940 43.9 885.0 733.9 83.0 17.0 1.948 Effect of heating rate (°C/min) $5 \ ^{\circ}C/min$ 1.510 48.8 750.0 633.2 84.4 15.6 1.931 $10 \ ^{\circ}C/min$ 1.290 63.0 708.0 599.0 84.6 15.4 1.926 $20 \ ^{\circ}C/min$ 1.150 51.8 688.0 577.0 83.9 16.1 1.944 Effect of nitrogen flow rate1X 1.030 38.0 590.0 490.5 83.1 16.9 1.949 $2X$ 1.010 59.4 642.5 540.4 84.1 15.9 1.943 $3X$ 1.050 72.3 703.1 586.0 83.3 16.7 1.943	850 °C	0.861	37.0	1656.5	1156.8	70.0	30.0	1.973	
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	<u>Effect of car</u>	bonization tin	<u>ne (h)</u>						
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	0.25 h	1.487	88.0	318.0	256.0	80.5	19.5	1.996	
$1.00 h$ 1.110 63.0 703.1 586.0 83.4 16.6 1.943 $2.00 h$ 0.980 61.0 750.0 593.0 79.0 21.0 1.950 $3.00 h$ 0.940 43.9 885.0 733.9 83.0 17.0 1.948 Effect of heating rate (°C/min) $5 \ ^{\circ}C/min$ 1.510 48.8 750.0 633.2 84.4 15.6 1.931 $10 \ ^{\circ}C/min$ 1.290 63.0 708.0 599.0 84.6 15.4 1.926 $20 \ ^{\circ}C/min$ 1.150 51.8 688.0 577.0 83.9 16.1 1.944 Effect of nitrogen flow rate $1X$ 1.030 38.0 590.0 490.5 83.1 16.9 1.949 $2X$ 1.010 59.4 642.5 540.4 84.1 15.9 1.943 $3X$ 1.050 72.3 703.1 586.0 83.3 16.7 1.943	0.50 h	1.072	78.0	469.0	378.0	80.6	19.4	1.970	
2.00 h0.98061.0750.0593.079.021.01.9503.00 h0.94043.9885.0733.983.017.01.948Effect of heating rate (°C/min)5 °C/min1.51048.8750.0633.284.415.61.93110 °C/min1.29063.0708.0599.084.615.41.92620 °C/min1.15051.8688.0577.083.916.11.944Effect of nitrogen flow rate1X1.03038.0590.0490.583.116.91.9492X1.01059.4642.5540.484.115.91.9433X1.05072.3703.1586.083.316.71.943	1.00 h	1.110	63.0	703.1	586.0	83.4	16.6	1.943	
3.00 h 0.940 43.9 885.0 733.9 83.0 17.0 1.948 Effect of heating rate (°C/min) 5 °C/min 1.510 48.8 750.0 633.2 84.4 15.6 1.931 10 °C/min 1.290 63.0 708.0 599.0 84.6 15.4 1.926 20 °C/min 1.150 51.8 688.0 577.0 83.9 16.1 1.944 Effect of nitrogen flow rate 1010 59.4 642.5 540.4 84.1 15.9 1.949 3X 1.050 72.3 703.1 586.0 83.3 16.7 1.943	2.00 h	0.980	61.0	750.0	593.0	79.0	21.0	1.950	
Effect of heating rate (°C/min) $5 \ ^{\circ}C/min$ 1.510 48.8 750.0 633.2 84.4 15.6 1.931 $10 \ ^{\circ}C/min$ 1.290 63.0 708.0 599.0 84.6 15.4 1.926 $20 \ ^{\circ}C/min$ 1.150 51.8 688.0 577.0 83.9 16.1 1.944 Effect of nitrogen flow rate $1X$ 1.030 38.0 590.0 490.5 83.1 16.9 1.949 $2X$ 1.010 59.4 642.5 540.4 84.1 15.9 1.943 $3X$ 1.050 72.3 703.1 586.0 83.3 16.7 1.943	3.00 h	0.940	43.9	885.0	733.9	83.0	17.0	1.948	
5 °C/min 1.510 48.8 750.0 633.2 84.4 15.6 1.931 10 °C/min 1.290 63.0 708.0 599.0 84.6 15.4 1.926 20 °C/min 1.150 51.8 688.0 577.0 83.9 16.1 1.944 Effect of nitrogen flow rate 1 1.030 38.0 590.0 490.5 83.1 16.9 1.949 2X 1.010 59.4 642.5 540.4 84.1 15.9 1.943 3X 1.050 72.3 703.1 586.0 83.3 16.7 1.943	Effect of heating rate (°C/min)								
10 °C/min 1.290 63.0 708.0 599.0 84.6 15.4 1.926 20 °C/min 1.150 51.8 688.0 577.0 83.9 16.1 1.944 Effect of nitrogen flow rate 1 1.030 38.0 590.0 490.5 83.1 16.9 1.949 2X 1.010 59.4 642.5 540.4 84.1 15.9 1.943 3X 1.050 72.3 703.1 586.0 83.3 16.7 1.943	5 °C/min	1.510	48.8	750.0	633.2	84.4	15.6	1.931	
20 °C/min 1.150 51.8 688.0 577.0 83.9 16.1 1.944 Effect of nitrogen flow rate 1 1.030 38.0 590.0 490.5 83.1 16.9 1.949 2X 1.010 59.4 642.5 540.4 84.1 15.9 1.943 3X 1.050 72.3 703.1 586.0 83.3 16.7 1.943	10 °C/min	1.290	63.0	708.0	599.0	84.6	15.4	1.926	
Effect of nitrogen flow rate1X1.03038.0590.0490.583.116.91.9492X1.01059.4642.5540.484.115.91.9433X1.05072.3703.1586.083.316.71.943	20 °C/min	1.150	51.8	688.0	577.0	83.9	16.1	1.944	
1X1.03038.0590.0490.583.116.91.9492X1.01059.4642.5540.484.115.91.9433X1.05072.3703.1586.083.316.71.943	Effect of nitrogen flow rate								
111.05050.050.0150.065.110.71.9492X1.01059.4642.5540.484.115.91.9433X1.05072.3703.1586.083.316.71.943	1X	1 030	38.0	590.0	490 5	83.1	169	1 949	
3X 1.050 72.3 703.1 586.0 83.3 16.7 1.943	2X	1 010	59.4	642.5	540.4	84 1	15.9	1 943	
	3X	1.050	72.3	703.1	586.0	83.3	16.7	1.943	

Table 6.1: Summary of microporous carbon fabrication process parameters.

* density of microporous carbon samples was calculated by pressing ~ 0.1 g of sample at 7000 psi to form pellets in a swagelok set-up.

⁺ % yield of product carbon was calculated by taking the ratio of amount microporous carbon obtained and the amount of anthracite coal initially used.

[‡] These parameters were calculated in a BET surface area measurement unit by taking approximately 0.1 g of sample for each experiment. The % mesoporosity is reported as the subtraction of micropore area from total BET area.

Adsorption pore diameter calculated by BET analysis using formulae: d = 4V(volume)/A(area).

6.3.1 Effect of chemical activating agent:

The activating agent plays a key role in chemical activation process [9]. The effect of activating agent (KOH) was studied varying the coal/ KOH ratio from 1:1 to 1:5. Upon carbonization (at 550 °C for 1h in steady N₂ flow), microporous carbons with different morphology and surface area ranging from 210~1240 m²/g were developed as shown by their adsorption isotherms (Fig 6.1). The overall surface area and micropore area increases gradually with higher amount of activating agent (from 1:1 to 1:5 KOH ratio). The KOH salt plays significant role in chemical activation, controlling both micropore surface area and micropore size distribution. Generally, the activation process comprises of two distinct phenomena: micropore formation followed by pore widening. When KOH is added to coal, it acts as a dehydrating agent at a lower temperature and uniformly impregnates the carbon structure. The subsequent removal of KOH upon carbonization (with heating) leads to the formation of porosity [10-13]. The small size of ionic salt leads to formation of microporosity. At high temperature, KOH-coal system evolves CO/CO₂ and ionic K⁺. During the chemical activation, several possible chemical reactions can occur as proposed below:

6KOH + C	← →	$2K + 3H_2 + 2K_2C$	2O ₃ (1)
$K_2CO_3 + C$	\longleftrightarrow	$K_2O + 2CO$	(2)
K_2CO_3	$ \longleftrightarrow $	$K_2O + CO_2$	(3)
$2K + CO_2$	\longleftrightarrow	$K_2O + CO$	(4)
$K_2O + C$	\longleftrightarrow	2K + CO	(5)
K(aq) + HCl(aq)	←→	$KCl + H_2O$ (neutralization step)

However, during carbonization, potassium ions (K^+) impregnates into carbon matrix at high temperature [13]. It leads to the widening of the spaces between carbon atomic layers and increases the pore volume. Additionally, a group of nearly-located pores may coalesce to trigger pore-widening that generates mesopores [10,11,13]. Thus, higher amount of KOH develops increasing amount of mesoporosity. In addition, higher KOH content leads to more aggressive chemical activation and severe burn-off of precursor carbon. Hence, even through the overall surface area increases, the final carbon yield continually decreases. Figure 6.1(b) shows the inverse relation between BET surface area and percentage carbon yield. From this study, we optimised the coal and KOH ratio at 1:3, which gives high surface area with minimum mesoporosity and maximum product yield (>60%).



Figure 6.1: (a) Comparative adsorption isotherms showing the development of high surface area microporous carbons with gradual increase in coal:KOH ratio from 1:1 to 1:5. (b) The inverse trend between BET surface area and percentage carbon yield with an optimum value at 1:3.

6.3.2 Effect of carbonization treatment:

The optimization of the carbonization treatment was attained through a study of the temperature (*Tc*) and carbonization duration (*tc*). Figure 6.2(a) presents the comparative adsorption isotherms of microporous carbon, processed at temperature ranging from 250 to 850 °C (Coal:KOH = 1:3, 1h carbonization in steady N₂ flow). With higher carbonization temperature, a more intimate carbonization process gradually develops the BET area from 250 to 1650 m²/g. Figure 6.2(b) shows the opposite trend in BET area and final carbon yield. An optimum processing occurs for the carbonization temperature of 550 °C.



Figure 6.2: (a) Comparative adsorption isotherms showing the development of high surface area microporous carbons with higher carbonization temperature (from 250 °C to 850 °C). (b) The inverse trend between BET surface area and percentage carbon yield with an optimum value for carbonization temperature of 550 °C.

Apart from carbonization temperature, longer carbonization duration greatly favors effective carbonization and resulting morphological development. Figure 6.3(a) shows the gradual increase in BET surface area with longer carbonization time (at 550 °C, Coal:KOH = 1:3 in steady N₂ flow). Increase in the carbonization time improves the BET area from 320~890 m²/g. The corresponding yield is given in figure 6.3(b), which shows the optimum product is obtained for carbonization duration of 1h.



Figure 6.3: (a) Comparative adsorption isotherms showing the development of high surface area microporous carbons with longer carbonization duration (from 0.25 h to 3 h). (b) The inverse trend between BET surface area and percentage carbon yield with an optimum value for carbonization duration of 1h.

6.3.3 Effect of rate of reaction gas removal:

Later, the effect of heating rate was studied (Fig 6.4.a), which shows an increase in BET area (from 690 to 750 m²/g) in MPC carbon with slower heating rate (at 550 °C, Coal: KOH = 1:3, duration =1h in steady N₂ flow). Slower heating rate shows similar effect as that of longer carbonization duration at elevated temperature.



Figure 6.4: (a) Comparative adsorption isotherms showing the development of high surface area microporous carbons with slower heating rate (from 20 °C/m to 5°C/m). (b) Comparative adsorption isotherms showing the development of high surface area microporous carbons with faster nitrogen purging.

The last parameter investigated was the effect of nitrogen flow rate during carbonization. Figure 6.4b shows the adsorption isotherms of carbons activated with different nitrogen flow rate (at 550 °C, Coal: KOH = 1:3, duration = 1h). A steady increase in surface area (from 590 to 700 m²/g) with higher N₂ flow rate is observed. For continuous activation reaction, it is crucial to remove the gaseous reaction products [12]. Faster removal of these gases ensures the exposure of fresh surfaces for further activation reaction and favors progressive micropores formation. As discussed in section 6.3.1, carbonization process forms K⁺ ions at high temperature and subsequently initiates various possible chemical reactions and gaseous products. The quicker removal of these gaseous products from reaction chamber (using N₂ flow)

displaces the equilibrium of the chemical reaction (section 6.3.1) in forward direction to facilitate continuous activation reaction between coal and KOH.

In general, chemical activation always retains microporosity that grows proportionally to the BET surface area (Figure 6.5a). The inherent micropores in these carbons account for most of the BET area (in excess of 80% microporosity, table 6.1). Hence, the average pore size of these carbons is found to be below 2 nm, confirming the formation of IUPAC type-I microporous carbon (Figure 6.5b).



Figure 6.5: (a) The graph showing direct relation between micropore area and overall BET area in microporous carbons fabricated at different operating conditions. Micropores majorly contribute to BET surface area. (b) The average pore size in chemically activated microporous carbons is around 1.9 nm that falls in the micropore regime.

6.4 Nature of iodation in microporous carbon:

When iodine is mechanochemically introduced into the microporous carbon (25 wt% I, milling time = 20 min), it results in significant reduction in the BET surface area (from 741 m²/g to 7.2 m²/g) as indicated by the drop in the type-I N₂ adsorption isotherm (Fig 6.6). Though the type-I nature is retained with iodation, all the micropores are completely filled leaving the mesopores unoccupied. The mesoporosity in carbon increases from 13% to 79% upon iodation. Thus, the average pore size increases from 1.9 nm to 5.2 nm in carbon-iodine nanocomposites. Figure

6.6 shows the comparative adsorption isotherms of pristine and iodated activated carbon for mesoporous (type-IV) and microporous (type-I) carbons with similar BET surface areas of 750 m²/g. Iodation notably modifies adsorption isotherms of carbons reducing its BET surface area. Specially, the surface area of microporous carbon drops by two orders of magnitude (from 750 to 7 m²/g) but the inherent mesopore surface area only changes from 90 to 6 m²/g. It indicates that iodine segregates into existing micropores of carbon.



Figure 6.6: The comparative N_2 adsorption isotherms illustrating the pore filling owing to chemical iodation in mesoporous and microporous carbons with same initial BET surface area (~750 m²/g). A drastic drop in adsorption isotherms is seen upon iodation, the effect being more pronounced in case of microporous carbon.

6.5 X-Ray diffraction and elemental analysis:

The X-ray diffractograms of some representative pristine microporous carbon is shown in figure 6.7(a). Besides the presence of some residual KCl the microporous carbon consists mostly of randomly oriented carbons, with little degree of graphitization. With increase in surface area, carbon tends to develop a peak around 44° (related to [100] plane) and a small degree of development around the (002) area at 26° suggesting lateral graphitic growth inside amorphous carbon matrix. At low angles, microporous carbons show a broad peak around 7°, which comes from carbon micropores. These peaks corresponds to the d spacing of 12~15 Å, confirming microporosity. The appearance of small-angle X-ray peaks around 7° implies a structural regularity with a vague periodicity of about 1.4 nm [13]. With the surface area increasing from 750 to 1150 m²/g, the degree of microporosity increases as revealed by increasing intensity of the 7° peak (Figure 6.7 a).

High-energy milling the neat carbon (BET area 750 m2/g) leads to the development of broad peaks around 26° and 44°, corresponding to (002) and (100) graphitic planes (figure 6.7b). High-energy milling develops localized graphitic ordering in carbon. This ordering phenomenon has earlier been observed in mesoporous carbons in a more pronounced manner [14-16]. However, when iodine is introduced into carbon structure, the resulting carbon-iodine chemical interaction destroys (002) and (100) peaks. The complete destruction of (002) and (100) graphitic peaks rules out any possibility of iodine intercalation inside graphitic layers. Iodine-induced order-disorder transition has been reported earlier for varieties of carbon [14-16]. Throughout the mechanochemical modification, the small angle X-ray peaks ~7° remains intact and gets more pronounced with iodation process.

Following, X-ray fluorescence (XRF) spectroscopy was employed to conduct the elemental analysis so as to identify iodine content and any impurity elements in the iodine–doped microporous carbons. Table 6.2 shows the XRF analysis data of modified carbons for three different precursor microporous materials. Iodine, being highly volatile, may escape the carbon structure by the localised heating during highenergy milling or during storage of sample. XRF analysis confirms the presence of iodine in all iodated carbon samples. XRF further confirm the presence of K (K- α =3.325 KeV) and Cl (K- α = 2.608 KeV), supporting the X-ray diffraction peaks of



Figure 6.7: Structural analysis of (a) pristine and (b) mechanochemically modified microporous carbon by X-ray diffraction showing the variation of microporosity (at lower angle) and order-disorder transition (at higher angle). (MM = milling time, following number represents duration in minutes).

KCl. The relative amount of iodine present can be semi-qualitatively analysed using the ratio of intensities of the iodine peak (L- α =3.938 keV) and silicon peak (K- α =1.739 keV). Table 6.2 confirms higher iodine content in carbons iodated with higher initial iodine feed. From XRF analysis, it was found the iodine content remains constant over a long period of storage.

Table 6.2: X-Ray Fluorescence elemental data of pristine and iodated microporous carbons

	MPC-1		1	MPC-2			MPC-3		
Materials	Cl/Si	K/Si	I/Si	Cl/Si	K/Si	I/Si	Cl/Si	K/Si	I/Si
Pristine	2.349	2.253		2.341	2.063		1.649	1.596	
HEM 20	4.290	1.241		2.744	2.405		1.834	1.189	
20 wt %I	2.141	1.473	5.239	2.113	1.882	5.106	1.774	1.066	3.124
40 wt %I	2.112	1.092	7.543	2.328	1.304	7.294	1.511	0.946	7.361
60 wt %I	1.764	0.740	8.160	1.163	0.944	8.728	2.014	1.067	10.30

6.6 Small-angle X-ray Scattering analysis:

SAXS was utilized as the pore size below 1 nm could not be accurately discerned through our multipoint BET experiments. The SAXS signal arises from the density differences between carbon matrix and underlying pores, hence it detects all kinds of pores (open and closed pore) of size as small as 0.1 nm (1 Å). In the low Q range (corresponding to micropores), the scattered intensity I(Q) is directly proportional to the carbon matrix-pores contrast and increases with total pore volume. The scattering intensity from microporous carbons can be expressed as:

$$I(Q) \approx 2\pi I_e \rho^2 SQ^{-4}$$

where, I_e being the intensity scattered by a single electron, ρ being the electron density difference between carbon matrix and vacuum (micropores), *S* being the interfacial surface area and *Q* being the scattering vector.

The SAXS scattering patterns and corresponding pore size distribution for pristine and modified carbons are shown in figure 6.8. Figure 6.8 (a-c) depicts the data for pristine microporous carbon with increasing surface area (700 \sim 1000 m²/g). In each case, a dispersed pore size range of $0.2 \sim 0.7$ nm $(2 \sim 7 \text{ Å})$ is observed. These chemically activated carbons are very rich in fine-micropore of size below 1 nm. With increase in surface area (hence micropore volume), the corresponding SAXS intensity gradually increases. The presence of finer micropores in carbon was also observed in the high-resolution TEM study. Some high-resolution TEM micrographs of a representative MPC (with surface area 700 m^2/g) are shown in figure 6.9 (a and b). A fairly uniform distribution of finer micropores (0.2~0.8 nm) is clearly observed. However, when iodine in introduced into these carbons (Fig 6.8 d), the SAXS peak disappears altogether. The fact that the intensity decreases suggests that a modification of the micropore structure may develop as the scattering intensity difference between the iodine and carbon should induce a discernable reflection. However, this process has been found to show some degree of reversibility as when the iodated carbon is partially deiodated by annealing at 300 °C under nitrogen flow, a small SAXS peak appears once again proving the formation of some open micropores (Fig 6.8 e). Chemical activation nucleates large number of fine-micropores, which can act as a host-site for iodine accumulation forming microporous carbon-iodine nanocomposites. Further morphological analysis of these carbons is discussed below.





Figure 6.8: Small-angle X-ray scattering (SAXS) patterns for pristine microporous carbon of different surface area (a) MPC-700 m²/g, (b) MPC-950 m²/g, (c) MPC-1000 m²/g. The increase in scattering intensity implies the presence of more micropore volume in higher surface area carbons. (d) When iodine is introduced into carbon, the scattering intensity sharply drops. (e) With partial removal of iodine from iodated carbon by thermal annealing, the scattering intensity once again grows. Figures (f-j) gives the pore size distribution, as calculated from corresponding scattering pattern by Fit2D software. A broad peak around Q range of 10-25 nm⁻¹ appears, which corresponds to fine micropore of size range 0.2~0.8 nm. This peak grows more intense with higher BET surface area (f-h) and disappears for iodated MPC (i) proving the micropore filling by iodine. The micropore peak reappears for partially iodated carbons (j).



Figure 6.9 (a): The effect of defocus on the void contrast. At Df=0 there is no contrast. For over-focus Df=250 nm and under-focus Df=-250 nm, a contrast appears associated with Fresnel type contrast. There is also a contrast reversal on going from over-focus to under-focus.



Figure 6.9 (b): High-resolution TEM images of chemically activated microporous carbons showing rich presence of fine micropores. Three particles are images with Fresnel defocus -250 and +250 nm.

6.7 Morphological analysis:

The morphology of pristine carbon is dramatically affected by introduction of any guest species. As per our previous research on mesoporous carbons, iodine was found to preferentially occupy the micropores [14-16]. In the current study on microporous carbon, the same phenomenon is more pronounced. The pore size distribution of pristine and iodated microporous carbon is compared in figure 6.10. Pristine microporous carbon of BET area 750 m²/g was used for iodine-incorporation (25 weight %) by mechanical milling for 20 minutes. While the fresh microporous carbon has a large peak in micropore/ small mesopore region, it is completely eliminated upon induction of iodine. This confirms the preferential adsorption of iodine into micropores. Micropores can be thought of as narrow cylindrical/ conical pores, which is highly reactive due to large specific surface energy and strong capillary behaviour. When carbon is exposed to iodine, the strong capillary force captures iodine molecules inside micropores forming monolayer of polyiodide compounds. With progressive iodation process, gradually all micropores are filled with polyiodides following the subsequent formation of multilayer.



Figure 6.10: The relative pore size distribution showing filling of micropores in pristine carbon upon mechanochemical iodation.

6.8 Raman spectroscopy analysis:

Microporous activated carbons are structurally amorphous (D: tetrahedral sp³ coordination) with embedded zone of crystalline graphitic (G: planar sp² coordination) zones. It leads to two distinct peaks, D peak (A_{1g} symmetry, ~1300 cm⁻¹) and G peak (E_{2g} symmetry,~1580 cm⁻¹). Further, the presence of polyiodides species gives evident peaks at low wave numbers. These peaks can shed light on the materials structure of iodated MPC carbons. The Raman spectra of pristine and iodated microporous carbons are shown in figure 6.11, showing (a) carbon D and G peaks (high wave number, 1100-1800 cm⁻¹) and (b) polyiodides peaks (low wave number, 0-300 cm⁻¹).

The broad spectrum and more intense D-band are consistent with the amorphous nature shown by XRD. Fig 6.11.a compares the pristine MPC to modified MPCs, where different amount of iodine was doped into carbon by mechanical milling for 20 minutes. No marked change in the D and G peaks (position and intensity) was observed in iodated carbons. As per x-ray studies, the presence of iodine leads to structural disordering in carbon. Although XRD study suggest complete disordering of carbon (disappearance of (002) and (100) peaks), Raman study retains the G bands unaltered, which proves the presence of confined disconnected graphitic nanoclusters of varying size inside MPC carbons.

The nature of chemical interaction between iodine (guest) and carbon (host) is captured in the low wave number Raman study. Molecular iodine has the characteristic peak at 180 cm⁻¹, which is absent in all modified carbons. It discards the existence of free iodine inside carbon. Iodated carbons give two broad polyiodide peaks at 115 cm⁻¹ (triiodide) and 160 cm⁻¹ (pentaiodide) (Fig 6.11.b) The triiodides and pentaiodide are formed by combination of molecular iodine (I₂, Lewis acid acceptor) and Γ or I_3^- (Lewis base donor) as basic building blocks. The pentaiodide (I_5^-) consists of two iodine molecules coordinated to an apical iodide $[I_5^- = (\Gamma)^2 I_2]$. With increasing degree of iodation, while the triiodide peak intensity remains constant, the pentaiodide peak intensity gradually increases and becomes remarkable for 60 wt% iodation. Thus, with higher amount of iodine inside carbon, pentaiodide units are preferentially formed over triiodide units.



Figure 6.11: Raman spectra of pristine and iodine-modified microporous carbons showing (a) the carbon peaks (D and G) and (b) the polyiodides peaks (I_3 and I_5).

6.9 Thermal analysis:

The iodation induced polyiodide formation leads to distinct change in differential scanning calorimetry results. Figure 6.12 shows the DSC graphs of some representative iodated microporous carbon along with some iodated mesoporous carbons. The respective iodine content in these carbons is indicated along the DSC peaks. These iodated carbons were prepared via high-energy milling for 40 minutes. Iodine, if present inside carbon in molecular form (I₂), sublimes at ~110 °C showing a sharp exothermic peak (dashed line in Fig 6.12). However, in all iodated carbons, the absence of any such peak discards the existence of molecular iodine inside carbon, in good agreement with the Raman study. In contrast, sharp exothermic peaks well

above 350 °C are observed, which we have previous attributed to the formation of polyiodide groups [14-16]. For microporous carbons, the increase in iodine content (from 40 to 60 wt%) reduces the onset point of exothermic reaction from 480 °C to 450 °C. As per Raman study, higher iodine content supports higher order polyiodide formation, which resembles closer to molecular iodine and decomposes at lower temperature. Similar trend was earlier marked in mesoporous carbons. Furthermore, the comparison between iodated mesoporous and microporous carbon clearly proves stronger carbon-iodine bonding in case of microporous carbon, which shifts the exothermic reaction to higher temperature. In figure 6.12, microporous carbons have higher degree of iodation. The stronger carbon-polyiodide bonding in microporous carbons can be attributed to the inherently strong capillary force of smaller micropores (0-2 nm).



Figure 6.12: Differential scanning calorimetry curves of iodated microporous carbons showing the exothermic peak confirming strong carbon-iodine chemical bonding inside the nanocomposites. The comparison between iodated mesoporous and iodated microporous carbon is shown. The number inside brackets indicates the amount of iodine content in carbon.

6.10 Electrochemical properties of iodated microporous carbon 6.10.1 Galvanostatic analysis:

As described in earlier sections, chemical iodation instigates significant physico-chemical modification in microporous carbons causing some intrinsic change in materials chemistry. It is reflected in the electrochemical properties of iodinemodified carbons. Figure 6.13a shows the comparative discharge voltage profiles of pristine and modified carbon. Like the earlier study on mesoporous carbon [14-16], iodation initiates negligible non-faradaic change but significant faradaic modification in microporous carbon. Mechanochemical iodation has almost no effect on zone I in the voltage profile (Figure 6.13a). The non-faradaic zone $(4 \sim 3.2 \text{ V})$ involves the formation of large size BF₄⁻ anion layers in the mesopores of carbon interface in the voltage profile. As per literature [17], the increase in space charge (electronic conductivity or DOS) inside carbon favors higher degree of interfacial ionic layers. The fact that iodation does not modify the non-faradaic behaviour suggests chemical iodation does not improve the electronic conductivity or DOS of microporous carbons. With further discharge, iodation increasingly changes the slope of activated carbons. It is associated with the adsorption of smaller Li^+ ion into the micropores of carbon. As per Raman spectroscopy, the micropores are filled with I_n^- type compound. This negative polyiodides attracts the Li^+ ions. With increase in iodine content, the degree of polyiodide increases resulting in more effective attraction of Li^+ cations. The adsorption of smaller Li⁺ cations into micropores containing polyiodide compounds prompts the electrochemical reaction at 3.1 V in faradaic zone $(3.2 \sim 2.8)$ V), which involves the presumed conversion reaction forming lithium iodide (LiI) from carbon polyiodide (CI_x). With increase in the iodine content, the degree of 3.1 V faradaic plateaus steadily increases. All these electrochemical reactions were found to

be extremely reversible in nature. The loosely connected polyiodide bonds favour the electrochemical reaction with good reaction kinetics.

On another note, to show the 3.1 V faradaic reaction is indeed due to inherent polyiodides and not due to any possible electrochemical development of electrode during charging segment, figure 6.13(b) shows the discharge profile of an iodated carbon, without any charging. Even for this case, the same degree of 3.1 V faradaic plateau arises at exactly same voltage. It proves the pseudocapacitive reaction is surely related to inherent polyiodide compounds in MPC carbons.



Figure 6.13: Comparative voltage discharge profile of microporous carbon-iodine nanocomposites with different degree of iodation. A clear development of 3.1 V faradaic plateau is observed for higher iodation leading to higher energy density. (b) Even if the electrode is discharge from its open circuit voltage without charging, it develops faradaic plateau around 3.1 V.

Combining the change in non-faradaic and faradaic zone, we get drastic improvement in the gravimetric capacity of pristine carbon. Also, the inherent nature of iodine makes the nanocomposites very dense thus improving the volumetric capacity of modified carbons. Figure 6.14 depicts the gradual improvement in the gravimetric/ volumetric capacity of microporous carbon-iodine nanocomposites.

Upon iodation of carbon with a particular surface area, microporous carbon provides better volumetric capacity than mesoporous carbons. Some key electrochemical parameters of iodated commercial mesoporous and in-house fabricated microporous carbon are listed in table 6.3.



Figure 6.14: Steady increase in gravimetric/ volumetric capacity of microporous carbon upon iodine inclusion and faradaic pseudocapacitance development.

	Carbon Materials								
Materials Properties	Commercial Activated carbon		Norit ASupra (Iodated)	Erachem ASP (Iodated)	Timcal SP (Iodated)	Microporous Carbon (Iodated)			
Capacity (n	nAh/g)	50.1	30.2	37.5	7.0	40			
Vol. Capaci	ity (mAh/cc)	4.03	44.2	58.0	18.4	71			
Capacitance	e (F/g)	158.4	73.3	56.0	4.1	110			
Vol. Capaci	itance (F/cc)	95.2	107.2	111.5	10.528	132.3			
Density (g/g	cc)	0.805	1.46	2.08	2.632	2.10			
Rate (500 n	nÁ/g) (W/kg)	1440		1600				
BET area (r	$n^2/g)$	2300	1720	732	61	754			
Micropore a	area (m^2/g) *	1648 (77)	320 (60)	66 (29)	5.4 (5)	684 (88)			
Mesopore a	rea (m^2/g) *	486 (23)	210 (40)	164 (71)	98 (95)	87 (12)			

Table 6.3: Table comparing some major electrochemical parameters of iodated microporous carbon with that of other existing carbon system.

* The number in bracket presents the percentage of microporosity in carbon.

6.10.2 Potentiodynamic analysis:

Pristine and iodated microporous carbons show different potentiodynamic profiles as shown in figure 6.15. Pristine microporous carbon, which involves non-faradaic charge storage throughout the operation, yields a smooth potentiodynamic curve. However, carbon polyiodides, the product nanocomposites involve both non-faradaic double layer formation and development of faradaic psuedocapacitance. As a result, the iodated carbons show a spike around 3.1 V, corresponding to the inception of faradaic reaction between polyiodide and lithium. With increase in iodine content, the degree of faradaic reaction increases, thereby increasing the potentiodynamic loop bigger with bigger 3.1 V spike. These cyclic voltammetry loops were found reversible in nature indicating the reversibility of chemical reaction involving repeated formation and destruction of polyiodide compounds. Iodated carbon involves higher specific current than pristine carbon, which is in good agreement with its higher galvanostatic capacity.



Figure 6.15: Typical cyclic voltammetry plots comparing pristine and iodated microporous carbon electrodes. The reversible spikes around 3.5 and 3.2 V corroborate the corresponding galvanostatic modification.

6.10.3 Cycling stability study:

The microporous carbon-iodine nanocomposites electrodes were finally tested for cycling stability. Figure 6.16 compares the volumetric capacity over initial cycling stage of pristine and iodated microporous and mesoporous carbon. The iodinemodified carbon not only delivers high volumetric capacity, but also retains the capacity over initial stage of cycling. As discussed earlier, the electrochemical cycling involves reversible faradaic conversion of polyiodide to lithium iodide around 3.1 V. As seen, the volumetric capacity retains its high values, thus proving the reversibility of conversion reaction and little permanent leaching of iodine from carbon.



Figure 6.16: The initial cycle life study of iodated microporous carbons. The high volumetric energy density is fairly retained over cycling even though it involves reversible conversion of polyiodide and lithium iodide.

The cycling stability of these iodated carbons relies on the retention of polyiodide species during reversible conversion reaction. For the iodated microporous carbon (in Figure 6.16), a comparative voltage discharge profile for different cycles is
shown in figure 6.17 (a). The presence of 3.1 V faradaic peak even after long cycling proves the presence of polyiodides. However, a clear drop in 3.1 V faradaic plateau (and hence capacity) occurs.



Figure 6.17: (a) Comparative voltage discharge profiles (cycled between 4 to 2.8 V) of iodated microporous carbon electrodes after different cycles. The numbers close to the voltage profiles indicate the cycle index. (b) The normalized iodine XRF signal for different cycles at different state of discharge. The presence of iodine signal proves the retention of polyiodide species.

Further, ex-situ x-ray fluorescence study of iodated electrode tapes was conducted at different intermediate discharge voltages during different cycle. These electrodes were specially prepared using equal amount of iodated carbons and aluminum powders (as reference) as active material. The resulting data are presented in figure 6.17 b. The amount of iodine inside electrode remains constant throughout the discharge cycle. With longer cycling, the amount of iodine gradually decreases that can be due to leaching of some physisorbed iodine into electrolyte during cycling.

6.11 Conclusions:

IUPAC type-I microporous carbon (0~2 nm) was fabricated by a low-cost chemical activation method from anthracite coal precursor. Various activation process

parameters were studied and optimized to fabricate carbon with tunable area from 250 to 1700 m²/g with well above 80% microporosity. These microporous carbons were mechanochemically modified to produce carbon-iodine nanocomposites. Microporous carbon was found to be favourable precursor carbons for accommodating high amount of iodine into micropores. Iodation process had profound effect on the structural, morphological and electrochemical properties of pristine carbons. These physical and electrochemical developments were studied in depth using variety of characterization tools. Iodation results in structural disordering and polyiodide formation inside, which triggers faradaic pseudocapacitive reaction and improve the electrochemical capacity of modified carbons. We observed very high gravimetric capacity (~39 mAh/g) and volumetric capacity (80 mAh/cc) in microporous carbon-iodine nanocomposites. These microporous carbon-iodine nanocomposites form an interesting system for electrochemical study for hybrid capacitor and low voltage battery-type applications.

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VII: EXTENSION OF CHEMICAL HALIDATION CONCEPT TO HIGHLY REACTIVE BROMINE: EFFECT OF BROMINATION ON ELECTROCHEMICAL PROPERTIES OF ACTIVATED CARBONS

7.1 Introduction:

The effect of chemical iodation on electrochemical development in carbons has been elucidated for various commercial activated mesoporous carbons (Chapter 3 & 4), crystalline graphitic carbon (Chapter 5) and chemically activated microporous carbons (Chapter 6). The iodine-induced structural development and corresponding 3.1 V faradaic plateau development is generalized for different kind of carbons. In the current chapter, the concept of carbon-halide nanocomposites is extended from iodine to bromine. Bromine is unique among halide elements in many aspects. It is the middle element in gr-VII (in periodic table) and is the only liquid halide element. In comparison to iodine, bromine has smaller ionic size, higher chemical reactivity, large electronegativity, higher redox potential and higher charge transfer ability (table 7.1) [1, 2]. The charge transfer ability is presented by charge transfer per carbon atom (f_c), which is defined as the number of charge carriers (holes) created in any individual carbon atom upon addition of one bromine atom. Higher f_C value implies higher chemical reactivity. Due to its high reactivity, bromine may show more pronounced chemical interaction with activated carbons. This chapter examines the effect of bromination on physical and electrochemical properties of activated carbons.

Table 7.1: Some	comparative p	roperties of	bromine	and iodine	(Gr-VII	halides)	[1,2]
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Element Properties	Iodine (I)	Bromine (Br)
Density (g/cm ³)	4.933 (solid)	3.1028 (liquid)
Melting point (Kelvin)	386.85	265.80
Crystal structure	Orthorhombic	Orthorhombic
Oxidation states	±1, 5, 7 (acidic)	-1, 1, 3, 4, 5 (acidic)
Electronegativivity (Pauling scale)	2.66	2.96
Electrical resistivity $(\Omega.m)$	1.3×10^7	$7.8 \ge 10^{10}$
Thermal conductivity (W.m ⁻¹ K ⁻¹)	0.449	0.122
Charge transfer per carbon atom (f_C)	0.0005	0.001
Redox potential (vs Li)	3.1 V	3.5 V

7.2 Fabrication of carbon-bromine nanocomposites by solid-state mechanical milling route:

Commercially available activated carbon (trade name ASP, Timcal Inc) was taken as precursor carbons. ASP carbon was mechanochemically modified via highenergy milling (0~1 h) and bromine incorporation (0~30 wt%), as described in chapter 2. For bromination, liquid bromine (Alfa-aeser Inc) was added to pre-weighed amount of carbon drop-wise by a glass pipette. As per calculation, one drop of bromine was equivalent to 0.1 g (density, ρ of Br = 3.1028 g/cm³). All materials loading and collecting modified carbon from milling cells were performed inside ventilated hood in a dry room to ensure no external contamination or hydrolysis. The physical and electrochemical modification of carbon-bromine nanocomposites was examined using varieties of techniques as described in chapter 2.

7.3 Structural analysis (XRD) of carbon-bromine nanocomposites

As described in chapter 4, when iodine vapor was introduced into pre-milled activated mesoporous carbons of different morphology, it adversely affects any localized graphitic ordering inside amorphous carbon matrix [3]. The iodine-induced structural disordering was further observed in graphites and microporous carbons [4]. In order to study the effect of bromination on carbon structure, X-ray diffractograms of bromine-modified carbons are shown in figure 7.1 for different milling duration. The related lattice parameters, calculated to approximate values, are enlisted in table 7.2. The peak around 18° originates from sample holder. Overall amorphous nature of carbon presents spectra with two broad peaks around 25° and 44° related to (002) and (100) Bragg reflections. It indicates the presence of randomly oriented small graphitic zones in all carbon samples. These peaks become sharper and intense with longer mechanical milling of carbon precursor, which has been described in chapter 3 and 4.



Diffraction angle (20) Figure 7.1: X-ray diffractograms showing the order-disorder transition in activated carbon upon bromination for milling duration of (a) 20 min, (b) 40 min, (c) 60 min.

When the pristine carbon is chemically modified by different degree of bromination, distinct modification of the diffractograms is observed that can be attributed to bromine. Special care was taken in sample handling and analysis to ensure accurate comparisons between pristine and modified carbons. For all milling duration (Fig 7.1), bromination sharply destroys the (100) peak (~44°) even for very small bromine content of 10 wt%. Any further bromination only yield slight reduction of (100) peak. It indicates the destruction of lateral dimension (along c axis) of nanographene zones in carbon. However, in comparison to iodine (Chapter 3 and 4), bromination induces lesser degree of structural disordering. Here, even with very high bromination, very small/ broad (100) peaks are retained in carbon, whereas for similar degree of iodation, complete destruction of (100) peak has been observed. The interplanar distance between individual graphene planes is 0.34 nm. The relatively smaller size of bromine (0.185 nm, [2]) and polybromide (0.3041~0.3197 nm, [5]) is less destructive to the lateral graphitic dimension than polyiodide species (size of polyiodide = 0.58 nm).

Coming to the longitudinal dimension of graphitic domains (related to (002) peak around 26°), bromine-incorporation destroys the graphitic ordering. From table 7.2, with 10 wt% bromine-introduction, the longitudinal lattice parameter (L_a) drops from 50 to 19 Å (for 20 min milling), 80 to 20 Å (for 40 min milling) and 96 to 22 Å (for 60 min milling). With further bromination, there is minimal change in L_a parameter. It is marked that gradual bromination leads to slight increase in (002) peak position and corresponding d spacing. However, in spite of bromination induced disordering, X-ray diffractograms retains the (002) peaks, unlike for chemical iodation. Overall, bromination leads to lesser degree of structural disordering than iodations.

Materials	peak p (002)	oosition (100)	d space (002)	ing (Å) (100)	La (Å)	L _c (Å)
		· /		· /	. ,	~ /
ASP Pristine	24.648	43.282	3.647	2.096	30.5	37.2
ASP BM 20	24.700	44.161	3.631	2.068	50.0	25.2
ASP BM 40	24.752	44.420	3.543	2.036	80.2	29.3
ASP BM 60	24.596	44.420	3.529	2.040	96.1	34.4
A CD D. (20 100/ D	24.051	42 452	2 500	2 001	10 (1	22.04
ASP BM 20 10% Br	24.851	43.453	3.580	2.081	19.61	33.04
ASP BM 20 20% Br	24.954	43.505	3.565	2.078	20.28	35.27
ASP BM 20 30% Br	25.159	43.607	3.537	2.074	22.47	36.93
ASP BM 40 10% Br	24 800	43 710	3 587	2.069	18 48	30 37
ASP BM 40 20% Br	25 262	43 453	3 523	2.009	20.85	34.15
ASP BM 40 30% Br	25.416	43.505	3.502	2.078	21.24	35.37
	• • • • •			• • • •		
ASP BM 60 10% Br	24.748	44.378	3.595	2.040	17.42	33.01
ASP BM 60 20% Br	25.005	43.402	3.558	2.083	19.80	32.65
ASP BM 60 30% Br	25.108	43.762	3.544	2.067	21.28	33.20

Table 7.2: The summary of X-ray diffraction of brominated carbon materials.

Bromine is highly volatile (M.P, t_m = 55°C), which may escape carbon structure during high-energy milling and resulting heat generation. X-ray fluorescence study was conducted on brominated carbon, taking metallic Fe as reference material. As detailed in table 7.3, bromine is present in each brominated carbons and the relative degree of bromination gradually increases with higher bromine feed. This holds true for all milling duration. In addition, XRF study (with Fe powder as reference element) confirms the absence of any foreign elements and very slight Fe impurity in carbon-bromine nanocomposites for longer milling duration.

Table 7.3: The X-ray fluorescence data (Br/Fe ratio) of brominated activated carbons.

	Bromine Content (weight %)				
Milling duration (min)	10%	20%	30%		
20	0.3036	0.7753	1.2341		
40	0.3977	0.8554	1.5897		
60	0.3548	0.8419	1.4667		



Figure 7.2: X-ray Photoelectron (XPS) Spectra showing carbon and bromine (a) survey scan showing C1s and O1s peak for pristine and halidated carbons, (b) bromine 3p and (c) bromine 3d peaks respectively.

The surface chemistry of bromine-doped carbons was conducted by XPS analysis. Figure 7.2a shows the XPS scans of pristine and bromine modified activated carbons. The C1s and O1s peaks are due to carbon and oxygen impurities. A longer scan delivers peaks related to 3p orbitals (Fig 7.2b) and 3d orbitals (Fig 7.2c) of bromine, which matches well with previous literature [6, 7]. These XPS peaks prove the presence of molecular bromine (Br₂) in carbon-iodine nanocomposites.

7.4 Raman spectroscopy study of brominated carbons:

Activated carbons largely consist of tetrahedral sp³ diamond structure with embedded sp² graphitic structure and linear sp¹ structure. Further investigation of mechanochemical bromination on carbon was conducted focusing on two distinct peaks; the A_{1g} symmetry D peak (~1300 cm⁻¹) and the E_{2g} symmetry G peak (~1580 cm⁻¹) of Raman spectra [8]. The comparative Raman spectra of brominated carbons are given in figure 7.3 for different milling time showing the high wave number window (800~1800 cm⁻¹, carbon peaks) and low wave number window (100~700 cm⁻¹), bromine peaks). Some Raman spectroscopy data are summarized in table 7.4.

In the low wave number window, pristine activated carbon is featureless [9,10]. However, bromination gives some distinct peaks that become more intense with gradual bromination (Figure 7.3 a,b,c). For 10 wt% case, it is very difficult to detect bromine peaks due to very low bromine content in amorphous carbon. But for higher bromine content, a peak arises around 220 cm⁻¹, which is assigned to Br-Br stretching vibration mode [11-13] in bonded state (Br-Br), proving the presence of bromine inside activated carbons. Yet, this peak is different than solid bromine (300 cm⁻¹) and gaseous bromine (324 cm⁻¹) [14]. A careful observation reveals the 2nd and 3rd harmonic peaks related to Br-Br vibration (2ω and 3ω) around 400 cm⁻¹ and 600 cm⁻¹. These Br-Br molecular Raman peaks have been observed in graphites and nanotubes [15,16]. Apart from these Br-Br bands, highly brominated carbons lead to a peak around 270 cm⁻¹ that becomes intense with higher bromination. It is assigned to polybromide peaks corresponding to Br³⁻ (Br₂+Br⁻) or Br⁵⁻ (2Br₂+Br⁻) types bonding [5,12,17,18] possibly with carbon. In all cases, the characteristics 323 cm⁻¹ band corresponding to free bromine (Br₂) [13] is missing. Thus, bromination of activated carbons leads to the parallel formation of Br-Br vibrational bonds or polybromide.



Figure 7.3: Raman spectra of bromine-doped activated carbons: The bromine bands at low wave number windows for mechanical milling duration of (a) 20 min, (b) 40 min, (c) 60 min, and the variation of D and G bands at high wave number window for mechanical milling duration of (d) 20 min, (e) 40 min, (f) 60 min.

*	High	wave number	r window	Capacity
Materials	I _D /I _G ratio	D peak	G peak	(mAh/g)
	(cm^{-1})	(cm^{-1})		
ASP	1.8245	1303.0	1592.5	10.9000
ASP BM 20				8.6053
ASP BM 40				6.4324
ASP BM 60				6.4580
ASP BM 20 10% Br	1.3004	1326.4995	1597.2518	17.2000
ASP BM 20 20% Br	1.2083	1328.0855	1595.2660	17.6770
ASP BM 20 30% Br	1.4226	1328.4855	1591.0732	18.0600
ASP BM 40 10% Br	1.2704	1325.7507	1593.1205	16.0000
ASP BM 40 20% Br	1.1892	1332.4401	1593.1205	16.2440
ASP BM 40 30% Br	1.2303	1334.5306	1593.1205	17.5440
ASP BM 60 10% Br	1.2613	1324.6558	1593.4459	10.9910
ASP BM 60 20% Br	1.3081	1328.6947	1593.4459	16.8880
ASP BM 60 30% Br	1.2669	1330.7142	1593.4459	17.0960

Table 7.4: Raman spectroscopy data of brominated activated carbons.

Coming to the high wave number window, the D and G bands of brominated carbons are shown for different milling duration (Fig 7.3 d,e,f). Overall, amorphous nature as proved by XRD is observed with broad and intense D peak. Bromine intercalation in crystalline carbons forms a small G shoulder peak (~1600 cm⁻¹) [11], which is missing in case of amorphous activated carbons. It proves little degree of bromine intercalation in carbon-bromine nanocomposites. Unlike iodated carbons, in case of brominated carbons, gradual bromination leads to upshift of D band position and downshift of G band position, i.e. the D and G band approach to each other. This hints at possible charge transfer reaction and alteration in electronic structure. When highly electronegative bromine is introduced into carbon via mechanical milling, it can trigger a valence electron transfer from carbon to bromine, thus creating holes in carbon. This in turn reduces the C-C bond in carbon and hardens the tangential vibrational phonon modes [19-22]. The gradual cross shift in D and G bands (table 7.4) is an indication of bromination induced charge transfer reaction in carbons.



7.5 Morphological modification on activated carbons upon bromination:

Figure 7.4: (a) Intermediate magnification image of mesoporous ASP activated carbon taken at a defocus value of Df = -250 nm, and highly magnified defocused images showing wide mesopores in ASP carbons for (b) Df=-250 nm, (c) Df=250 nm.

High surface area with mesoporosity leads to effective double-layer formation and ionic rate capability in carbon. ASP is chemically activated mesoporous carbons (pore size: 15-30 nm) with high surface area (762 m²/g). Figure 7.4 shows some TEM images of ASP carbon having large, distributed mesopores. Any mechanochemical modification affects these morphological parameters. The effect of mechanochemical bromine-incorporation on carbon morphology is given in figure 7.5. The mechanical milling and iodine-induced reduction in BET area of ASP carbon was earlier discussed in chapter 4. A similar effect was observed for bromination. When bromine is introduced into carbon, it tends fills up existing pores. Thus gradual bromination decreases the BET surface area (Fig 7.5a). Further, using t-plot analysis, the change in micropore area in brominated carbons is presented in figure 7.5b. Similar to the case of iodation, bromination progressively reduces the micropore area. The smaller bromine particles tend to fill up the smaller micropores, thus reducing the micropore area. The net decrease in micropore area is almost equal to the decrease in overall BET area for all modified carbons. Thus preferential micropore filling mostly accounts for overall decrease in BET area. Although the morphological change from bromination follows similar trend of iodation, bromination yields lesser reduction in surface area due to its inherently small size. Some morphological properties of brominated carbons are listed in table 7.5.

Figure 7.5c shows the average pore size of bromine-modified activated carbons for different milling duration. Generally, they are mesoporous in nature (mesopores: 2-50 nm). Even through BET area and micropore area of pristine carbon decreases with longer milling, the average pore size remains same around 3 nm. When different amount of bromine is included into carbon, the average pore size slowly increases. As bromine preferentially fills up the micropores in carbon, it leaves the inherent mesopores open. As a result, the average pore size increases. The modification in porosity with bromination is further elucidated in figure 7.6. It shows the pore volume distribution for pristine and brominated carbons. For pristine carbon, a broad small peak shows the presence of pore in the mesopore range of 10-50 nm. With increasing amount of bromine-doping, this mesopore volume increases significantly, confirming higher degree of mesoporosity. This is in agreement with larger average pore size and relative decrease in carbon microporosity.



Figure 7.5: The effect of mechanochemical modification by high energy milling and gradual bromine-incorporation on (a) BET surface area, (b) micropores surface area and (c) average pore size as determined by BET equation and t-plot equation.

Materials	density (g/cc)	resistivity (Ohm-cm)	y BET) area (m ² /g)	micropore area (m²/g)	pore size (nm)	OCV (V)
ASP	0.359	0.7272	761.07	119.07	4.58	3.3178
ASP BM 20	1.518	1.0472	445.00	192.44	3.27	3.3203
ASP BM 40	1.974	1.4800	360.00	145.45	3.16	3.3100
ASP BM 60	2.050	1.6850	297.35	165.83	3.06	3.3494
ASP BM 20 10% Br	1.137	2.0944	435.10	122.77	4.22	3.3377
ASP BM 20 20% Br	1.170	2.6255	401.96	102.55	4.41	3.4362
ASP BM 20 30% Br	1.244	2.2958	319.71	75.48	4.26	3.6233
ASP BM 40 10% Br	1.224	2.1767	354.67	153.28	3.40	3.3145
ASP BM 40 20% Br	1.326	2.1177	324.55	108.34	3.54	3.4845
ASP BM 40 30% Br	1.447	2.7989	258.76	76.32	3.43	3.6198
ASP BM 60 10% Br	1.447	2.5806	285.62	148.28	3.10	3.3838
ASP BM 60 20% Br	1.530	2.3562	252.99	87.82	3.28	3.5885
ASP BM 60 30% Br	1.990	2.4847	221.48	66.50	3.34	3.6693

Table 7.5: Some physical/ morphological properties of brominated activated carbons.



Figure 7.6: Graph showing the relative pore volume in pristine and brominated carbons (fixed milling duration = 20 min). Gradual bromination leads to mesopores development i.e. micropores are preferentially filled by bromine particles.

7.6 Electrochemical study of carbon-bromine nanocomposites: 7.6.1 Galvanostatic study:

The carbon-bromine interaction at nanoscale brings significant modification in the structure, morphology and other physical properties [23, 11]. As revealed by Raman spectroscopy and earlier literature [20,21], the highly reactive bromine is a good oxidizer that can trigger charge transfer reaction (CT) with carbon. The extent of CT reaction increases with higher bromine content. It is reflected in the corresponding open circuit voltage (OCV) of brominated carbons (Figure 7.7). The OCV of activated carbon lies around 3.32 V (vs. Li). When bromine is introduced into carbon structure, the OCV values gradually increases from 3.32 to 3.62 V. This trend holds good for different milling duration (yielding different morphology). The higher OCV values hints at progressive oxidation of activated carbons with bromination. Iodine, being a very weak acceptor, leads to lesser degree of CT reaction and oxidation of carbon.



Figure 7.7: The effect of bromination on open circuit voltage (OCV) of activated carbons. Bromination induced charge transfer reaction oxidizes the carbon that leads to higher OCV. This phenomenon is true for all milling duration.



Figure 7.8: Comparative galvanostatic voltage discharge profile for activated carbons (milled for 60 min) with different degree of bromination ($0\sim30$ wt%). Bromination leads to sharp increase in slope (hence non-faradaic development) and development of 3.1 V pseudocapacitive plateaus (hence faradaic development).

The chemical bromination makes the galvanostatic voltage profile non-linear in nature. As shown in figure 7.8, bromine induces a two-fold modification (a) developed slope in (linear) non-faradaic zone (4~3.2 V) and (b) appearance of a faradaic plateau around 3.1 V (current rate = 15 mA/g). The brominated carbon can have higher space charge development due to CT reaction. It leads to higher degree of ionic adsorption/ desorption (of electrolyte), thus developing higher slope. In the faradaic zone, the appearance of a faradaic plateau can be due to cathodic reaction of bromine (or polybromide) with lithium. These non-faradaic and faradaic modification results in improved electrochemical capacity as discussed below.

The galvanostatic capacity of pristine and brominated carbons is shown in figure 7.9 (cells cycled at 15 mA/g, 2.8~4 V). The capacity of pristine carbon decreases with longer milling solely due to decrease in mesoporous surface area. But,



Figure 7.9: Histograms showing the electrochemical improvement in activated carbons with mechanochemical bromine modification (a) gravimetric capacity (mAh/g), (b) specific capacitance (μ F/cm²) and volumetric capacity (mAh/cc).

in case of carbon-bromine nanocomposites, the capacity sharply rises (>100% rise) when 10 wt% of bromine is introduced. Further bromination (up to 30 wt%) slightly increases the capacity. This capacity improvement comes in spite of lower amount of carbon and lower BET surface area. It is due to the combination of non-faradaic capacity increment and faradaic plateau development.

Following, the specific capacitance of carbon samples was calculated by normalizing the non-faradaic capacitance (μ F/g, 4~3.2 V) with corresponding BET surface area (m²/g) (Figure 7.9b). Bromination improves the leads to 50-100% improvement in specific capacitance. Further, the volumetric capacity of pristine and bromine-doped activated carbon was calculated by multiplying the discharge capacity (mAh/g) (4~2.8 V) with corresponding density of carbon pellets (g/cm³) pressed at 7000 psi. Bromination and high-energy milling leads to higher density as shown in table 7.5. The combination of higher discharge capacity and higher density gives rise to higher volumetric capacity in brominated carbons (Figure 7.9c). Volumetric capacity improves as high as 100~150%. A point to note that bromine is lighter and produces milder faradaic pseudocapacitance than iodine. Hence, brominated carbons have much smaller gravimetric and volumetric capacity than iodated carbons.

Interestingly, bromination process triggers a faradaic pseudocapacitive reaction at 3.1 V like chemical iodation. Due care was taken during materials preparation and handling to avoid any iodine contamination. Further, XRF and XPS study on brominated carbons ensure no iodine contamination. From Raman study and hint about Br-Br (and polybromide) compounds, the following faradaic conversion reactions from polybromide to lithium bromide are proposed:

$$2 C + 3 Br_2 \leftrightarrow 2 Br_3 + 2 C^+$$
$$nLi^+ + ne^- + C^+ + Br - Br^{(-)} \leftrightarrow C + n LiBr$$

7.6.2 Potentiodynamic study

Following the galvanostatic study, potentiodynamic study was performed on some key carbon-bromine nanocomposites of different composition. The comparative cyclic voltammograms (CV) of pristine and brominated activated carbons are shown in Figure 7.10. Pristine carbon delivers typical square type CV, where charge storage in entirely non-faradaic in nature. With brominated activated carbons, a sharp peak around 3.1 V appears due to the inception of faradaic reaction. Also, a small peak was noted at 3.5 V, which may be due to some faradaic reaction. This voltage is perfectly consistent with the reduction of molecular Br_2 by the reaction 2 Li + $Br_2 \rightarrow 2$ LiBr. Considering that there was spectroscopic evidence for the presence of molecular bromine, this mechanism is entirely plausible and likely. These peaks are found to be reversible with longer cycling. Higher degree of bromination (from 10 to 30 wt %) favors higher specific current (3~4 V range). In comparison to iodation, brominated carbons have less specific currents and smaller area covered by cyclic voltammograms. Never the less, bromination produces lesser degree of oxidation/ corrosion at higher voltage unlike iodation.



Figure 7.10: Comparative cyclic voltammograms showing sharp 3.1 V peak corresponding to the onset point of pseudocapacitance reaction. The peak intensity increases with higher degree of bromination.

7.7 Summary and Conclusions

The concept of chemical halidation of activated carbon was extended to bromine. Activated carbon was mechanochemically brominated with varying degree of bromine feed. The resulting structural, morphological and electrochemical properties of brominated carbons were investigated and compared to corresponding iodated carbons. The highly reactive bromine leads to possible charge transfer reaction which is indicated by (i) decrease in the G band position (Raman spectroscopy) and (ii) increase in open circuit voltage owing to oxidation of carbon. Similar to iodation, chemical bromination led to graphitic disordering, polybromide formation (Br-Br), reduction in BET and micropore area and improvement in electrochemical capacity. However, bromination modified the physicochemical properties of carbon to a lesser degree. As bromine is toxic, corrosive and unsafe to handle, its industrial usage in electrochemical modification of carbon is not viable. Nonetheless, carbon-bromine nanocomposites form an interesting system for deciphering some fundamental issues regarding chemical halidation process.

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VIII: SUMMARY AND CONCLUSIONS

In an effort to improve the electrochemical properties of activated carbons for supercapacitor application, a novel 'mechanochemical halide modification route' was proposed and investigated. This method modifies the electrochemical properties of carbons by combining morphological modification with simultaneous inception of faradaic pseudocapacitance.

(*a*) At the outset, the chemical halidation was employed on various commercial mesoporous carbons, by solid-state and vapor phase iodine-incorporation. The structure, morphology and chemical bonding in these iodated carbons were investigated with suites of techniques. Iodation was found to destroy any internal graphitic ordering as detected by x-ray diffraction and Raman spectroscopy. Further, using thermal analysis and Raman study, formation of polyiodide compounds (I_3^-, I_5^-) was confirmed in iodated carbons. Consequently, the effect of mechanochemical iodation on electrochemical properties of modified carbons was investigated. In general, the net electrochemical capacity was improved by development of non-faradaic capacity and by inception of a faradaic conversion reaction around 3.1 V. As a result, substantial improvement in gravimetric, surface-normalized and volumetric capacity was observed. Specially, the volumetric capacity improved from 8 mAh/cm³ to 57 mAh/cm³ (200-500% rise), thus forming a very high energy density electrode.

(b) Later, the effect of iodation of crystalline graphite was studied. A vague hint of charge transfer reaction between carbon and iodine was found from Raman spectroscopy. Graphite-iodine system confirmed the results of mesoporous activated

carbons and faradaic conversion reaction at 3.1 V between polyiodide and lithium iodide. Even for low surface area carbon like graphite, chemical halidation markedly improved its gravimetric and volumetric capacity.

(c) In all mesoporous carbons, BET study indicates about preferential iodine segregation inside existing micropores. To decipher the effect of pore size in activated carbon on carbon-iodine interaction and final electrochemical properties, microporous carbon with tunable morphology was fabricated by chemical activation process using anthracite coal precursors. The microporous carbons were found to accommodate more iodine due to presence of micropores. The structure, morphology and chemistry of these iodated microporous carbons was analysed using XRD, DSC, BET, SAXS and TEM. Microporous carbon-iodine nanocomposites developed very high faradaic pseudocapacitance, thus giving volumetric capacity exceeding 80 mAh/cm³.

(*d*) Eventually, the chemical halidation process was extended from iodine to bromine. Generally, bromination led to similar structural and morphological development in carbons but to a smaller degree. Bromine leads to graphitic disordering, polybromide formation and reduction of BET/ micropore area. Particularly, charge transfer reaction was more evident for bromine as indicated by Raman scattering studies and variation in open circuit voltage (OCV). Like iodine, bromine too develops a 3.1 V faradaic pseudocapacitive reaction, leading to higher electrochemical capacity.

On the whole, there was a striking dearth of literature related to the physical properties of carbon-iodine composites and none that we could find relating to the electrochemical properties. Regarding the former, no compounds have been found between macro graphite/ carbon and iodine. This is due to the lack of energetic driving force for the intercalation of the iodide/polyiodide within the bulk or between the basal planes of the graphite material. However, one paper by Enoki did stand out where it was shown that a weak charge transfer interaction between iodide and nano graphite edges as seen in neat nano graphite and nano grapheme within activated carbons. The conclusions presented above for various carbons in the present work give physical/electrical evidence for the observation by Enoki in (1) the formation of polyiodide species which cannot form without some strong degree of polarization or charge transfer, (2) the systematic increase of OCV as a function of polyiodide formation consistent with the oxidation of carbon, (3) The very near physical locale of the polyiodide species to grapheme edges within the micro pores, (4) the formation of a Faradaic 3.1V plateau which cannot be related to the conversion of Lithium with polyiodide (voltage 0.3V above theoretical), but would require the reduction of C^+ centers. Indeed, the same 3.1V Faradaic charge transfer was seen in the polybromated samples. If the redox was due to the polyhalide, the voltage should be much higher than that of the polyiodide. However, if the voltage is due to the reduction of the C^+ the two polyhalide compounds (eg $C^+:I_n$ and $C^+:Br_n$) should give the same voltage. (5) The fact that the compound shows very high stability towards decomposition in the DSC study.

Very interesting is that when the voltage is decreased below the redox that should be induced by the polyiodide (approx 2.7V), we do not observe a redox reaction. This strongly suggests that the polyiodide is not accessible for redox with the lithium. In deed the charge transfer may be delocalized such that Li⁺ may satisfy the redox at sites delocalized from the micropore area where the polyiodide resides. This needs to be investigated further.

Finally, these new materials must be discussed from a practical standpoint. Although the focus was to establish a new material for symmetric/asymmetric supercapacitors, the relatively low 3.1V plateau where most of the polyhalide induced voltage resides is too low to be of practical use in such systems. However, the good capacity, very high reversibility and power may make this material class be one of interest for high power long cycle life battery systems.

IX: FUTURE WORKS

Chemical halidation produced 'carbon-halide nanocomposites' form a special class of activated carbon based electrode system, showing unique combination of morphological and electrochemical properties. The current project was the first step to formulate and investigate these carbon-halide nanocomposites electrodes. It lays a foundation for many future research works, some of which are proposed below.

(a) Halides (and polyhalides) give rise to a faradaic pseudocapacitive reaction at 3.1V, involving reversible conversion reaction. A fundamental study on the underlying reaction mechanisms involving in-situ x-ray diffraction, in-situ Raman spectroscopy and ex-situ solid state ¹³C-NMR and x-ray absorption spectroscopy can be done.

(*b*) While mesopore favors effective non-faradaic double-layer formation, micropore yields efficient halidation and development of faradaic pseudocapacitance. The optimal combination of mesopores and micropores in activated carbons for chemical halidation can be studied to get the best carbon-halide nanocomposites.

(c) Although the carbon-polyhalide compounds were found to be chemical stable, some capacity loss in early-stage cycling was observed. As supercapacitor demands robust cycling, it will be worthwhile to study the possible failure mechanisms in carbon-halide nanocomposites electrodes.

(*d*) The very addition of extremely-electronegative halides into carbon can develop charge-transfer (CT) reaction. There were some hints of halide-induced CT in activated carbons. Thorough study is needed to verify CT reaction and its effect on electrical conductivity and space charge development in carbons. Both these

parameters are central for supercapacitor performance. A synergistic approach combining experimental and computational tools is proposed.

(*e*) The halidation concept can be extended to compound halidation (e.g. different combination of iodine and bromine into activated carbons forming $C_xI_{1-x-y}Br_y$ composites). Bromine seems to improve electronic conductivity while iodine gives very high pseudocapacitance. Their combination can further improve the capacity.

(*f*) These carbon-halide nanocomposites can be further studied using various electrolytes of different ion size and concentration.

(g) The high-temperature and low-temperature stability of these halidated carbons can give an idea of possible temperature range for safe operation.

(*h*) Finally, attempt should be taken to implement these carbon-halide nanocomposites in asymmetric hybrid supercapacitors (e.g. with counter electrode like $Li_4Ti_5O_{12}$) and low voltage battery configurations. In both cases, due care should be taken for proper electrode-optimization and pre-lithiation of electrodes.

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PUBLICATIONS

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