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# Capacitance Evolution of Electrochemical Capacitors with Tailored Nanoporous Electrodes in Pure and Dissolved Ionic Liquids

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## Abstract

A homologous series of ionic liquids (IL) with 1-alkyl-3-methylimidazolium cations of different lengths of alkyl chain was used to study the effect of cation size on the capacitive response of two carbons with a tailored pore size distribution. The results reveal a clear ion-sieving effect in pure ILs, while the effect is heavily mitigated for the same salts used in solution, most likely due to somewhat stronger geometrical flexibility of dissolved ions. For the electrode material showing the ion-sieving effect in solution, the gravimetric capacitance values are higher than in pure ILs. The dissimilarity of capacitance values between pure and dissolved ILs with ion-sieving carbons highlights their respective advantages and disadvantages in terms of energy density: whereas pure ILs can potentially provide a larger working voltage window, the corresponding dissolved salts can access smaller pores, mostly contributing to higher capacitance values.

**Keywords:** Activated carbon, ionic liquid, electrolyte, electrochemical capacitor, double-layer capacitance, ion sieving, pore size.

# 1 Introduction

The increasing demand for highly effective energy storage devices has stimulated intensive research efforts on electric double-layer capacitors (EDLCs). In the energy/power spectrum, EDLCs are located between dielectric capacitors and batteries, having higher energy density than capacitors and higher power density than batteries [1, 2]. Ongoing research on EDLCs is in particular connected with a growing interest in electric and hybrid vehicles [3] where EDLCs are used for providing the peak power required during acceleration.

EDLCs store charge by electrosorption of ions on an active surface, mainly by electrostatic forces without phase transformations in the electrode material. Owing to the high reversibility of electrosorption, EDLCs can withstand a large number of charge/discharge cycles without significant performance fading. Porous carbons have been extensively employed as electrode material for EDLCs due to their low cost, environmental friendliness and established electrode production technologies [4, 5, 6].

Aqueous, non-aqueous and solid polymer electrolytes have mainly been investigated for EDLCs. Organic electrolytes, mostly solutions of tetra-ethylammonium tetra-fluoroborate and other tetra-alkylammonium salts in acetonitrile or propylene carbonate, are predominantly employed in industrial systems: they provide a higher working window (2.7 V) than the aqueous ones (about 1 V) and, correspondingly, a higher energy density.

Room temperature ionic liquids (RTILs), which are liquids exclusively made up of cations and anions, have been probed as electrolytes for EDLCs (see, e.g., [3, 7]). RTILs have been favored because they should increase both the safety (non-volatile and non-flammable properties) and the working voltage window of a device. Unfortunately, generally high viscosity and low electrolytic conductivity limit the high-power performance of the devices, especially at low temperature [7].

Studies on different RTILs showed that the 1-ethyl-3-methylimidazolium cation (EMI) possesses an exceptionally high ionic conductivity as compared with cations containing longer alkyl chains [8]. A variety of anions have been employed in pair with EMI for supercapacitor electrolytes, in particular, bis(trifluoromethylsulfonyl)imide, bis(perfluoroethylsulfonyl)imide, hexafluoroarsenate, hexafluorophosphate, and tetrafluoroborate [9, 10].

A pure ionic liquid is also attractive as a convenient model electrolyte for studying the effects of ion size on capacitance [11, 12]: the size of a bare ion can be assessed with greater precision as compared to that of a solvated ion in electrolytic solutions. In particular, it was established using a 1-ethyl-3-methylimidazolium-based ionic liquid that the maximum values of capacitance per unit surface area are achieved for carbons with an average pore size of 0.7 nm [12], corresponding closely to the cationic dimension of 0.76 nm. Earlier studies also

evidenced a trend between the capacitance and the anion size of ILs dissolved in propylene carbonate, which was also attributed to the ion-sieving effect [13].

In this paper, we present an experimental study of the cation effect on the capacitive response by using a series of salts based on homologous 1-alkyl-3-methylimidazolium cations. We discuss the differences in performance of supercapacitors based on pure and dissolved ionic liquid together with the effect of electrode pore size distribution. We used electrodes from chemically activated carbons of different pore size distribution, which additionally allows assessing the possible effect of ion/pore size compatibility on capacitance.

## 2 Experimental

### 2.1 Preparation and characterization of electrode materials

Activated carbons were produced by chemical activation of mesophase pitch PR21 (Mitsubishi Gas Chemical Co.) with potassium hydroxide. Mixtures of KOH and pitch (KOH:pitch ratios of 1:1, 2:1) were ball-milled for 15 min at 350 rpm. They were then heat-treated in a muffle furnace under a nitrogen flow of 200 mL min<sup>-1</sup>. The heating and cooling steps were carried out at a ramp of 2.5 °C min<sup>-1</sup> with an intermediate 1 h isothermal step at 700°C. Potassium hydroxide was removed from the materials by consecutive treatments with diluted hydrochloric acid and water until neutral pH. The dry materials were ground in a mortar to a particle size less than 0.1 mm and further treated with hydrogen in a tubular furnace as follows: heating/cooling steps at 20 °C min<sup>-1</sup> to 700 °C under a nitrogen flow of 280 mL min<sup>-1</sup>, and a 1 h holding step at 700°C under a mixed nitrogen and hydrogen flow (280 mL min<sup>-1</sup> for N<sub>2</sub> + 40 mL min<sup>-1</sup> for H<sub>2</sub>). The resulting nanoporous carbons are referred to as C1-1, C2-1, according to the KOH to pitch ratio in the precursor mixture.

Nitrogen adsorption isotherms were recorded at -195.8°C for relative pressure ( $P/P_0$ ) in the range of 10<sup>-6</sup> to 1, using an Autosorb-1 (Quantachrome) instrument. Preliminarily, the samples were outgassed for 12 h at 300°C. The values of DFT specific surface area are 1214 m<sup>2</sup> g<sup>-1</sup> for carbon C1-1 and 2202 m<sup>2</sup> g<sup>-1</sup> for carbon C2-1. The pore size distribution (PSD) obtained according to the quenched solid density functional theory (QSDFT) approach [14] is represented in Figure 1. The PSD is widened and shifted to larger pores as the KOH to pitch ratio in the precursor mixture increases. It is also remarkable that the carbon C1-1 does not contain pores over 1 nm. The PSD of the carbon 2-1 presents a main maximum at about 0.6 nm, and the pore size distribution extends up to 2 nm.

## 2.2 Electrolytes

The electrolytes were high purity (>99 %) imidazolium salts from Merck, 1-ethyl-3-methylimidazolium (EMI) trifluoromethanesulfonate (TFMS), 1-butyl-3-methylimidazolium (BMI) trifluoromethanesulfonate and 1-hexyl-3-methylimidazolium (HMI) trifluoromethanesulfonate. They were used either as pure ionic liquids or as the salts dissolved in acetonitrile (0.5 mol L<sup>-1</sup>). Experiments on pure ionic liquids (ILs) were conducted at 60°C as suggested in [11] to decrease the cell resistance. The conductivities of the ionic liquids at 25 °C are 0.92 S m<sup>-1</sup> for EMI TFMS, 0.37 S m<sup>-1</sup> for BMI TFMS and 0.25 S m<sup>-1</sup> for HMI TFMS.

## 2.3 Electrochemical characterization

The electrode mass was prepared as a mixture of activated carbon with polyvinylidene fluoride binder and conductivity additive (PUREBLACK®, Superior Graphite, USA). Carbon electrodes were then formed as pellets (10-15 mg) from the electrode mass. Electrochemical tests were conducted on two-electrode cells (without reference electrode) using two identical carbon pellets, titanium current collectors, a porous membrane separator and a Teflon Swagelok® airtight system. The assembling was carried out in a glove box under argon atmosphere with O<sub>2</sub> and H<sub>2</sub>O content less than 1 ppm. The electrochemical measurements (cyclic voltammetry and galvanostatic charge-discharge cycling) were performed using a VMP multichannel generator (Biologic, France). The gravimetric capacitance was calculated per electrode from the formula:

$$C = 2I/(dV/dt)/m \quad (1)$$

where  $C$  is the gravimetric capacitance per electrode, (F g<sup>-1</sup>),  $I$  the current, (A),  $dV/dt$  is the sweep rate, (V s<sup>-1</sup>),  $m$  the mass of active material per electrode, (g).

## 3 Results and discussion

### 3.1 Ion-sieving effect in pure ionic liquids

Figures 2A and 2C represent the cyclic voltammograms for carbons C1-1 and C2-1, respectively, using the pure ILs. The voltammograms for the carbon C1-1 (Figure 2A) demonstrate a decrease in gravimetric capacitance as the cation's alkyl chain increases. For the carbon C2-1, there is a decrease only from EMI to BMI-based electrolyte, whereas the characteristics in BMI and HMI-based media are comparable.

The differences in capacitance for the carbons C1-1 and C2-1 can be clarified based on the analysis of pore size distribution and ions geometry. The maximum possible dimensions of ions can be estimated through direct measurement from software visualization models by probing different conformations and taking into account the van der Waals radii of the terminal atoms [12]. The longest possible dimension of the imidazolium cations (Figure 3) can be evaluated as 0.76 nm, 0.86 nm, 0.95 nm for EMI<sup>+</sup>, BMI<sup>+</sup>, HMI<sup>+</sup>, respectively, the two other dimensions being approximately equal to 0.43 nm and 0.37 nm for any of the cations. The largest possible dimension of the anion can be estimated to be about 0.7 nm, which is smaller than the largest dimension of any of the cations. Charge storage in a two-electrode cell is described by formula (2) for two capacitors in series:

$$1/C = 1/C_+ + 1/C_- \quad (2)$$

where  $C$  is the cell capacitance,  $C_+$  and  $C_-$  the respective capacitance values of the positive and negative electrodes. According to this formula, the overall capacitance  $C$  is mostly influenced by the lowest value between  $C_+$  and  $C_-$ . Literature data on electrosorption on non-porous glassy carbon and gold electrodes reveal that the EMI cation is adsorbed vertically on the electrode surface [15] in a potential range from  $-1.3$  to  $+0.6$  V vs.  $Ag/Ag^+$  (as evidenced by FTIR on a gold electrode), whereas 1-butyl-3-methylimidazolium adopts a tilted position close to the vertical at positive potentials [16-19]. Because the cations are bulkier than the anion when entering the porosity almost perpendicularly to the pore walls, we can assume that  $C_+ > C_-$ , and consequently the cell capacitance is essentially controlled by the negative electrode.

The values of gravimetric capacitance,  $C_g$ , for microporous carbons can approximately be governed by the recently-developed formula for an electric wire-in-cylinder capacitor [20, 21]:

$$C_g = A \epsilon_r \epsilon_0 / [b \ln(b/a_0)] \quad (3)$$

where  $\epsilon_r$  is relative dielectric constant of the electrolyte,  $\epsilon_0$  the permittivity of vacuum,  $A$  the interphasial surface area,  $b$  the micropore size, and  $a_0$  the effective size of the counterions. Formula (3) was found to correctly describe the experimental capacitance values of various microporous carbons. The interphasial surface area can be adopted to be the accessible surface area, i.e. the surface area of pores larger than the largest cation dimension [22,23]. Therefore, it appears obvious that a tilted or vertical orientation of the cations with respect to the pore wall would result in different values of accessible surface area for the series of imidazolium cations, because of their differences in the largest dimension. Accordingly, this would give rise to dissimilar values of gravimetric

capacitance, i.e. the shorter the alkyl chain, the higher the accessible surface area and, consequently, the higher the gravimetric capacitance.

In fact, the smaller capacitance evolution with C2-1 as compared to C1-1 when the length of the alkyl chain increases could be explained by the relationship between ion and pore sizes. Indeed, the pore size distribution of the carbon C1-1 does not extend over 1.2 nm, and a very small portion of pores is above  $\sim 1$  nm. Therefore, cations with the largest dimension close to 1 nm, especially HMI and BMI, would have difficulties penetrating the porosity of such carbon if their largest side were close to perpendicular to pore walls (Figure 3). By contrast, for carbon C2-1, the accessible porosity extends up to 2 nm (Figure 1), so ion-sieving becomes less apparent than for carbon C1-1 due to less hindered access of larger cations to porosity. It is also likely that there is no strong effect of dielectric permittivity on the observed differences in capacitance since the same electrolyte should normally possess the same  $\epsilon_r$  value independently of the electrode material. Since capacitive responses vary strongly in the series of ionic liquids for carbon C1-1 only, such dissimilarity in capacitance evolution is most likely due to the effect of pore size distribution.

A recent study using ionic liquids with the chloride anion [24] and a non-porous glassy carbon electrode has shown the differential capacitance to follow the order  $\text{HMI} < \text{BMI} < \text{EMI}$  in ionic liquids, which is attributed to the denser double layer for smaller imidazolium cations (the shorter the alkyl chain length, the closer the approach to the electrode surface). For nanoporous electrodes, our study brings out a similar trend, but for the gravimetric capacitance data of two-electrode cells. Since this trend is much more spectacular for the carbon C1-1, it is heavily strengthened by the effect of pore size distribution of this carbon, which excludes the larger cations.

### 3.2 Comparison between pure and dissolved ionic liquids.

The most striking and unexpected result of our study is the capacitive behavior of the carbons C1-1 and C2-1 when using ILs solutions in acetonitrile (Figures 2B and 2D). As distinct from the case of pure IL electrolytes, dissolved ILs exhibit little or no difference in capacitive response whatever the carbon used. In fact, for the C1-1 carbon (Figure 2B), the capacitance of the dissolved HMI-based system is only slightly smaller than that of the dissolved EMI or BMI-based ones; it is also noteworthy that the voltammograms for the EMI- and BMI-based electrolytes virtually overlap. Another important result is significantly lower capacitance values using pure ILs in comparison to their dissolved salts. However, this can be seen only for the carbon C1-1 (see Figure 4A for the pure or dissolved HMI solution) whose feature is a closer fit of pore and ion sizes. For the carbon C2-1, having



larger micropores than the carbon C1-1, the capacitance values with the IL-based systems are not quite different from the respective systems using dissolved electrolyte even for the IL having the cation with the longest alkyl chain, i.e. HMI (Figure 4B). At the same time, the voltammograms with pure ILs are more resistive, which arises naturally from their higher resistivity in comparison to their respective solutions (Figure 4).

Hence, the ion-sieving effect is markedly distinguishable with pure ionic liquid electrolytes for the carbon C1-1, but disappears virtually when the same salts are used in dissolved state in a capacitor with the same carbon C1-1. This suggests that, even for the carbon C1-1, virtually the same surface area  $A$  (see formula 2) is accessible for any of the three cations moving out of acetonitrile into the electrode pores, *i.e.* there is almost no difference in pore accessibility among the cations. This could plausibly arise due to non-rigid alkyl chains being freer to move in solution than in pure ILs. In other words, dissolved cations, especially BMI and HMI, could more readily adopt a geometry that provides no or little difference in cation size before penetrating the pores. As a result, the overall cation size could easily be minimized for the non-rigid cations to fit smaller pores. Thus, in the case of dissolved electrolytes, a larger part of specific surface area would become available for charge storage, which consequently enhances the gravimetric capacitance.

Lower capacitance values with pure ILs in comparison with their dissolved use were observed for phosphonium-based salts [25], but this study did not focus on the effect of pore size distribution on capacitance, which prevents a detailed comparison with our work. On the other hand, the ion-sieving effect was demonstrated using a series of phosphonium-based ionic liquids [11], but the behavior of dissolved salts was not studied, which also precludes a deeper analysis in comparison with our data.

A distinctive feature of ion-selective electrosorption is a clear kinetic effect, which can be manifested by a stronger decrease in the charge storage rate when there is a good size fit between pores and ions [26-28]. In fact, Figure 5 shows that the capacitance values undergo a stronger enhancement at a lower scan rate for pure ILs than for dissolved electrolytes (compare the difference between the voltammograms at 0.2 mV/s and 1 mV/s in Figure 5A and B for the pure HMI-based IL and dissolved IL). It is an additional proof for the stronger ion-sieving effect in pure ionic liquid medium.

In summary, our results show that the use of dissolved ionic liquids is beneficial in terms of gravimetric capacitance due to the likely effect of more flexible cations in solutions, which makes more porosity available to charge storage.

## 4 Conclusion

We have demonstrated a clear ion-sieving effect in pure ionic liquids, in agreement to other related studies [11, 12], but the most important and novel result is a strong difference in capacitive responses between pure and dissolved ionic liquids for ion-sieving carbons. We have also evidenced that the ion-sieving effect, clearly observable in pure ILs, is heavily mitigated for the same salts used in solution, most likely due to somewhat stronger geometrical flexibility of dissolved ions. Furthermore, for the electrode materials showing the ion-sieving effect, the gravimetric capacitance values of dissolved salts are higher in comparison to pure ionic liquids. The dissimilarity of capacitance values between pure ionic liquids and dissolved salts in ion-sieving carbons highlights their respective advantages and disadvantages in terms of energy density: whereas purely ionic electrolytes can potentially provide a larger working voltage window, the corresponding dissolved salts can access smaller pores, mostly contributing to higher capacitance values. Thus, this finding should be of use in the optimization of prospective industrial systems using both pure ionic liquids and their respective solutions.

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## Figure Captions

**Figure 1.** QSDFT pore size distribution of the nanoporous carbons C1-1 and C2-1.

**Figure 2.** Cyclic voltammograms at  $1 \text{ mV s}^{-1}$  for the EDLCs using the carbons C1-1 (A, B) and C2-1 (C, D). The left-hand side graphs are for the pure ionic liquids, and the right-hand side ones for their solutions in acetonitrile. Numerals indicate: 1-EMI; 2-BMI; 3-HMI.

**Figure 3.** Structure and size of 1-alkyl-3-methylimidazolium cations used in the ionic liquids. The thickness perpendicular to the ion plane direction is 0.37 nm.

**Figure 4.** Comparison between cyclic voltammograms at  $1 \text{ mV s}^{-1}$  for the EDLCs using the HMI cation and the carbons C1-1 (A) and C2-1 (B). 1: pure IL; 2:  $0.5 \text{ mol L}^{-1}$  solution.

**Figure 5.** Cyclic voltammograms for the EDLCs using the carbon C1-1 and the HMI-based pure (A) and dissolved (B) ionic liquid. 1:  $1 \text{ mV s}^{-1}$ ; 2:  $0.2 \text{ mV s}^{-1}$ .

Figure 1

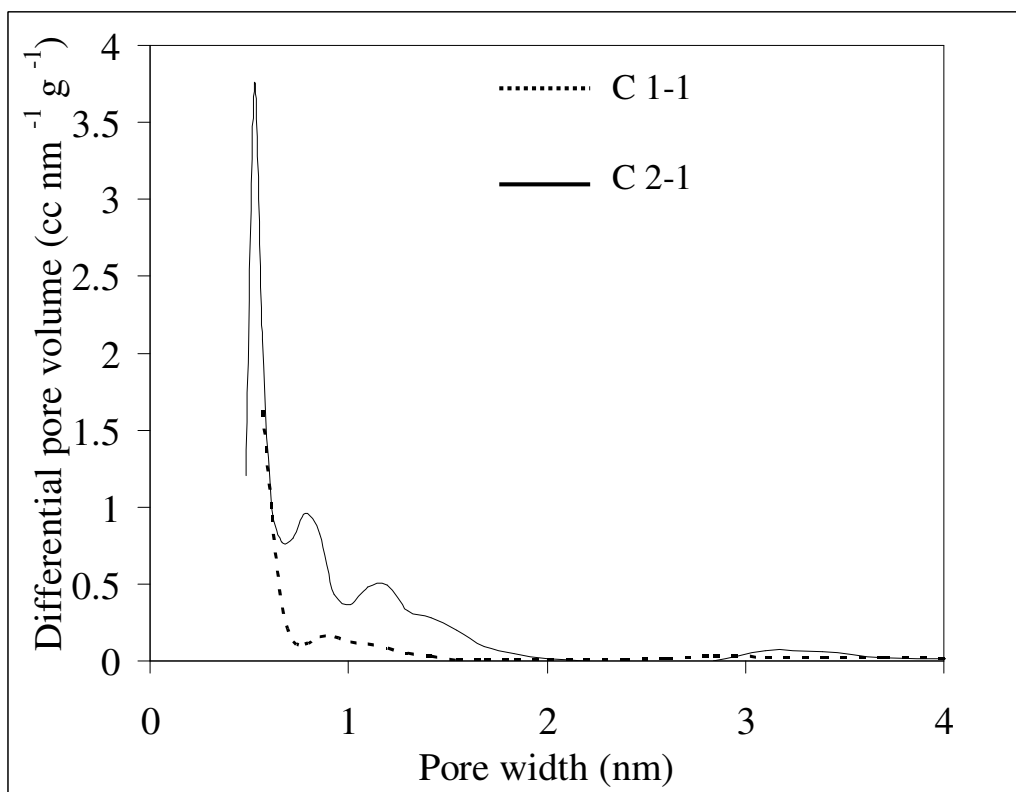


Figure 2

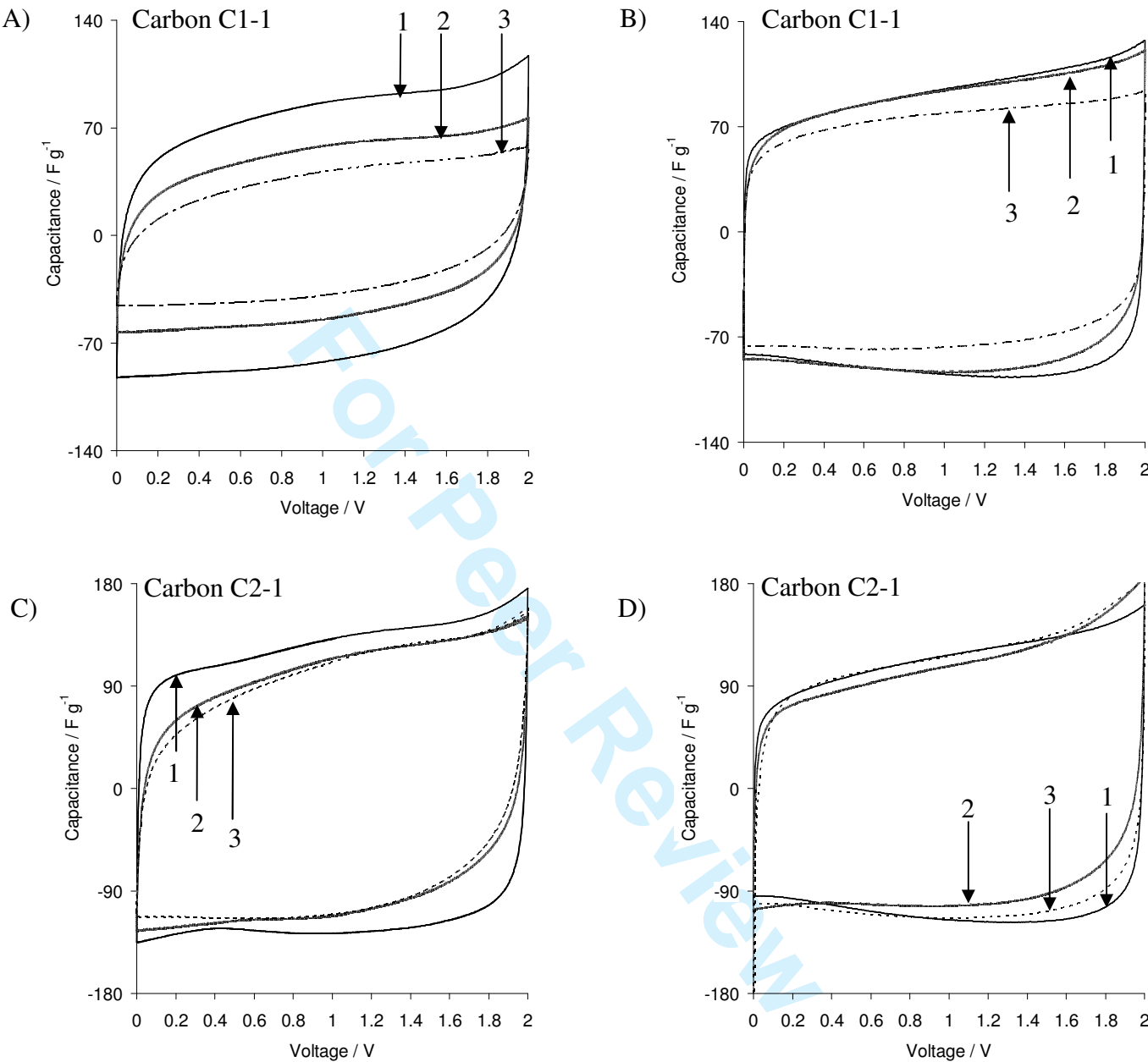


Figure 3

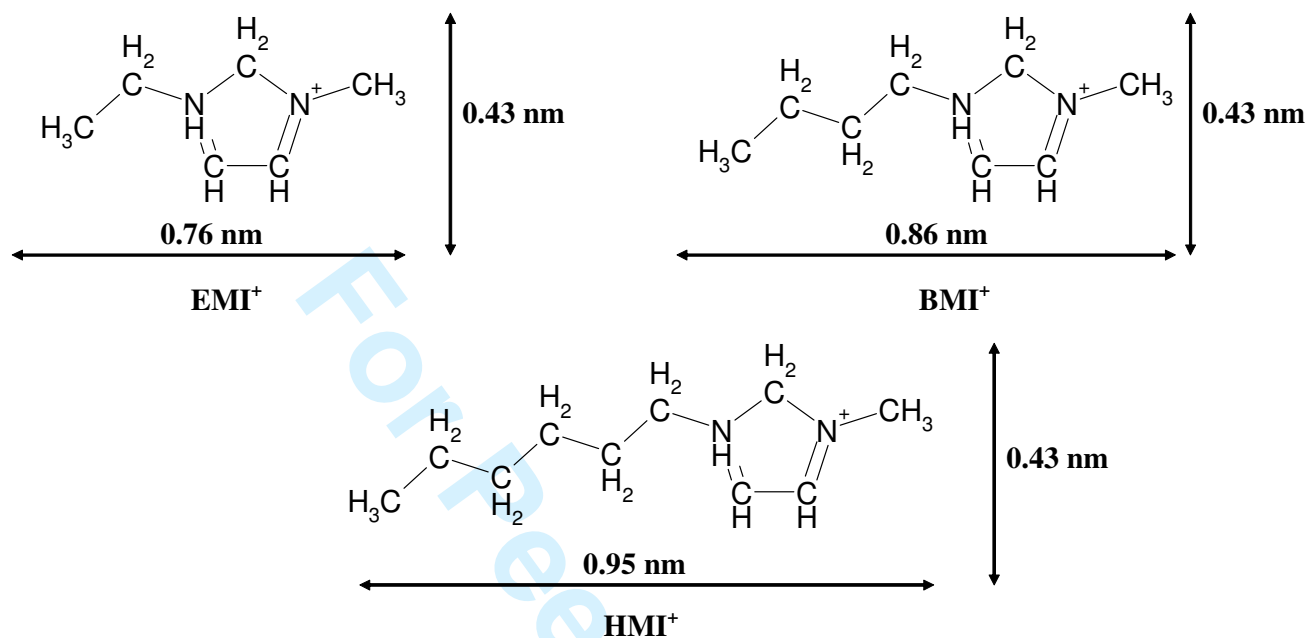




Figure 4

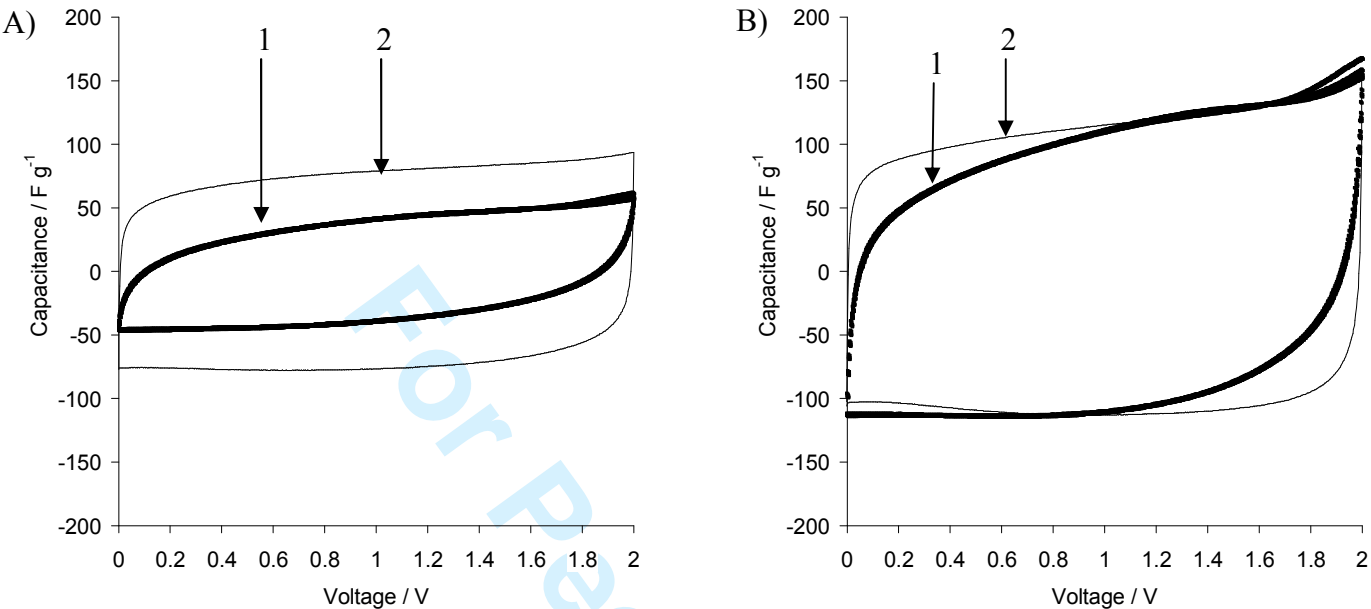


Figure 5

