A combined salt-hard templating approach for synthesis of multi-modal porous carbons used for probing the simultaneous effects of porosity and electrode engineering on EDLC performance

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Abstract

A new approach, based on a combination of salt and hard templating for producing multi-modal porous carbons is demonstrated. The hard template, silica nanoparticles, generate mesopores (~22 nm), and in some cases borderline-macropores (~64 nm), resulting in high pore volume (~3.9 cm³/g) while the salt template, zinc chloride, generates borderline-mesopores (~2 nm), thus imparting high surface area (~2100 m²/g). The versatility of the proposed synthesis technique is demonstrated using: i) dual salt templates with hard template resulting in magnetic, nanostructured-clay embedded (~27% clay content), high surface area (~1527 m²/g) bimodal carbons (~2 and 70 nm pores), (ii) multiple hard templates with salt template resulting in tri-modal carbons (~2, 12 and 28 nm pores), (iii) low temperature (450 °C) synthesis of bimodal carbons afforded by the presence of hygroscopic salt template, (iv) easy coupling with physical activation approaches. A selected set of thus synthesized carbons were used to evaluate, for the first time, the simultaneous effects of carbon porosity and pressure applied during electrode fabrication on EDLC performance. Electrode pressing was found to be more favorable for carbons containing hard-templated mesopores (~87% capacitance retention at current density of 40 A/g) as compared to those without (~54% capacitance retention).

1. Introduction

Recently, there has been considerable attention devoted towards understanding and tailoring the material properties [1-10] and electrode processing conditions [11-18] to enhance the performance of porous carbons used as electrode materials for supercapacitors. Among the various carbon material properties, the pore size distribution has been shown to play a very significant role [1-4, 6-10]. Hierarchically porous carbons comprised of interconnected

macropores (> 50 nm), mesopores (2-50 nm) and micropores (< 2 nm), have appeared as promising candidates for electrode materials for supercapacitors [5-9, 19-23]. In general, the micropores provide sites for electrosorption, whereas the mesopores and macropores act as electrolyte reservoirs as well as provide pathways for electrolyte transport [9, 24]. Among the various reported studies aimed at probing the effect of carbon porosity on its supercapacitor performance, there appears to be a consensus on the favorable effect of microporosity on electrical double-layer capacitance (EDLC) performance, with higher microporosity leading to higher surface area and thus higher EDLC capacitance, as long as the pores are accessible to the electrolyte ions [2]. However, the favorable effect of mesoporosity continues to be debated. Some studies indicate that the presence of mesoporosity leads to enhanced capacitance retention at higher current densities, but other studies have suggested otherwise [1, 3, 25-27].

The electrode processing conditions have also been shown to have a significant effect on the EDLC performance [11-18, 28]. For example, forced electrolyte infiltration was found to overcome, to some extent, the capacitance retention problem at high current densities associated with primarily microporous carbons [28]. Similarly, applying pressure and forcing the electrolyte into the pores was also found to play a favorable role in enhancing the capacitive performance and lowering IR drop, with the effect of applied pressure being different for different size electrolyte ions [11, 12]. On the other hand, Ruoff et. al. reported that electrode compression led to an enhanced equivalent series resistance and low EDLC performance (on gravimetric basis), which was ascribed to the loss of a fraction of mesopores in the electrode [18]. In another study, application of pressure during electrode preparation was found to have no effect on the capacitance, while resulting in reduced ohmic drop [13]. Based on the above, there is not a

consensus in the literature on the effect of application of pressure during electrode fabrication on the EDLC performance. Moreover, most of the studies aimed at understanding the effects of carbon porosity and electrode fabrication on EDLC performance, have been carried out independently. To the best of our knowledge, there are no studies exploring the effects of both - carbon porosity and electrode processing conditions simultaneously. In fact, probing the effect of carbon porosity while simultaneously exploring the wide electrode fabrication parameter space, could help shed light in understanding the sometimes contradictory experimental findings reported in the literature.

In this study, we investigate for the first time, the simultaneous effects of carbon porosity and electrode engineering on EDLC performance. To explore the effects of different levels of porosity, four different sets of porous carbons produced using a newly developed technique were tested. Specifically, (i) micropore, (ii) mesopore, (iii) micropore-mesopore, and (iv) micropore-macropore dominated carbons were tested and evaluated. In addition, for each carbon, the EDLC performance was measured as a function of increasing pressure applied during electrode manufacturing.

Multi-modal porous carbons have been gaining recently a lot of attention as high performance materials for supercapacitors and other fields including batteries, water purification, CO₂ capture, sensors, fuel cells, and hydrogen storage [5, 19, 20, 29-38]. A significant effort has been devoted towards developing efficient synthesis approaches for producing hierarchically porous carbons [5, 20, 29, 30, 39-43]. The most commonly used methods for producing multi-modal porous carbons usually involve two steps: (1) synthesis of a mesopore/macropore

dominated carbon (through either hard [44] or soft templating or sol-gel) and (2) introduction of microporosity through a second step of activation (either physical or chemical activation) [5, 19, 20, 45-49]. Although, such techniques can ensure a tight control on porosity at different levels, they often add complexity and make the synthesis highly energy intensive. For practical applications a simple, one step approach for synthesis is highly desirable [29, 30, 39, 50-52].

Recently, salt templating, has emerged as a highly simple and sustainable technique for producing functional porous carbons [53-57]. Salt templating involves the carbonization of a carbon precursor around molten salt at an elevated temperature. However, the technique mainly results in the generation of micropores and some small mesopores, with the pores generated after washing the salt nano-clusters [53]. Herein, we demonstrate a new approach, based on a combination of salt templating and hard templating, for producing high surface area multi-modal porous carbons. The approach involves mixing a solution of an inorganic salt (ZnCl_2) with a carbon precursor (glucose) and an inorganic hard template (colloidal silica) suspension, followed by vacuum assisted drying and carbonization. The salt (ZnCl_2) initially melts during carbonization with the glucose precursor forming a carbon matrix around the molten ZnCl_2 nano-pools, which eventually boil off during carbonization at elevated temperature (1000 °C), generating micropores and small mesopores. On the other hand, the removal of colloidal silica through etching with NaOH generates the mesopores. Different size mesopores, macropores and even tri-modal porous carbons can be generated by using colloidal silica of different sizes and combinations thereof. By using a mixture of two salts, we also demonstrate that the technique can be used for the synthesis of a nanostructured clay embedded, high surface area multi-modal porous carbon. Also, a combined technique involving salt templating-hard templating-physical

activation, is also demonstrated for the production of very high surface area ($\sim 2500 \text{ m}^2/\text{g}$) multi-modal porous carbons. While we have focused here on the effect of porosity on EDLC performance, the inherent flexibility of the synthesis can provide a family of carbons with tailored porosity potentially suitable for specific applications in many energy fields and beyond.

2. Experimental

2.1 Material Synthesis

For easy reference the overall synthesis approach is schematically depicted in Figure 1. In a typical synthesis, 10 g of a 30 wt% suspension of 22 nm colloidal silica and 3 g of glucose D are mixed in a plastic centrifuge tube. Then 6 g of ZnCl_2 salt dissolved in 6 mL of MilliQ Water is added to the solution and shaken well. After mixing, the sample is vacuum dried until completely dry. The glucose-silica- ZnCl_2 composite is then pyrolyzed at 1000°C , at a ramp rate of 3°C min^{-1} for a dwell time of 2 h under nitrogen. During the course of pyrolysis, ZnCl_2 acts as an in-situ nano-template finally boiling off and leaving behind secondary micropores and small size mesopores. The obtained carbon-silica composite is then stirred first in a 3M NaOH solution at room temperature for 4 hours and then the mixture is kept at 95°C for 24 hours in an autoclave, to etch out the silica. The sample is finally washed with copious amounts of deionized water and dried at 130°C for at least 12 hours before use. For convenience, the samples are denoted by PC x - y - z , where PC stands for porous carbon, x represents the average colloidal silica size (nm) and y ($= 0$ or 1) represents the mass ratio of silica to glucose in the original suspension, and z ($= 0$ or 2) represents the mass ratio of ZnCl_2 to glucose. For the purposes of this study, five different carbons were synthesized and tested: (i) PC produced by salt templating alone: PC 0-0-2, (ii) PCs produced by only hard templating alone: PC 4-1-0, PC 22-1-0, (iii) PCs produced by

combined salt templating-hard templating: PC 4-1-2, PC 22-1-2. Commercially available colloidal silica suspensions in water with different average size silica: 4 nm (15 wt% , Alfa Aesar), 22 nm (40 wt%, Ludox TM-40) were used as received.

Figure 1. Schematic showing the basic steps involved in the carbon synthesis. The four steps shown clockwise from bottom left are: (1) preparing a glucose-colloidal silica aqueous suspension, (2a) salt addition (ZnCl_2) to the glucose-silica suspension, which results in controlled aggregation of silica nanoparticles, (2b) vacuum drying resulting in the formation of silica nanoclusters embedded in the glucose-salt matrix, (3) carbonization yielding micropores from boiling of ZnCl_2 nano-pools, and (4) silica etching to produce mesopores. For simplification the pores are not shown as interconnected.

For carbon materials produced through the combined salt templating-hard templating-physical activation procedure, the synthesis procedure is exactly the same as described previously, except for the carbonization at 1000 °C, the inert nitrogen gas is replaced with CO_2 . A low energy intensity synthesis was also explored, whereby the glucose-silica-salt mixture is

carbonized at 450 °C at a ramp rate of 3 °C min⁻¹ for a dwell time of 2 h under nitrogen. The resulting carbon-silica-salt composite is then treated with 1M HCl at 85 °C for 4 hours to etch out the ZnCl₂ salt, followed by washing with copious amounts of MilliQ water. The silica nanoparticles are etched out using the same procedure as described above. Finally, porous carbons using a multi salt mixture were also demonstrated. In this synthesis, first a solution of glucose-colloidal silica-ZnCl₂ is obtained as described above. Then 1 g of cobalt nitrate hexahydrate solution (dissolved in 2 mL MilliQ water) was added to the glucose-colloidal silica-ZnCl₂ solution, mixed well and vacuum dried. The dried glucose-silica-ZnCl₂-Co(NO₃)₂ composite was then carbonized at 1000 °C at a ramp rate of 3 °C min⁻¹ for a dwell time of 2 h under nitrogen. The obtained carbon-silica-cobalt composite was immersed in NaOH to remove the silica template. The etched out silica monomers/oligomers react with the embedded cobalt nanoparticles resulting in the formation of cobalt phyllosilicates embedded within the multi-modal porous carbon. The nanostructured cobalt phyllosilicates can further be etched out by using 1M HCl solution at 85 °C for 24 hours.

2.2 Material Characterization

2.2.1 Surface area and pore size measurement

Nitrogen adsorption-desorption tests were carried out at 77K using a Micromeritics TriStar II 3020 analyzer. Prior to gas adsorption, the samples were degassed at 180 °C under N₂ for at least 12 hours. The specific surface area was calculated using the Brumauer-Emmett-Teller (BET) method. The pore volume was estimated from single point adsorption at a relative pressure of 0.994. The pore diameter was determined from the adsorption curve, according to the Barrett-Joyner-Halanda (BJH) method.

2.2.2 Transmission Electron Microscopy (TEM)

TEM specimen was prepared by dispersing the carbon powders in ethanol and dropping the resulting suspension onto a 400-mesh holey carbon-coated copper grid. Bright-field TEM and high-angle-annular-dark-field (HAADF) scanning (S)TEM images were carried out on FEI Titan ST electron microscope ($C_s=1.2$ mm; $C_c=1.5$ mm; 300 kV). EDX spectra were collected under STEM mode. The probe size of the microscope was approximately 2.0 Å for STEM imaging and EDX analysis. Energy-filtered transmission electron microscopy (EF-TEM) mapping, energy dispersive X-ray spectroscopy (EDX) mapping, and electron energy loss spectroscopy (EELS) mapping were performed on the same microscope equipped with a GIF system operated at 300 kV.

2.2.3 Electrode preparation and electrochemical characterization

For electrode preparation, the PCs were first ground using a mortar and pestle. Then 92.5 wt% of PC and 7.5 wt% polytetrafluoroethylene (PTFE) (60 wt% PTFE obtained from Sigma Aldrich) were mixed in ethanol to form a slurry. The PC-PTFE-ethanol slurry was sonicated for ~30 minutes and then dried by placing in an oven at 80 °C for an hour to obtain a dough-like paste. The paste was then rolled into a film (~2mg/cm² of active carbon material) and then pressed onto a stainless steel mesh (Alfa Aesar) at a pressure of 1bar, using a hydraulic press.

Electrochemical performance and galvanostatic charge-discharge (GCD) measurements were carried out at room temperature using a two electrode configuration at different current densities ($I/2m$, where m is the mass of a single electrode), with 1M H₂SO₄ as the electrolyte in the potential range between 0-1V. The effect of pressure (applied using a hydraulic press, in line with Masarapu et al. [11] defined as force applied using the hydraulic press divided by the plate area dimensions) on supercapacitor performance was measured by successively pressing the

electrodes at increasing pressure values under three different conditions– (i) in the presence of electrolyte soaked cotton, (ii) in the presence of MilliQ water soaked cotton, (iii) in the presence of dry cotton. The pressing was done in between successive EDLC measurements, using a cotton square (~1cm by 1.5cm) placed in between the two electrodes, with the carbon film side facing the cotton square. The specific capacitance, energy density, power density, and total resistance were calculated using the following formula:

$$E = \frac{1}{8} C_s (V - V_{drop})^2 \quad (1)$$

$$P = \frac{1}{2} (V - V_{drop}) \left(\frac{I}{2m} \right) \quad (2)$$

$$C_s = 2 \left(\frac{I}{m} \right) \left(\frac{dt}{dV} \right) \quad (3)$$

$$R_t = \frac{V_{drop}}{I} \quad (4)$$

where

m is the mass of single electrode

I is the current

V is the maximum applied potential (1V)

V_{drop} is the IR drop

dV/dt is the rate of potential decline during the discharge (excluding IR drop)

C_s is the specific capacitance of the material

E is the specific energy density

P is the specific power density

R_t is the total resistance

The capacitive frequency response was calculated from the Electrochemical Impedance Spectroscopy (EIS) data using the following formula:

$$C = \frac{1}{j\omega Z} = \frac{1}{j\omega(\text{Re}(Z) + j\text{Im}(Z))} \quad (5)$$

$$|C| = \left[\{\text{Re}(C)\}^2 + \{\text{Im}(C)\}^2 \right]^{1/2} \quad (6)$$

$$\alpha = 2\pi f \quad (7)$$

The electrochemical impedance spectroscopy measurements were performed at 0 V using a sinusoidal signal of 10 mV over the frequency range from 100 kHz to 100 mHz. Following established procedures the total resistance is divided into two main components – (i) R_s - series resistance comprising of electrolyte resistance, intrinsic resistance of carbon film and contact resistance at the interface of carbon film/current collector and (ii) R_i – Ionic resistance, attributable to ion migration within the carbon film and carbon pores. The series resistance, R_s , is given by the first intersection point of the Nyquist spectrum in the high-frequency region. The ionic resistance, R_i , is the difference between total resistance (R_t) and series resistance (R_s).

3. Results and Discussion

3.1 Physical Characterization of synthesized porous carbon materials

The textural and physical characteristics of the various PCs are presented in Table 1 and Figure 2 (a, b). There are three important things to note from the porosity data. First, PC 0-0-2 (produced through salt templating alone), has very high surface area arising from the presence of secondary micropores and mesopores with a size around ~2 nm. Second, PC 4-1-0 and PC 22-1-0 (produced through hard templating alone), have large pore volumes arising from the presence of large size mesopores ~7 nm and ~26 nm generated through their respective silica template. Third, PC 4-1-2 and PC 22-1-2 (produced through combined hard templating-salt templating) show both high surface areas and very high pore volumes. The high surface area arises from the presence of secondary micropores and mesopores around 2 nm generated through the carbon matrix formed around the salt (ZnCl_2) nanoclusters. The mesopores and macropores (~22 nm and ~64 nm for PC 4-1-2 and PC 22-1-2 respectively) are produced through the removal of silica nanoparticle clusters. The silica nanoparticle clusters are formed as a result of the controlled aggregation of silica after addition of ZnCl_2 to the glucose-silica suspension. Since the

carbonization proceeds under solvent free conditions, no further phase segregation appears to take place, enabling the mesopores/macropores generated from silica etching to still retain a relatively sharp peak in their respective pore size distributions. The solution-free carbonization strategy prevents uncontrolled phase segregation of the hydrophilic silica nanoparticles within the carbonizing (and increasingly becoming hydrophobic carbon precursor matrix) and thus alleviates the need for using costly surfactants [58], fast stirring speeds and/or dilute carbon precursor concentrations [59]. In order to confirm this finding, another set of carbonization experiments were performed, where the glucose-colloidal silica-salt solution was directly subjected to carbonization without removing the solvent through the vacuum drying step. As can be seen in Figure 2 (c, d), the carbons produced show a very broad pore size distribution indicative of uncontrolled phase segregation, unlike the relatively sharp peak obtained for carbons produced from vacuum drying of glucose-colloidal silica-salt solution.

Table 1. Surface Area and Porosity Characteristics of the various synthesized PCs

Synthesis Procedure		Sample	BET Surface Area (m ² /g)	N ₂ adsorption pore volume (cm ³ /g)
Vacuum assisted drying	Salt templating alone	PC 0-0-2	2062	1.12
	Hard templating alone	PC 4-1-0	1457	2.56
		PC 22-1-0	979	2.23
	Combined salt templating-hard templating	PC 4-1-2	2013	3.91
		PC 22-1-2	2096	3.87
Heat assisted drying	Hard templating alone	HePC 4-1-0	1257	3.19
		HePC 22-1-0	865	2.83
	Combined salt templating-hard templating	HePC 4-1-2	1954	4.34
		HePC 22-1-2	1846	3.30
Combined Hard Templating-Salt Templating-Physical Activation		PCP 4-1-2-10	1908	4.30
		PCP 4-1-2-17	2517	4.26
		PCP 4-1-2-25	2404	3.55
		PCP 22-1-2-17	2579	3.57
Combined hard templating-salt templating low Temperature carbonization (450 °C)		PCL 22-1-2	2108	3.24
PC stands for porous carbons produced through vacuum assisted drying, HePC stands for porous				

carbons produced through heat assisted drying, PCP stands for porous carbons produced through combined hard templating-salt templating-physical activation, PCL stands for porous carbons produced at lower carbonization temperature (450 °C).

For PC x - y - z - α (if used), x represents size of silica nanoparticle, y represents mass ratio of silica/glucose, z represents mass ratio of ZnCl_2 /glucose, α for the case of physically activated samples represent the flow rate (ml/min) of CO_2 .

The multi-modal porosity of carbons produced through the combined hard-salt templating, could translate in both high energy density and high retention capability when used as supercapacitor electrodes. High surface area typically leads to high energy density while the the presence of big mesopores (~22 nm in case of PC 4-1-2) or macropores (~64 nm in case of PC 22-1-2) could lead to high retention capability, since they could act as both electrolyte reservoirs and highways for efficient electrolyte transport.

Figure 2. N_2 sorption isotherm and pore size distribution for porous carbons synthesized through vacuum assisted drying (a, b) and direct carbonization (heat assisted drying) (c, d).

Another important feature of our synthesis technique is that very high surface area multi-modal carbons can be produced using a combination of salt templating-hard templating-physical activation. The only difference in the synthesis procedure in this case is that during the hold at 1000 °C, the inert nitrogen gas is replaced with CO₂. CO₂ activation is known to proceed through reactions between CO₂ and the carbon matrix, thus leaving behind pores within the carbon matrix in the process [60]. The porosity (produced in-situ due to the boiling off of the ZnCl₂ nanoclusters) facilitates the easy in-diffusion of CO₂ to active sites and out-diffusion of reaction products [61]. The presence of ZnCl₂ also ensures a higher degree of carbonization of the glucose-silica composite. Note that combined hard templating-physical activation (i.e. in the absence of ZnCl₂), under same thermal conditions and CO₂ flow rates, resulted in almost zero yield. The much lower yield is attributed to the lower degree of carbonization of silica-glucose composite, which leads to higher gasification rate upon reaction with CO₂ [61]. The nitrogen sorption isotherms and pore size distribution results for samples produced through combined salt templating-hard templating-physical activation, with varying CO₂ flow rates, are shown in Figure 3. For the combined hard templating-salt templating-physical activation, the degree of physical activation can be easily controlled by varying the CO₂ flow rate. At high CO₂ flow rates (e.g. 25 ml/min), the carbon matrix between adjacent silica nanoparticles also seems to react with CO₂, resulting in merger and enlargement of adjacent spherical mesopores, as can be seen in Figure 3 (b).

Another advantage of the combined salt templating-hard templating approach is that the carbonization can be achieved at a much lower temperature. The ZnCl₂ salt, apart from acting as an in-situ template around which carbon matrix is formed, also acts as a dehydrating agent

ensuring effective carbonization of glucose even at a low temperature, such as 450 °C. In the absence of ZnCl₂ salt, (i.e., when hard-templating alone is used), carbonization is incomplete at such low temperatures and the whole carbon matrix collapses upon etching of the silica template. This lack of porosity in low temperature carbonization of silica-glucose composites is highly evident from N₂ porosimetry, as shown in Figure 4 (a, b). In contrast, a very high degree of porosity is obtained when a combination of salt-hard templating is used, in spite of the lower carbonization temperature. Such multi-modal low temperature (and thus highly energy efficient) carbonized samples could be highly useful candidates for water purification applications or as polymer impregnated supports for CO₂ capture. Since the carbonization is carried out at a very low temperature, these samples have low electrical conductivity as compared to their respective high temperature (1000 °C) carbonization counterparts, and, are thus, less attractive for electrochemical applications.

Figure 3. N₂ sorption isotherm and pore size distribution for porous carbons synthesized using a combined salt templating-hard templating-physical activation approach. For the physical activation part, during the hold at 1000 °C, the inert nitrogen gas is replaced with CO₂. (a,b) show the effect of CO₂ flow rate (10, 17, 25 ml/min) on the carbon porosity, (c,d) represents the sorption isotherm and pore size distribution for sample produced with 22nm silica and activated at CO₂ flow rate of 17 ml/min.

Figure 4. N₂ sorption isotherm and pore size distribution for porous carbons synthesized through low temperature carbonization. The carbonization is carried out at 450 °C, followed by etching with 1M HCl to remove ZnCl₂, followed by etching with 3M NaOH to remove SiO₂.

Lastly we discuss one more advantage of this new synthesis technique: the possibility of using a combination of different metallic salts. In this situation one salt acts as a template to produce porous carbons, while the other can act as a precursor for the formation of metallic phyllosilicates embedded within the carbon matrix. One example of such a synthesis is demonstrated using a combination of ZnCl_2 and a $\text{Co}(\text{NO}_3)_2$. The nitrogen sorption isotherm and the corresponding pore size distribution for the nanostructured cobalt phyllosilicate embedded in high surface area multi-modal carbon is shown in Figure 5 (a, b). In spite of having high metal clay content ($\sim 27\%$, calculated before and after HCl etching), the carbon has a very high surface area ($\sim 1527 \text{ m}^2/\text{g}$) and pore volume ($\sim 3.63 \text{ cm}^3/\text{g}$). The ZnCl_2 salt, not only helps in generating high surface area by producing secondary micropores and mesopores, but because ZnCl_2 boils off at the carbonization temperatures used in this synthesis, it eliminates the need for acid washing. It is important to avoid post-synthesis acid washing as it can also cause etching of the nanostructured phyllosilicate. The TEM image and the corresponding EDX spectrum are shown in Figure 6. The cobalt, silicon and oxygen mapping results confirm that the nanostructures in the TEM image are cobalt phyllosilicates. The presence of cobalt phyllosilicate within the carbon matrix imparts magnetic behavior to the composite material, as confirmed in Figure 6(f). Such metallic nanostructured clay embedded in multi-modal porous carbons could be used as magnetically-recoverable sorbents for water purification.

Figure 5. (a) N₂ sorption isotherms and, (b) BJH pore size distributions – for (i) nanostructured cobalt phyllosilicate embedded in bimodal porous carbons (surface area – 1527 m²/g and pore volume – 3.63 cm³/g) and (ii) bimodal porous carbon after cobalt phyllosilicate etching (surface area – 1767 m²/g and pore volume – 4.32 cm³/g)

Figure 6. (a) TEM image for nanostructured cobalt phyllosilicate embedded in multi-modal porous carbon, (b) Selected area for EDX analysis, EDX mapping results for (c) cobalt (red), (d) silicon (blue), (e) oxygen (pink), where the green color represents the carbon matrix, (f) digital photograph confirming the magnetic nature of the material.

3.2 Electrochemical performance

Detailed characterization measurements were carried out to investigate the interrelated effect of the carbon's porosity as well as the effect of pressure applied during electrode fabrication on the EDLC performance. We start by comparing the EDLC performance for each carbon as a function of increasing electrode fabrication pressure. For understanding the effects of porosity and electrode fabrication pressure, three different EDLC performance assessment measures are considered. First, we use the specific capacitance of the electrode as a function of increasing current density. Both, the absolute value of the specific capacitance as well as its retention as a function of increasing current density are considered. Second measure is the energy density and power density of the electrode, commonly plotted as a Ragone plot. Third is the evolution of the EIS spectra as a function of pressure applied during electrode fabrication. The contribution of different electrode components to the overall resistance as well as the capacitive frequency response for the various electrodes as a function of electrode fabrication pressure were also evaluated.

Figure 7 shows the variation of specific capacitance as a function of current density for PCs with different pore size distributions for varying pressures applied during electrode fabrication. There are three important things to note from Figure 7. First, for the lowest current density measured, i.e. 0.5 A/g, under various electrode pressing conditions, the specific capacitance increases with increasing electrode fabrication pressure mainly for carbons having microporosity and small size borderline mesopores produced from salt templating, i.e., PC 0-0-2, PC 22-1-2 and PC 4-1-2. For carbons having only large size mesopores, produced from hard-templating alone, the capacitance at low current densities increases only marginally with

increasing electrode fabrication pressure. These results can be rationalized as follows: low current densities imply slow charge-discharge conditions. And low fabrication pressure implies low electrolyte filling, which consequently increases with increased fabrication pressure, as suggested by previous studies [11, 12]. Thus, at low current densities, in spite of the low electrolyte filling (at low electrode fabrication pressure), there is enough time for the electrolyte to diffuse in the mesopores. Thus, the capacitance improvement with increased electrolyte filling (with increased electrode fabrication pressure) is only marginal in the case of hard templated mesoporous carbons, as most of the mesopores are easily accessible through diffusion alone. On the other hand, for carbons with microporosity and small size mesopores, the diffusion within the micropores and small size mesopores is slow, even at the lowest current density tested, resulting in incomplete utilization of the available porosity. Thus, as electrolyte filling increases with increasing pressure, the diffusion length and time needed to access the micropores and small size mesopores decreases, thus resulting in enhanced capacitance. At high current densities or fast charge-discharge conditions, the electrolyte diffusion is not fast enough to warrant complete porosity utilization offered by even big size mesopores. Thus, the increased electrolyte filling leads to an increase in capacitance for all the carbons, associated with reduced diffusion lengths and timelines. Capacitance retention shown in Figure S3 (defined as the ratio of capacitance at any current density to that at lowest current density) also increases with increased electrolyte filling within the pores. However, for PC 0-0-2, containing only micropores and small size mesopores, although the capacitance retention increases with increasing electrode fabrication pressure, it only reaches a maximum value of 54%. For all the other carbons containing mesopores from hard templating, capacitance retention in the order of 80% is achieved. The low capacitance retention for PC 0-0-2 implies that it may not be possible to completely fill the

micropores and small mesopores, in contrast to previous reports [11]. This different extent of electrolyte filling within carbons with varying porosity while applying the same amount of pressure can also be explained by the fact that the applied pressure has to overcome both the capillary pressure, which is inversely proportional to the pore size, as well as the trapped air pressure [11]. Moreover, if complete or high-level of electrolyte filling was possible for micropores and small mesopores, then a much higher capacitance retention should be obtained at higher electrode fabrication pressures for PC 0-0-2, just like in the case of mesoporous carbons (PC 4-1-0 and PC 22-1-0) and multi-modal carbons (PC 4-1-2 and PC 22-1-2). This is because if the electrolyte filled completely all the pores, then the ions would only need to migrate to the pore wall to form the double layer and thus capacitance retention should be independent of pore size, which is not the case.

Figure 7. Specific capacitance as a function of current density for electrodes fabricated using different pressures in the presence of 1M H₂SO₄ electrolyte.

Figure 8 shows the Ragone plot for the various PCs with different pore size distributions as a function of increasing pressure applied during electrode fabrication. There are two important things to note from Figure 8. First, the energy and power densities for the various carbons increase with increasing electrode fabrication pressure, reaching a maximum value at an optimum pressure before it starts falling. The energy density increases as a result of both – an increase in capacitance as well as a decrease in IR drop as a result of a decrease in resistance with increasing electrode fabrication pressure. The power density increases with increasing electrode fabrication pressure as a result of decrease in resistance. The existence of an optimum pressure beyond which the performance starts falling can be explained on the basis of collapse of big size pores beyond a certain electrode fabrication pressure[18]. Secondly, as can be seen in Figure S5, among the various PCs, at any electrode fabrication pressure, the multi-modal carbons, PC 22-1-2 and PC 4-1-2, prepared through combined hard-salt templating, provide the highest energy density for both high and low power applications. Comparing the salt templated carbon (PC 0-0-2) with hard templated ones (PC 4-1-0 and PC 22-1-0), the former shows high energy density for low-medium power applications, while the latter, despite their lower surface area, show high energy storage for high power applications. PC 0-0-2 has a micropore (and borderline mesopore) dominated pore size distribution, which as explained earlier, leads to only partial electrolyte filling, even with increasing electrode fabrication pressure. Thus, PC 0-0-2 has a higher ionic resistance associated with it, as confirmed in Figure 10c (vide infra), which results in higher IR loss and thus lower energy density (see equation 2) at high current densities. On the other hand, the hard-templated carbons (PC 4-1-0 and PC 22-1-0) have an abundance of larger

mesopores, which become increasingly filled with the electrolyte as a function of electrode fabrication pressure. This feature leads to low ionic resistance and thus lower IR drop and high-energy storage even at high current densities. We conclude that carbons produced via hard/salt templating combine the high surface area from salt templating and big size mesopores (or macropores) from hard templating result in high energy storage at both low and high current densities.

Figure 8. Ragone plots for electrodes fabricated at different pressures in the presence of 1M H_2SO_4 .

The EIS results are presented in Figure 9. The deconvolution of the total resistance into different components is presented in Figure 10. There are two important things to note from the resistance break-up plot. First, the total resistance is highest for the salt-templated carbon, PC 0-0-2, containing only secondary micropores and small mesopores, with the bulk of the contribution coming from ion migration resistance. On the other hand, the hard-templated

carbons having relatively larger mesopores show low ion migration resistance. These results suggest that the extent of electrolyte filling decreases with decreasing pore size. Second, the ion migration resistance decreases with increasing pressure. Both findings could be attributed to the increased filling of electrolyte within the pores as a result of applying increasing pressure during electrode fabrication. Increased electrolyte filling results in reduced diffusion length and time required for ion migration to the pore wall for forming the electrochemical double layer, thus resulting in low ionic resistance. Apart from analyzing the resistive behavior, the impedance spectra can also be used to determine the capacitive response as a function of modulation frequency. A sample normalized capacitive frequency response (calculated using equations 4, 5, 6) for an electrode made with PC 4-1-0 is shown in Figure S7. The frequency at which the normalized capacitance becomes half, for the various carbon electrodes manufactured at different fabrication pressures, is given in Figure 10(d). As can be seen in Figure 10(d), the frequency corresponding to 50% capacitance retention, increases with increasing electrode fabrication pressure, as a result of higher utilization of the available area in line with the results from the GCD measurements. Also the frequency values is highest for hard-templated carbons having big mesopores and lowest for salt-templated carbon having only secondary micropores and small size/borderline mesopores.

Figure 9. Electrochemical impedance spectroscopy for electrodes fabricated at different pressures in 1M H₂SO₄.

Figure 10. Pressure dependent variation of (a) total resistance (R_t), (b) series resistance (R_s), (c) ionic resistance (R_i), (d) capacitive frequency response (frequency corresponding to 50% capacitance retention, calculated from the EIS measurements).

As demonstrated above, superior EDLC performance can be obtained by pressing the electrodes in the presence of the electrolyte. It is important to note that two things can happen simultaneously as a result of applying pressure in the presence of electrolyte. First, the carbon

particles can come together as a result of compression, thus reducing the contact resistance [13]. Second, the electrolyte can fill the pores, thus reducing the ion migration resistance [11]. In order to understand which resistance gets affected the most, two more set of tests were performed: (i) pressing in the presence of MilliQ water, and (ii) pressing under dry conditions. Performance enhancement for pressing under dry conditions can be safely ascribed to reduction in contact resistance only. On the other hand, pressing in the presence of MilliQ water, is expected to decrease the ionic resistance. This decrease is because, when the water filled electrodes come in contact with the electrolyte solution, the ion diffusion into the water filled pores is enhanced due to concentration gradient. Never the less, the decrease in resistance as a result of compression in MilliQ water case should be lower than when pressed in the presence of the electrolyte. Thus, the performance of pressing in MilliQ water is expected to be intermediate between the dry pressing and pressing in the presence of the electrolyte.

The results (Ragone plot, capacitance measurement, EIS plot, resistance composition and capacitive frequency response) for all the three pressing conditions – (i) pressing in presence of electrolyte, (ii) pressing in presence of MilliQ water and (iii) pressing in dry conditions are presented in Figure 11. The tests were conducted for the best performing carbon, PC 22-1-2. The EDLC performance for the three different testing conditions at their respective optimum pressing pressure follows the order – (electrolyte pressing) > (MilliQ water pressing) > (dry pressing). The electrodes prepared by the dry pressing procedure, exhibit both low capacitance as well as high resistance, leading to poor energy and power density. The break-up of resistance into different components suggests that R_s is the same for both electrolyte pressing and MilliQ water pressing case. Whereas the R_i is slightly lower for the electrolyte pressing case compared to the MilliQ water pressing case. This lowered R_i results in superior EDLC performance, likely due to

the presence of ions within the carbon particles and carbon pores when electrodes are fabricated under pressure in the presence of the electrolyte. For electrodes fabricated under pressure in the presence of MilliQ water, the ions need to diffuse through the solvent present between the carbon particles and within the carbon pores. The R_i for electrodes fabricated in the presence of electrolyte as well as the MilliQ water is much lower compared to the dry fabrication method. This can be explained on the basis of diminished ion diffusion through the compacted carbon particles and within empty carbon pores.

Figure 11. (a) Ragone plot, (b) specific capacitance, (c, d, e) EIS spectrum, (f) total resistance (R_t), (g) series resistance (R_s), (h) ionic resistance (R_i), (i) capacitive frequency response (frequency corresponding to 50% capacitance retention, calculated from the EIS measurements), for electrodes fabricated under pressure in the presence of H₂SO₄ electrolyte, MilliQ and under dry conditions.

4. Conclusion

In summary, we have demonstrated a new approach, based on a combination of salt templating and hard templating for producing bimodal micropore-mesopore dominated carbons. The synthesized bimodal carbons have both high surface areas arising from the presence of secondary micropores and small size mesopores produced from salt templating, and high pore volumes arising from large size mesopores produced from hard templating. The synthesis technique is highly versatile and offers the ability to produce a range of porous carbons by using different combinations of salts and hard templates. In addition, the use of ZnCl_2 as the salt template also makes low temperature (450 °C) carbonization feasible because of the hygroscopic nature of ZnCl_2 . The technique can also be easily combined with physical activation for producing very high surface area ($\sim 2600 \text{ m}^2/\text{g}$) multi-modal porous carbons through single-step carbonization alone. The synthesized (i) microporous, (ii) mesoporous, (iii) bimodal (micropore-mesopore dominated) carbons produced through salt templating alone, hard templating alone and combined salt-hard templating respectively, were used as electrode to compare the simultaneous effects of porosity and pressure applied during electrode fabrication on EDLC performance. The combined salt-hard templated carbons exhibited highest energy storage for both low and high power applications. The effect of pressure applied during electrode fabrication on EDLC performance was more favorable for carbons containing hard templated mesopores. This result was attributed to increased electrolyte filling within the hard-templated mesopores as compared to micropores. GCD and EIS measurements carried out for three different configurations (i) pressing in the presence of electrolyte, (ii) pressing in the presence of MilliQ water, (iii) dry pressing, confirmed that reduced ion migration resistance (because of ion filling within the

pores) followed by reduced contact resistance (because of electrode compression), were responsible for the improved EDLC performance upon pressing.

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