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Steric effects in adsorption of ions from mixed electrolytes into microporous carbon

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ABSTRACT

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With the goal to improve the capacitance in electrochemical double-layer capacitors (EDLCs) many studies on pore size/ion size relationship have been undertaken to achieve a better understanding of the charge storage mechanism in the electrochemical double-layer in confinement. A significant capacitance increase was achieved by using carbon electrodes with micropores (<1 nm), when the carbon pore size was close to the ion size. In this paper, the accessibility of narrow pores is investigated by selecting a carbon with a small pore size (<0.7 nm) and electrolyte mixtures with different ion sizes. It has been shown that the adsorption capacitance limitation observed for large cations and anions could be overcome by adding ions with a smaller effective size. This result demonstrates that the pores are accessible when their size matches the effective ion size and contradicts the surface saturation assumption; effective ion size which exceeds the pore size leads to current limitation. This work confirms that the steric effect is involved when ions are adsorbed into pores and highlights the importance of controlling ion size/pore size relationship for optimisation of the capacitive performance of EDLC devices.

1. Introduction

Our generation faces increasing energy demands due to human activities and the associated environmental concerns. To address this challenge, research activities are directed towards the development of efficient technologies for storing and delivering energy. Electrochemical double-layer capacitors (EDLCs), also called supercapacitors, can meet the demand of high power during few seconds and, along with batteries, provide the energy storage for renewable energy sources.

Based on electrostatic adsorption of ions from an electrolyte onto porous carbon electrodes with large specific surface area (1000–2000 m^2/g), EDLCs have high power density and can store more charge than conventional capacitors. However, their energy density is far below that of batteries and the energy density of EDLCs must be increased for broadening their range of applications.

Recent studies showed that a large increase of capacitance [1] was obtained in micropores by using carbide derived carbons (CDCs) as model materials, which have controlled, narrow pore size distributions below 1 nm [2]. Several studies of carbons with tailored subnanometer porosity showed that during the electrochemical charge storage, the double-layer capacitance can be limited for some pore sizes due to a sieving effect [3–11]. More specific studies have shown that the limitations in both the capacitive behaviour and the

ion transport increased when the carbon pore size decreased below the effective ion size of the electrolyte [9,10,12]. This result was explained by a steric limitation due to ion size effect. At the same time, recent work attributed this capacitance decay at small carbon pore size to a surface saturation of the micropores [13,14]. This paper aims to clarify the ion adsorption mechanism in confined pores of charged carbon structures by determining the origin of the limitation of the capacitive behaviour reported in previous studies [9,10,13,14].

2. Material and methods

CDC powders (Y-Carbon, USA) with controlled, fine-tuned pore size distributions were synthesised from Titanium Carbide (TiC) powder (Alfa Aesar #40178, particle size 2 μm) which was chlorinated 3 h at 500 °C in a horizontal tube furnace. The chlorination process was followed by annealing treatment 3 h at 600 °C to remove any chlorines or chlorides remaining in the carbon pores [2]. The structural characterisation of TiC-CDC as well as specific surface area (SSA) and the pore size distributions (PSD) calculated by the nonlocal density functional theory (NLDFT) [15] have been reported elsewhere [1,2,16].

Three electrolytes were investigated in this study (i) 1.5 M solution of tetraethylammonium tetrafluoroborate (NEt$_4$BF$_4$) (Acros Organics, CAS #429-06-1) in acetonitrile (AN) (Acros Organics, CAS #75-05-8, H$_2$O <10 ppm) solvent, (ii) 2 M solution of 1-ethyl-3-methylimidazolim bis(trifluoromethane-sulfonyl)imide (EMI,TFSI) (Solvionic company) in AN and (iii) 2 M solution of 1-ethyl-3-

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methylimidazolium tetrafluoroborate (EMI,BF$_4$) (Sigma Aldrich, CAS #143314-16-3) in AN.

Electrochemical tests were performed using a cavity microelectrode (CME) technique [17,18]. The CME used in this study consists of a glass tube in which a platinum wire was sealed and one of its extremities was dissolved in aqua regia to create a cavity with a diameter of 150 μm and depth around 50 μm. The active material was packed inside the cavity by pressing the powder onto a glass plate. The counter electrode was a 1 cm^2 rolled platinum foil and the quasi-reference electrode was a silver rod. The electrochemical cells were assembled in a glove box under Ar atmosphere with less than 1 ppm of water and oxygen content.

Cyclic voltammetry (CV) measurements were done at room temperature with a multi-channel potentiostat/galvanostat (VMP3, Biologic).

3. Results and discussion

### 3.1. Additions of EMI,BF$_4$ to NEt$_4$BF$_4$-based electrolyte

Fig. 1A shows the CVs recorded at 20 mV.s^{-1} for a TiC-CDC prepared at 500 °C, with a pore size of 0.68 nm and a specific surface area of 1140 m^2/g, in 1.5 M NEt$_4$BF$_4$ in AN electrolyte with addition of various concentrations of EMI,BF$_4$, the CVs were normalised for comparison purpose. For the CV measured in 1.5 M NEt$_4$BF$_4$ in AN without any addition of EMI,BF$_4$, the open circuit voltage (OCV) was found to be around +0.3 V/Ref for this material. In the potential range between +0.3 and +0.9 V/Ref where BF$_4^-$ anions are adsorbed, the current response exhibits a rectangular shape typical for a capacitive behaviour.

Table 1
Neat, solvated and effective ion sizes.

	Cation size (nm)		Anion size (nm)	
	NEt$_4^+$ [9]	EMI$^+$ [10]	BF$_4^-$ [9]	TFSI$^-$ [10]
Chemical formula	(CH$_2$CH$_3$)$_4$N$^+$	(CH$_3$)$_2$(CH$_3$)$_4$N$_2^+$	BF$_4^-$	(SO$_2$CF$_3$)$_2$N$^-$
Neat ion	0.68	0.76	0.48	0.79
Solvated ion in AN	1.30	1.77	1.16	2.24
Effective ion size in pores	0.8 < d < 1	≈ 0.7	≤ 0.68	≈ 0.75

Conversely, in the potential range between −1.4 and +0.3 V/Ref, where NEt$_4^+$ cations are adsorbed, the distortion of the CV is attributed to a limitation in the NEt$_4^+$ adsorption. This current limitation observed in such small pores was assigned to a steric hindering because the pores are too narrow to accommodate these cations (effective ion size estimated between 0.8 and 1 nm, Table 1) [9].

In the +0.3 to +0.9 V/Ref voltage window (anion adsorption), the capacitive response is not affected by addition of EMI,BF$_4$, which was expected since the anion of the additional electrolyte (EMI,BF$_4$) is the same as the supporting electrolyte (NEt$_4$BF$_4$). However, in the −1.4 to +0.3 V/Ref potential range, the current increases with the concentration of EMI,BF$_4$, thus more ions can access the pores. In a 1.5 M NEt$_4$BF$_4$ in AN electrolyte, the effective ion size of the NEt$_4^+$ cations adsorbed in the CDC pores was estimated between 0.8 nm and 1 nm (Table 1) [9]. From electrochemical measurements in 2 M EMI, TFSI in AN electrolyte, the EMI$^+$ effective cation size was found to be around 0.7 nm (Table 1) [10], that is smaller than that of NEt$_4^+$ cations. Accordingly, the current increase observed in Fig. 1A with
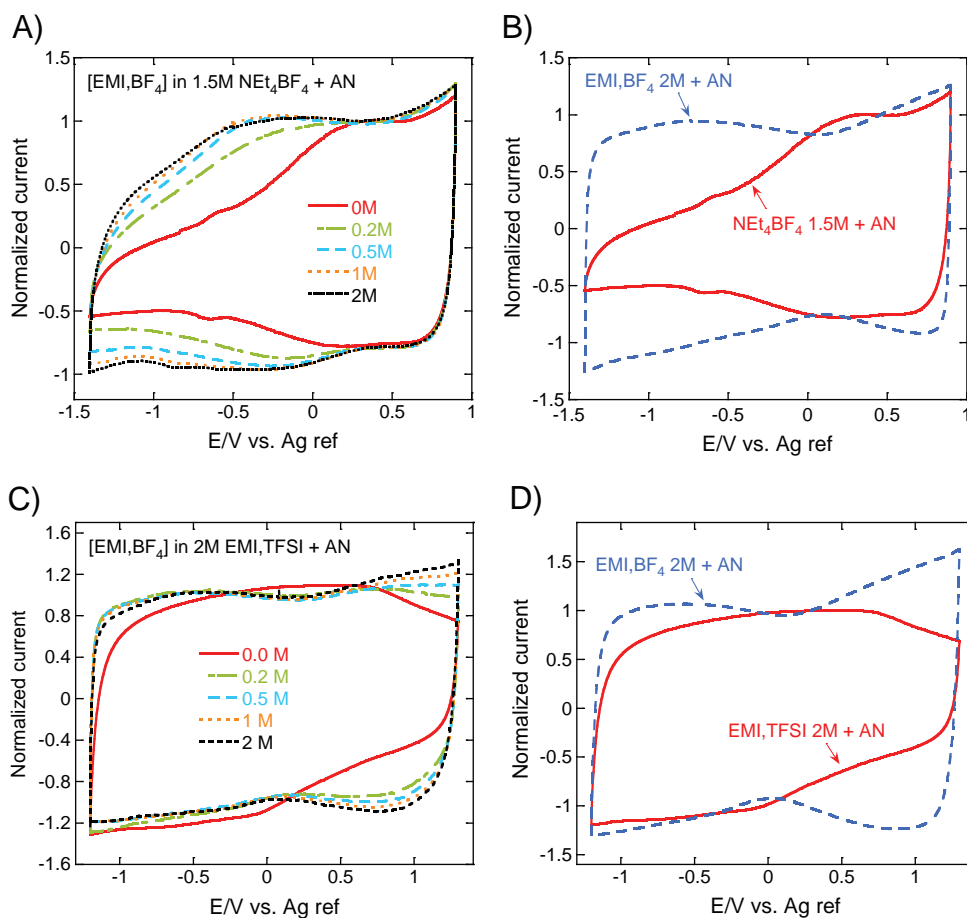
Fig. 1. Normalised CVs of TiC-CDC with 0.68 nm pores in 1.5 M NEt4BF4 in AN (A) and 2 M EMI,TFSI in AN (C) with addition of different amounts of EMI,BF4 and comparison of 1.5 M NEt4BF4 in AN (B) and 2 M EMI,TFSI in AN (D) with 2 M EMI,BF4 in AN. CVs were measured at 20 mV.s^{-1} (A and B) and 100 mV.s^{-1} (C and D).

increased concentration of EMI,BF$_4$ originates from the adsorption of the EMI$^+$ ions that, being smaller than NEt$_4^+$ cations, can access the micropores of the carbon, whilst the bigger NEt$_4^+$ cations are blocked. This sieving effect, already reported by many authors, is then assumed to be linked with a volumetric limitation (size effect) rather than a charge saturation proposed recently [13,14]. In Fig. 1A, it can be seen that whatever the concentration of EMI,BF$_4$ added to the EMI,TFSI electrolyte, there is still a slight distortion from the ideal capacitive behaviour at low potential on the reverse scan. This is explained by the increased interactions between the different cations present in the solution since the ionic strength of the electrolyte was not kept constant. It is also necessary to take into account that the pore size distribution has a certain width [16] and pores smaller than the size of EMI$^+$ ions are present in CDC along with pores that are larger than NEt$_4^+$ ions.

CV curves of the 0.68 nm TiC-CDC sample in the two electrolytes containing the same anion, 1.5 M NEt$_4$BF$_4$ in AN and 2 M EMI,BF$_4$ in AN, are shown in Fig. 1B. Currents were normalised in these experiments, since the amount of carbon powder packed in the micro cavity varies between the two tests [9]. At voltages beyond the OCV value (+0.2 V/Ref), where the BF$_4^-$ anion adsorption can be seen, both CVs exhibit a capacitive behaviour. As previously mentioned, in the −1.4 to +0.3 V/Ref potential window, NEt$_4^+$ cation adsorption is limited in 1.5 M NEt$_4$BF$_4$ in AN. On the other hand, the CV in 2 M EMI,BF$_4$ in AN shows a rectangular shape typical from a pure capacitive behaviour, thus indicating that EMI$^+$ cations are adsorbed into the pores without any limitation and fully participate in the electrochemical charge storage. This supports again the volumetric limitation for the cation adsorption into the carbon pores.

3.2. Additions of EMI,BF$_4$ to EMI,TFSI-based electrolyte

Fig. 1C shows the normalised CVs of the same TiC-CDC sample with 0.68 nm pore size recorded between −1.2 and +1.3 V/Ref at 100 mV.s^{-1} in 2 M EMI,TFSI dissolved in AN containing increased concentration of EMI,BF$_4$. In 2 M EMI,TFSI in AN without any addition of EMI,BF$_4$, the rectangular shape of the CV can be seen in a potential range from −1.2 to +0.2 V/Ref (OCV), where the EMI$^+$ cations are adsorbed, which is typical for a pure capacitive behaviour. However, the CV is distorted in the potential range where adsorption of larger TFSI$^-$ anions occurs (+0.2 to +1.3 V/Ref). The limitation in current observed at high potential evidences a limitation in the anion adsorption [10]. As a result, in the present experiments, a carbon pore size of 0.68 nm is large enough for EMI$^+$ adsorption but, on the other hand, shows a capacitance limitation for TFSI$^-$ adsorption.

In the −1.2 to +0.2 V/Ref (OCV) potential range where cations are adsorbed, the rectangular CV shape is preserved, as expected, after additions of EMI,BF$_4$ since the same cation (EMI$^+$) is added to the electrolyte. In the +0.2 to +1.3 V/Ref potential window, where the TFSI$^-$ anion adsorption is observed, the current increases when EMI,BF$_4$ is added to the electrolyte. In a 1.5 M NEt$_4$BF$_4$ in AN electrolyte, the effective BF$_4^-$ anion size seen by a carbon electrode during ion adsorption is smaller than 0.68 nm (Table 1) [9]. The effective TFSI$^-$ anion size estimated from electrochemical experiments from a 2 M EMI,TFSI in AN electrolyte was about 0.75 nm (Table 1) [10]. In Fig. 1C, the current limitation previously observed for the TFSI$^-$ adsorption is now suppressed by additions of BF$_4^-$ to the electrolyte. This shows that pores are accessible to BF$_4^-$ ions, in good agreement with the smaller size of the BF$_4^-$ ion compared to the TFSI$^-$. These experiments conducted on the anion adsorption confirm that the ion sieving effect observed for the 2 M EMI,TFSI in AN electrolyte is linked to steric effect (volumetric saturation) and not to a saturation of the carbon surface by the ions. Finally, a comparison of the electrochemical signature of the 0.68 nm pore size CDC sample in EMI,TFSI and EMI,BF$_4$ dissolved in AN is presented in Fig. 1D. The electrochemical signature of the 0.68 nm pore size sample in the 2 M EMI,BF$_4$ in AN

electrolyte shows a typical capacitive behaviour for both the anion and cation adsorption, thus demonstrating that a careful selection of the electrolyte/carbon couple is needed to optimise the charge storage in carbon nanopores. In our previous studies [19] and work of others [20], optimisation of capacitance has been done by changing the pore size of CDC. We show here that it is also possible to tune the electrolyte composition to match a specific pore size of the carbon electrode.

4. Conclusions

Cyclic voltammetry on TiC-CDC with a narrow distribution of pores with the average size of ~0.68 nm has been used for screening the adsorption of different cations and anions in the carbon pores. NEt$_4^+$ and TFSI$^-$ ion adsorption limitations were first observed in acetonitrile-based electrolytes. Current increase obtained after addition of EMI$^+$ to NEt$_4^+$ and BF$_4^-$ to TFSI$^-$ shows that the pore accessibility is controlled by the size effect: limitations observed for NEt$_4^+$ and TFSI$^-$ adsorption are not due to a charge saturation of the carbon surface inside the pores by the ions, but to a steric (volumetric) effect. This work helps in understanding the ion adsorption mechanism and supports the importance of matching the pore size of the carbon electrode and the effective ion size of the electrolyte ions for enhancing the capacitance of the system.

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