Insights on the Behavior of Imidazolium Ionic Liquids as Electrolytes in Carbon-based Supercapacitors: an Applied Electrochemical Approach

Paulo F. R. Ortega^{c*}, Garbas A. dos Santos Junior^b, João P. C. Trigueiro^d, Glaura G. Silva^b, Noemí Quintanal^a, Clara Blanco^a, Rodrigo L. Lavall^{b*}, and Ricardo Santamaría^{a*}

- a. Instituto Nacional del Carbón, INCAR-CSIC, Apdo. 73, 33080-Oviedo, Spain
- b. Departamento de Química/ICEx, Universidade Federal de Minas Gerais, Av. Antônio Carlos, 6627, Pampulha, CEP 31270-901, Belo Horizonte - MG, Brazil
- c. Departamento de Química, Centro Federal de Educação Tecnológica de Minas Gerais, Av. Amazonas, 5253 – Nova Suíça, CEP 30421-5169, Belo Horizonte - MG, Brazil
- d. Instituto Federal de Minas Gerais - Campus Betim, Rua Itaguaçu, 595, São Caetano, CEP 32677-562, Betim - MG, Brazil

***Corresponding authors.**

E-mail address: pauloortega@cefetmg.br (Paulo F. R. Ortega), rodrigo.lavall@qui.ufmg.br (Rodrigo L. Lavall), riqui@incar.csic.es (Ricardo Santamaría).

ABSTRACT

This study aims to increase the knowledge on the interactions that occur at the electrode/electrolyte interface in carbon-based electric double layer capacitors (EDLC) when solvent-free ionic liquids are used as electrolytes. Many previous studies found in the literature are conducted using theoretical approaches and they are unable to model all the variables and the complexity of an actual device with a complex carbon surface and an ionic liquid (IL). Here, the compatibility between imidazolium ionic liquids and different carbon materials – an activated carbon (AC), a mesoporous carbon (MES), multi-walled carbon nanotubes (MWCNT), and reduced graphene oxide (RGO) - is empirically investigated applying synchronous chronopotentiometric tests to various symmetrical EDLCs. The study of the simultaneous evolution of the cell and electrode potentials of the various carbon/ILs cells, monitoring the evolution of specific capacitances and electrical resistances for each independent electrode, allows inferring about the ion-electrode compatibility, the limiting factors for charge accumulation and its impacts on the performance of the global cell. The results indicate that the sp^2 structures of MWCNT and RGO favor interactions with the EMI^+ cation on the negative electrode. In the positive electrodes, MES and AC favor interactions with the BF_4^- and $TFSI^-$ anions, respectively, yielding a higher specific capacitance and lower resistance.

INTRODUCTION

Over the last few decades, electric double-layer capacitors (EDLC), also known as supercapacitors, have been the focus of numerous studies due to their complementary characteristics to that of batteries.¹⁻² Although not yet rivaling batteries in energy density, supercapacitors are more suitable for applications with peak demands due to their higher power densities. This ability to store and release energy at high charge rates is due to its operating mechanism that is based on the accumulation of ions from the electrolyte at the surface of electrodes under polarization.³ Besides, in this mechanism, there is no occurrence of chemical reactions and it is essentially electrostatic so that the electrodes have less chemical stresses.²⁻³ This also justifies the greater cyclability of EDLCs in relation to batteries.

The main challenge in the applied supercapacitor research is to increase the capacitance and energy density of these systems to obtain a single device that meets the high demands for energy and power. Since the energy density of EDLCs is proportional to both the capacitance (C) and the square of the cell potential (V), it is possible to maximize the energy density of the cell by optimizing these two parameters.²

Capacitance is a property that depends primarily on the electrode/electrolyte interface and it maximizes using materials with a high specific surface area and with a porous structure suitable for the insertion of the electrolyte ions.⁴ It is also common to obtain higher C values with the use of pseudocapacitive materials (such as conductive polymers, metal oxides, and metal nitrides), which are capable of storing charge similarly to batteries but through rapid and reversible redox reactions occurring at the interface.³ Since the capacitance (or capacity) of faradic reactions is greater than that of the electrical double layer, it is possible to combine these mechanisms in supercapacitors constructed with carbon materials in three basic ways:³⁻⁷ (i) modifying the surface (functionalization) of carbons with redox-active groups; (ii) coupling a battery-type electrode and an EDLC-type electrode in a hybrid device; (iii) adding to the electrolyte species that can be adsorbed and be capable of transferring electrons at the interface (redox-shuttle). Although these approaches abruptly increase the capacitance of the cells, they usually reduce the cyclability over conventional EDLC.⁴

On the other hand, the cell potential is specified, at first, by the electrochemical stability window of the electrolyte.⁴ The most stable electrolytes at high potentials are the most used in EDLCs, especially the organic ones based on acetonitrile or propylene carbonate as solvents that are capable of operating at 2.7 – 3.0 V.^{1, 4, 8} However, characteristics such as volatility, flammability and toxicity are inherent in these electrolytes that can become dangerous in situations of overpotential, for example.¹ Aqueous electrolytes are an interesting alternative because they are cheap, safer, but with a limited stability window that normally does not exceed 1.2 V.^{1, 4, 8} In this sense, ionic liquids (ILs) are strategic because they have the largest electrochemical stability windows and ideal physicochemical properties for building safe cells: low vapor pressure and non flammability.^{4, 8}

Although ILs have properties that, in theory, allow maximizing the energy density of supercapacitors (as they can operate in wide ranges of potentials), the construction of cells based on these electrolytes requires more than simply combining them with high specific surface area electrodes.⁹ ILs are viscous electrolytes, have low conductivity and its high theoretical stability window (> 5.0 V) is not supported by conventional carbon electrodes.⁹ Our group has recently published a paper discussing the conditions that should be taken into account to determine the maximum cell potential ($V_{\max}$) in EDLCs based on ILs and the consequences of the selection of this $V_{\max}$ to the cell efficiencies (energy and coulombic).⁹ The paper shows that even in favorable conditions that allow the cells to work in high stability windows and with coulombic efficiencies close to 100%, the high viscosity of ILs increases the resistance of the device, decreasing the rate capability and energy efficiency at high current densities and ambient temperature.⁹

At the microscopic level, ILs are even more complex because they have voluminous cations and anions that present strong ion-ion electrostatic interactions.¹⁰ Regarding the electric double layer formation, ILs cannot be considered as ideal electrolytes, and sometimes their behavior is quite intriguing.¹¹ Also, their structures are complex, quite far from the ideal spherical form, and the concept of solvation shell is now not easy to define.^{10, 12-13} As a consequence of this, the interaction and insertion of IL ions into the structure of a porous material is dramatically affected, and the selection of electrode materials taking into account only a high surface area and high pore volume does not guarantee the highest capacitance.

The knowledge of the microscopic structure is undoubtedly a key point for the use of ILs in actual electrochemical devices. Some theoretical investigations and calculations have shown that ILs present ion arrangements with some local order even in the liquid phase, generating supramolecular structures. This is one of the reasons that make difficult the correlation between the structure and physicochemical properties of the ILs.^{10, 12, 14} Besides, these supramolecular structures can be affected by the presence of an electric field.^{10, 12} This effect is little known and should affect the performance of electrochemical devices that use IL as electrolytes and that are subjected to high voltages. Furthermore, theoretical studies have shown the ions of an electrolyte interact specifically within the pores of the carbon electrodes.^{11, 15-17} Unfortunately, these microscopic considerations are addressed mainly in theoretical studies that simulate conditions very different from those to which the real devices are subject.

The electrochemical parameters of real cells such as capacitances and resistances are affected by numerous variables that are difficult to compile in theoretical simulations. For example, the surface of the electrodes has heterogeneous porous networks with rich surface chemistry that impacts the adsorption and diffusion of ions. Ion-pore interactions can also be different in two electrodes of an EDLC that present symmetrical configuration (with the same material and the same mass in both electrodes).⁵ Then, the same material can present different resistances and specific capacitances while operating as a positive or negative electrode. Such differences are accentuated in EDLC based on ILs, especially due to the size of the ions (which can form aggregates by strong ion-ion interactions when accessing the pores). Additionally, the ILs present complex structures that could be formed by several functional groups, aromatic rings, and hydrophobic and/or hydrophilic parts - elements that can interact with the surface of the carbon electrodes quite differently. In light of these considerations, it is not well understood how these interactions affect the electrochemical properties of the EDLCs. Besides, these microscopic effects are not properly considered in the several experimental researches published in the literature.

The present study investigates the performance of EDLCs based on IL focusing on the behavior of each electrode individually and mainly in the compatibility of each IL with the different carbon materials using an applied electrochemistry approach. For this purpose, two ionic liquids were selected:

the 1-ethyl-3-methylimidazolium bis(trifluoromethane)sulfonamide (EMITFSI) and the 1-ethyl-3-methylimidazolium tetrafluoroborate (EMIBF₄); and four carbon materials: activated carbon (AC), mesoporous carbon (MES), multi-walled carbon nanotubes (MWCNT), and reduced graphene oxide (RGO). The main goal of this study is to understand how the structures of the ILs interact and affect the behavior of four electrode active materials having different surface areas, pore sizes and surface chemistry using synchronous chronopotentiometric tests. Finally, in this work, we present a set of data critically evaluated and discussed with the intention of enlightening particularities of IL-based EDLCs to build more efficient cells with improved performance.

EXPERIMENTAL

Materials. Two ionic liquids (ILs) were employed as electrolytes: EMITFSI (Sigma-Aldrich, >99%, Spain) and EMIBF₄ (Io-Li-Tec, >98%, Germany). Multi-walled carbon nanotubes (MWCNT) were obtained from Sigma-Aldrich with 95% purity, average length ~5 μm , and a diameter between 6-9 nm.

Reduced graphene oxide (RGO) was obtained by oxidative treatment of graphite using a modified Hummers method.¹⁸ Concentrated H₂SO₄ (400 mL) was added to a mixture of graphite (15 g) and NaNO₃ (7.5 g) and then cooled below 0 °C using an ice bath. After that, KMnO₄ (45 g) was added slowly in small doses to keep the system always below 20 °C. The ice bath was then replaced by a water bath and the solution was heated to 35 °C and magnetically stirred for 1 h.

To obtain the AC, the mesophase pitch produced by Mitsubishi Gas Chemicals has been chemically activated with KOH. The mesophase pitch was mixed with the activating agent in a proportion of 5:1 (mass ratio between KOH and carbon) by hand-grinding in a mortar. Then, the sample was carbonized at 700 °C for 1 h, in a nitrogen atmosphere, with an initial heating rate of 2.5 °C min⁻¹. After heat treatment and with the sample at room temperature, it was neutralized with 3 M HCl solution and washed with distilled water until neutral pH. Finally, the resulting CA was dried at 110 °C in vacuum for 24 h.

Mesoporous carbon (MES) was synthesized based on a method well established in the literature (template method).¹⁹⁻²⁰ 1.0 g of silica gel (Sigma-Aldrich, 550 m² g⁻¹, particle size: 63-210 mesh, pore size: 60 Å, pore volume: ~0.8 cm³ g⁻¹ - information provided by the manufacturer) was stirred for 1 h in

a solution of 0.5 M p-toluenesulfonic acid (PTS), and then filtered and dried for 3 h at 80 °C. This procedure was used to impregnate PTS inside the silica gel to act as a catalyst for the polymerization of furfuryl alcohol. After that, 0.95 g of furfuryl alcohol (Sigma-Aldrich, 98%) was added to the dried silica/PTS and heated at 80 °C for 24 h (in this step the polymerization of furfuryl alcohol to polyfurfuryl alcohol occurs). Next, the material (silica impregnated with polyfurfuryl alcohol) was carbonized at 800 °C for 1 h at 3 °C min⁻¹, under nitrogen flow. Finally, the silica was etched using an HF aqueous solution where it was kept for 24 h. The resultant material (MES) was filtered, washed with distilled water, and dried at 120 °C for 2 h.

Materials characterization. The textural characteristics of the carbon materials were obtained from their N₂ isotherms at 77 K, which were carried out in a Micromeritics ASAP 2420. Different methods were used to evaluate the textural properties of the carbon materials, where Brunauer-Emmett-Teller (BET) was used to calculate the specific surface area (S_{BET}) and Dubinn-Radushkevich methods have been used to micropore analysis. To evaluate the pore size distribution, different models were used to suit the specificities of each material: Quenched Solid Density Functional Theory (QSDFT) was used for the analysis of GRO, AC, and MES and Kruk-Jaroniec-Sayari (KJS) method was used for MWCNT.

The C, N, and H content were quantified from the combustion (at 1050 °C) of 1 mg of the corresponding sample using a LECO-CHNS-932 microanalyzer. The total oxygen content of the samples was determined in a LECO-TF-900 furnace coupled with the previous equipment. The electrical conductivity was measured on the shaped discs prepared by mixing 90 wt.% of the carbon material and 10 wt.% of polytetrafluoroethylene using a four-point probe system (Keithley Instruments, Model 238 High Current Source Measure Unit, USA).

Preparation of electrodes and supercapacitor cells. The electrodes were prepared by mixing 90 wt.% of the carbon material and 10 wt.% of polytetrafluoroethylene as the binder. The mixture was prepared in a mortar and pressed into disk-shaped electrodes (weighing approximately 30 mg, with a diameter of 1.13 cm² and a thickness of about 0.4 mm). Symmetric cells were built with glass fiber separators and gold current collectors, using a “T-type” Swagelok® cell. The Ag/AgCl/3.5M KCl reference electrode

was used as a third-end connection to record the potentials of the electrodes and all cells were assembled and sealed in a dry box containing argon atmosphere.

Electrochemical characterization. The electrochemical measurements were carried out at 25 °C in a BioLogic VMP3 Multichannel Potentiostat/Galvanostat. The electrochemical behavior of the devices was evaluated by synchronous cyclic chronopotentiometry, where the cell voltage and the potential of each electrode are recorded simultaneously. The galvanostatic tests were performed at different current densities (50 – 500 mA g⁻¹ concerning the active mass of the electrodes) and at a cell potential of 3.0 V. The values for the cell capacitance (C_{cell}), energy density (E_{sp}), power density (P_{sp}), coulombic efficiency (ϵ), specific capacitance of each electrode (C_+ or C_-), equivalent series resistance for cell and each electrode were calculated from the results of the galvanostatic experiments (details of the calculations can be found in Supporting Information).

RESULTS AND DISCUSSION

Characterization of the carbon materials. Figure 1 shows the N₂ adsorption/desorption isotherms for the four materials studied. The main quantitative textural data are summarized in Table 1.

Figure 1. N₂ adsorption/desorption isotherms and pore size distribution (inset) of (a) MWCNT, (b) RGO, (c) AC, and (d) MES.

The isotherms of MWCNT and RGO are both type II isotherms but important differences are found. In this type of isotherms, the formation of the adsorption monolayer is reflected as a small step in the low pressures range due to its low surface area (**Figure 1a, b**). In MWCNT, after this first step, the increase in the adsorbed amount is due to the adsorption in multilayer and then, at high pressures, due to the condensation of liquid nitrogen in interparticular holes. The S_{BET} calculated for this material is 256 m² g⁻¹ presenting mainly an open surface, with no development of porosity. RGO presents a higher specific surface area (454 m² g⁻¹) and a more complex structure, as shown by the strong hysteresis curve, a mixture of H3 and H4 types.²¹ This RGO is characterized by the presence of a wide range of mesopores diameters, mainly several tens nm in diameter (**Figure 1b** - inset). The shape of the pores is also relevant for the performance of the carbons as electrode materials. In these two materials, the differences are evident taking into consideration their nature. The surface area in MWCNT arises from interparticular spaces between the individual nanotubes and bunches of nanotubes. The surface area in

RGOs is due to the miss stacking of single layers (or small packs of a few layers), giving place to slit-shaped cavities. Considering the lateral size of the graphene layer the adsorption paths are much larger than in MWCNT.

AC shows a type Ib isotherm, presenting a rather wide knee and a little hysteresis that reflects a wide micropore size distribution.²¹ The DFT curve of this material (**Figure 1c** - inset) shows that although most pores are centered in the diameters of 0.6-0.8 nm, there are some larger pores, with even a small amount of mesopores, in the 2-3 nm range (leading to a mesopore volume of 0.31 cm³ g⁻¹). AC has a high value of S_{BET} (2240 m² g⁻¹) with an important contribution of S_{micro} (1349 m² g⁻¹). Also, it is generally accepted that the pores in microporous carbons are slit-shaped and that the interaction of carbon surface with many adsorbates is strong as a result of the small size of the cavity.²¹

The mesoporous carbon (MES) also shows a typical isotherm for this kind of material (type IV-a), with an important hysteresis (type H2-b). The S_{BET} is high (1347 m² g⁻¹) and the pore-size distribution is centered at ~6 nm (**Figure 1d** - inset), but there is also a relevant amount of micropores ($V_{\text{micro}} = 0.52 \text{ cm}^3 \text{ g}^{-1}$, $S_{\text{micro}} = 457 \text{ m}^2 \text{ g}^{-1}$). Nevertheless, it is clear that this carbon presents mainly mesopores, with a $V_{\text{meso}} = 1.11 \text{ cm}^3 \text{ g}^{-1}$, and the shape of the pores in this template mesoporous carbons is cylindrical.²¹

Table 1. Quantitative textural data for the different porous carbon materials studied.

Carbon material	S_{BET} (m² g⁻¹)	S_{micro} (m² g⁻¹)	V_{total} (cm³ g⁻¹)	V_{micro} (cm³ g⁻¹)	V_{meso} (cm³ g⁻¹)
MWCNT	256	-	0.34	-	-
RGO	454	-	0.53	-	-
AC	2240	1349	1.10	0.79	0.31
MES	1347	457	1.63	0.52	1.11

*where S_{BET} is the specific surface area; S_{micro} is the specific surface area of the micropores; V_{total} is the total pore volume; V_{micro} and V_{meso} are the micropores and mesoporous volume, respectively.

Table 2 summarizes the elemental composition and DC resistivities for the materials under study. The oxygen content has an impact on the surface properties of the carbon material. Oxygenated functional groups make the surface more polarized and improve their wettability in polar electrolytes.

On the other hand, a higher content of such groups also increases defects on the carbon structure, which increases resistivity. MWCNT and RGO have the lowest oxygen content and, therefore, with the less defective surface. Their surfaces are formed by carbon atoms of the sp^2 type, which guarantee resistivities with orders of magnitude lower than those of CA and MES. As the resistivity is a macroscopic property, the flat surface of the RGO favors stacking with greater orientation between graphene layers, improving the conductivity. This justifies the lower ρ values for RGO (0.03 Ω cm) concerning MWCNT (0.13 Ω cm).

AC and MES have richer surface chemistry, with higher oxygen content. In the case of AC, this content is even greater (8.57%) as a result of the synthesis method that uses oxidizing agents (KOH). Besides, this AC is derived from mesophase pitch and carbonized at 700 °C, factors that favor obtaining a material with relevant content from graphitic domains with a local short-range order.²² On the other hand, MES comes from the pyrolysis of a non-graphitizable source (poly(furfuryl alcohol)), within a porous mold (silica gel), and no chemical activation is used for the generation of pores. For these reasons, MES has a low degree of graphitization,¹⁹ its oxygen content is lower (2.90%) and its resistivity (315.04 Ω cm) is much higher than AC (13.63 Ω cm).

Table 2. Quantitative textural data for the different porous carbon materials studied.

<i>Carbon material</i>	C (wt. %)	H (wt. %)	N (wt. %)	O (wt. %)	ρ (Ω cm)
MWCNT	95.59	0.16	0.16	1.40	0.13
RGO	97.60	0.32	0.27	1.29	0.03
AC	85.80	0.50	0.18	8.57	13.63
MES	93.03	0.99	0.12	2.90	315.04

*where C, H, N, O wt.% means the weight percentage of each indicated elements and ρ is the DC resistivity obtained by the four-point probe method.

Characteristics of the ionic liquids. The ILs used in this study are commonly found in the supercapacitor literature because they have large electrochemical stability windows and are some of the least viscous among this type of electrolytes.^{9, 13, 23-24} Even though they are both based on imidazolium salts, they have very different properties.²⁵ EMITFSI is a hydrophobic liquid with a viscosity of 35.6 cP, the conductivity of 10 mS cm^{-1} and their cations and anions have their largest diameter practically equal

(**Figure 2**). EMIBF₄ has the same cation as EMITFSI (EMI⁺) but, although the BF₄⁻ anion is smaller and less polarizable than TFSI⁻, surprisingly the IL is hydrophilic. Another curious behavior is the conductivity of EMIBF₄ that reaches 14 mS cm⁻¹ despite the higher viscosity (42.0 cP) than the EMITFSI. **Table 3** summarizes some important physicochemical properties of these ILs.²⁵

Figure 2. Structures and molecular sizes for the cations and anions of the EMITFSI and EMIBF₄.

Table 3. Physicochemical properties of EMITFSI and EMIBF₄ ionic liquids obtained at 25 °C.

Ionic Liquid	Viscos. / cP	Dens. / g cm ⁻³	Conduct. / mS cm ⁻¹	Molar mass / g mol ⁻¹	Other features
EMITFSI	35.6	1.52	10.0	391.31	Aprotic, water-insoluble
EMIBF ₄	42.0	1.24	14.0	197.97	Aprotic, water-soluble

Electrochemical performance of the EDLCs based on EMITFSI and EMIBF₄. **Figure 3** shows the performance of symmetric EDLCs constructed with different ILs and high surface area carbon materials in terms of specific cell capacitance (C_{cell}), energy density (E_{sp}) and power density (P_{sp}). All parameters were calculated with cells operating in the current density range of 50 - 500 mA g⁻¹ and with a cell potential of 3.0 V. These conditions were used to ensure that EDLCs operate with coulombic efficiencies greater than 95% (a necessary condition in practical cells,²⁶ preserving the excessive degradation of the components that occur at higher potentials and extreme current densities.⁹ The galvanostatic charge/discharge curves are shown in the Supporting Information.

Figure 3. Specific cell capacitance as a function of current density for the EDLCs with different porous carbon electrodes and with (a) EMITFSI and (b) EMIBF₄ as electrolytes. (c) Ragone diagram for all evaluated EDLCs.

It is important to emphasize here that the purpose of these studies is not to choose the cell with the best performance but to highlight the main electrochemical characteristics of these systems based on ILs. The first point to be highlighted is the capacitive behavior of these cells that present many anomalies. Note that AC has the highest S_{BET} values ($2240 \text{ m}^2 \text{ g}^{-1}$) and cells built with this material have the lowest capacitances, even lower than the MWCNT ($S_{\text{BET}} = 256 \text{ m}^2 \text{ g}^{-1}$), at almost all current densities and for both ILs. Obviously, AC has many small micropores that are not accessible to ILs ionic species. As previously discussed, DFT results reveal a large number of pores with sizes less than

0.6 nm that are incompatible with the diameter of the ions. However, this material still has many accessible pores (>1.0 nm) and the volume of mesopores of $0.31 \text{ cm}^3 \text{ g}^{-1}$.

The micropores have great importance for the accumulation of charge by supercapacitors, which has a significant impact on capacitance.²⁷ Chmiola et al. have shown that carbon materials with pores in the range of 0.6 to 1.2 nm are capable of operating with electrolytes containing solvated ions with larger diameters (1M NEt_4BF_4 in ACN; $\text{NEt}_4^+ = 1.7$ nm, $\text{BF}_4^- = 1.5$ nm - considering the diameters of solvated ions).^{4, 27} However, this also indicates that the ions access the microporosity desolvated. Other studies also support the idea that the ions can access pores having a similar size to their diameter and contribute to the capacitance.¹³ In the case of ILs, this access is difficult due to the absence of solvation (by the solvent) and strong ion-ion interactions that could prevent an ion from becoming individualized to access a small pore. This is one of the reasons that can worsen the performance of the microporous materials in the IL medium. In this particular case, it is clear that an important part of the surface of AC is not accessible to the large size ions of the ILs used.

The capacitance data show that mesoporous carbon electrodes are more suitable than the other carbon studied. Lower current density facilitates diffusion and the highest C_{cell} values are found for MES, which combines large surface area and the largest volume of mesopores ($1.11 \text{ cm}^3 \text{ g}^{-1}$). In EMITFSI at 50 mA g^{-1} , the following trend is observed: MES (26.86 F g^{-1}) $>$ RGO (8.18 F g^{-1}) $>$ MWCNT (6.35 F g^{-1}) $>$ AC (5.57 F g^{-1}). Under the same conditions for EMIBF₄, cells containing MES maintain similar C_{cell} (26.57 F g^{-1}), RGO has 10.02 F g^{-1} and the performance with AC (9.15 F g^{-1}) is slightly superior to MWCNT (6.96 F g^{-1}).

Ideally, an EDLC should meet the power demands, maintaining its energy density regardless of the charge/discharge rate.⁴ The data presented in **Figure 3** shows that this behavior cannot be easily achieved with ILs, especially with materials with a high microporous content (AC), and even MES suffers a severe drop in power density. By increasing the current density by 10 times (500 mA g^{-1}), the cell containing MES reduces its specific capacitance by 65% in EMITFSI and 47% in EMIBF₄, and the energy density equals the level of the EDLC based on MWCNTs using EMITFSI. Considering AC, again it is noted its poor compatibility with ILs since at 500 mA g^{-1} the C_{cell} and E_{sp} values reached by its cells are very low (EMITFSI: 0.63 F g^{-1} and 0.5 W h kg^{-1} ; EMIBF₄: 1.78 F g^{-1} and 1.4 W h kg^{-1}). On

the other hand, RGO and MWCNT have the best rate capabilities due to their greater conductivity and their highly accessible surface. Therefore, this shows that ILs operate better not only with materials with a high volume of mesopores (as in the case of MES) but also open and completely accessible surfaces are convenient for high power demands. As a consequence, the best performance in P_{sp} is obtained with MWCNT that exceeds 600 W kg^{-1} while MES and AC do not reach 400 W kg^{-1} at the same current density.

Up to this point, the global behavior of cells has been analyzed and correlated with the properties of the porous carbon electrodes. However, charge accumulation occurs on the separate electrodes that can behave differently even in a symmetric EDLC. It is important to note that failures in an EDLC can occur specifically in a single electrode.²⁸ Therefore, the knowledge of the behavior of each electrode allows knowing in greater depth the compatibility of an electrolyte with a given electrode, and such data can be used to optimize the design of cells. In the next sections, the studies will be centered at the electrode level trying to understand the particularities of each porous carbon material immersed in the imidazolium ILs.

Electrochemical study at electrode level for cells containing MWCNT. The behavior of the electrodes will be studied at two different current densities, the highest (500 mA g^{-1}) and the lowest (50 mA g^{-1}) ones tested. This study will focus on the specific capacitances of the electrodes and their resistances, whose values are summarized in **Figure 4-7**. As already attested, MWCNTs are the materials with the smallest specific surface area and high cell capacitances cannot be expected. However, its morphology and high conductivity guarantee a better rate capability and the best power performance at the cell level. Again, we emphasize that all the cells were built symmetrically, i.e., using the same mass of the same carbon in both electrodes. For the cell containing MWCNT and EMITFSI, this symmetry is manifested in the behavior of the electrodes that have similar capacitances in both evaluated current densities (**Figure 4**).⁵ This symmetry can also be seen in the galvanostatic curves that reveal equipartition of the operating potential windows in each electrode. So, this system behaves as it could be expected in a model EDLC.

On the other hand, when EMITFSI is substituted by EMIBF₄, the symmetry of the system is lost, as the capacitance of the negative electrode becomes larger ($C_- = 32.7 \text{ F g}^{-1}$) than the capacitance of the positive one ($C_+ = 24.3 \text{ F g}^{-1}$) at low current densities (50 mA g^{-1}), and the behavior is reversed at 500 mA g^{-1} ($C_- = 18.2 \text{ F g}^{-1}$, $C_+ = 23.6 \text{ F g}^{-1}$) as shown in **Figure 4**.

Figure 4. (a) Schematic representation of the porous structure of MWCNTs. (b, c) Evolution of the potentials of the electrodes at different current densities (50 and 500 mA g^{-1}) and (d) the specific electrode capacitances calculated from these galvanostatic curves. (e) Equivalent series resistances for cells and electrodes.

Considering the porous structure of the MWCNTs with a highly accessible open surface, the diameters for cations (d_{c+}) and anions (d_{a-}) for both ILs should be suitable for insertion into the cavities formed by MWCNTs bundles (EMITFSI: $d_{c+} \approx 1.5 \text{ nm}$, $d_{a-} \approx 1.6 \text{ nm}$; EMIBF₄: $d_{c+} \approx 1.5 \text{ nm}$, $d_{a-} \approx 0.4$

nm - diameters of unsolvated ions).^{13, 29-30} Thus, a spatial blocking hypothesis can be ruled out. For the MWCNT|EMIBF₄|MWCNT system, conventional thinking would lead to the prediction of higher values of C₊ (where BF₄⁻ forms the double layer) than C₋ (where EMI⁺ forms the double layer) due to the smaller size of the BF₄⁻ anion. But, in the experiments at 50 mA g⁻¹, C₋ is higher than C₊, a fact that needs to be explained.

The reasons that could explain the difference between the cells containing EMITFSI and EMIBF₄ (with MWCNTs as electrodes) can be found in the specific interaction of the different ions with the electrode surface, specifically the adsorption phenomena. Recently, Forse and collaborators have demonstrated experimentally and theoretically that the electrolyte ions can be specifically adsorbed on the electrode surfaces.³¹ Considering EMIBF₄, BF₄⁻ anion is considered to be quite inert with a compact tetrahedral structure and with the negative charge excess distributed and distributed between the four fluorine atoms and it is likely that the interaction with the MWCNT surface is weak. However, the positive charge of EMI⁺ and its planar aromatic ring favor interaction with the sp² structure of the nanotubes through π - π interactions. Thus, the adsorption of EMI⁺ ions is favored than the BF₄⁻ ions, explaining the differences in capacitance at low currents.

Looking at the resistance values (**Figure 4e**), again the cell containing EMITFSI shows a remarkable symmetry. This is a result of the similar sizes of the ionic species and indicates a similar electrosorption capacity between EMI⁺ and TFSI⁻ on the surface of the MWCNTs. In EMIBF₄ the differences are larger, with lower resistance for the positive electrode (1.50 Ω) and higher for the negative one (4.50 Ω). It is easy to accept that the BF₄⁻ presents low resistance due to the small size of the anions. This difference may explain the performance at the highest current density, where mobility becomes more important. Although EMI⁺ has a greater capacity for electrosorption, its access to the interface is more resistive, and this decreases the electrode performance at high charge rates, reducing the capacitance of the negative electrode in this case.

Therefore, the results obtained for MWCNT are interesting to understand the charge accumulation mechanism of an IL-based EDLC. Even for a completely open surface with free access to the ions, there may be interaction effects of ions with the material surface that limit a specific electrode performance and therefore, limit the cell performance.

Electrochemical study at electrode level for cells containing RGO. Even though RGO is another material with an open surface for electrolyte access, it has a morphology and pore shape (**Figure 5**) very different from MWCNTs. With this surface, even though EMITFSI has cations and anions with similar sizes, the performance of the electrodes is very different. For both ILs and regardless of the current densities evaluated, the positive electrode is the limiting one, presenting the lowest specific capacitances and the highest resistances (**Figure 5**), indicating the difficulties of the anions to form the electric double layer. The S_{BET} values for RGO are significantly higher ($454 \text{ m}^2 \text{ g}^{-1}$) than for MWCNT ($256 \text{ m}^2 \text{ g}^{-1}$), but this difference has little impact on the capacities of the positive electrodes of RGO-based cells in relation to MWCNT. Only the negative electrode develops greater capacitance on this better-developed surface. Therefore, it is the limitation of the positive electrode that justifies the small increase in C_{cell} and E_{sp} values of cells constructed with RGO in relation to MWCNT.

The asymmetries found in the results for RGO are more intriguing for EMIBF₄ since the BF₄⁻ anion is the smallest one and it should more easily access the positive electrode. Again, it is noted that the classic thesis of compatibility between the sizes of ions and pores is not sufficient to understand the mechanism of charge accumulation of EDLCs based on ILs. Probably the origin of these deviations is in the nature of the interaction between the ions and the surface. We can infer that the chemical structure of EMI⁺ (planar structure with a positive charge capable of interact with the π electrons of the graphene lamellae) facilitates the adsorption of this ion onto the RGO surface. These π -stacking interactions are not favored in the case of anions over RGO. Therefore, the intensity of the interaction is important and depends not only on the shape of the pores but also on the nature of chemical interactions of the ionic species with the electrode surface. Theoretical studies of the interaction of imidazolium and ammonium ILs on the graphene surface support this idea, revealing the dependence of the ion/surface interaction geometry with the energy involved in the process.³² Obviously, beyond the theoretical studies, the reality of the interactions on the surface of the supercapacitor electrodes is even more complex because there are important variables such as the heterogeneity and tortuosity of the surface and the presence of an electric field.

Figure 5. (a) Schematic representation of the porous structure of RGO. (b, c) Evolution of the potentials of the electrodes at different current densities (50 and 500 mA g⁻¹) and (d) the specific electrode capacitances calculated from these galvanostatic curves. (e) Equivalent series resistances for cells and electrodes.

Taking into account the structure and properties of BF₄⁻ and TFSI⁻, it is easy to accept that the smaller size of BF₄⁻ justifies the higher specific capacitance ($C_+ = 33.0$ and 18.7 F g⁻¹ at 50 and 500 mA g⁻¹, respectively) of the positive electrode in the cell-based on EMIBF₄ than EMITFSI ($C_+ = 27.2$ and 8.2 F g⁻¹ at 50 and 500 mA g⁻¹, respectively). The largest differences between C_+ at 500 mA g⁻¹ are the

result of resistance differences of the electrodes ($8.70\ \Omega$ for TFSI⁻; $4.30\ \Omega$ for BF₄⁻), revealing the difficulties of the TFSI⁻ anion to form the electric double layer and to diffuse on the RGO surface.

Electrochemical study at electrode level for cells containing AC. The behavior of the electrodes of cells containing AC is analyzed in this section. The results show that this is, undoubtedly, the least suitable material for building EDLCs with EMITFSI and EMIBF₄ despite its high surface areas and pore volume, and due to a large number of pores of small diameters (**Figure 1c**). As a consequence, the total resistance of the cells is very high (EMITFSI: $25.6\ \Omega$; EMIBF₄: $29.2\ \Omega$) and this justifies the poor performance in rate capability and power density since these properties are fundamentally correlated with resistance.⁹ Also, **Figure 6c** reveals the remarkable decrease in specific capacitance at the higher current densities in both electrodes with any IL.

Figure 6. (a) Schematic representation of the porous structure of AC. (b, c) Evolution of the potentials of the electrodes at different current densities (50 and 500 mA g⁻¹) and (d) the specific electrode capacitances calculated from these galvanostatic curves. (e) Equivalent series resistances for cells and electrodes.

Nevertheless, it is interesting to analyze the behavior of the cell-based EMITFSI at low current densities in the individual electrodes. In this system, the electrodes have very similar resistances that correlate well with the similarity of the sizes of the ions. However, contrary to the behavior observed for RGO and MWCNT, the C_+ value (32.3 F g⁻¹) is about two times larger than C_- (16.9 F g⁻¹), indicating a greater affinity of the CAs surface for the anion than for the cation.

The interactions in ACs must be very different from those in RGO and MWCNTs since this surface is much more heterogeneous, has a higher content of oxygenated groups and the ions within the pores are not only exposed to basal planes (as it mainly occurs in MWCNT and RGO) but they are also exposed to edges. At this point, it is important to note that electrodes with a high content of functional groups can also contribute to the energy density of cells through the presence of reversible redox reactions (pseudocapacitance).^{7, 33-34} This mechanism is faradic in nature and results in the presence of plateaus in the galvanostatic curves at specific potentials, promoting great distortions in the triangular profile of a supercapacitor.^{5, 35} It is well known that pseudocapacitance is more common and relevant in aqueous media, when acid or basic electrolytes are used.^{9, 36-37} However, EMITFSI and EMIBF₄ are aprotic ILs and the pseudocapacitive contribution in this work can be neglected.⁹

The resistances in both electrodes for EMIBF₄ are different from the negative electrode being the most resistive one (19.4 Ω) but it shows the highest capacitance (38.0 F g⁻¹). Intriguingly, this negative electrode favors the formation of the double layer with EMI⁺, which is not only the largest ion but also showed the worst performance when the electrolyte was EMITFSI. In an attempt to respond to this behavior, other considerations about the mechanism of formation of the electric double layer in EDLCs must be considered. First, it should be remembered that in microporous materials the larger ions can access the pores isolated without the solvation sphere.¹³ In the case of ILs, there is no solvent and the concept of a solvation sphere is inadequate. Two main mechanisms must be considered for IL ions to access the porosity:³¹

- i) for an ion to access a small pore, it is necessary to break the interactions with the co-ions in its neighborhood;
- ii) when the cell is discharged ($V_{\text{cell}} = 0$), both ions can occupy the pore. With the application of the electrical potential ($V_{\text{cell}} > 0$), the ions of the same charge in relation to the surface leave the pores and allow the entry of ions with opposite signal charges (counterions).

Scheme 1. Schematic representation of the mechanisms of ion insertion in micropores.

Scheme 1 shows a pictorial representation of these mechanisms that have an energy cost for the system. The study by Forse et al. supports the existence of these mechanisms through studies using nuclear magnetic resonance and computational modeling.³¹ Therefore, these important effects should impact the access of ILs into microporosity, changing the specific capacitance. In this context, for EMI^+ to access the small pores of the AC, ion-ion interactions are broken with TFST^- and BF_4^- which have different energies (mechanism *i*). On the other hand, in some pores, the anions must be desorbed with different energies for the entry of EMI^+ (mechanism *ii*). Also, elementary analysis reveals that the AC

has many oxygenated functional groups that must interact with different intensities with each anion. Therefore, this justifies the asymmetries in the behavior of the AC electrodes for the different ILs.

Finally, at 500 mA g⁻¹, the differences between the interactions become secondary in the EDLCs containing AC, since the formation of the double electrical layer is hindered at high charge/discharge rates due to the high resistance of the system, induced by the small pore diameter.

Electrochemical study at electrode level for cells containing MES. MES-based cells are the most suitable for the ILs, promoting the highest cell capacitances and energy densities. MES combines a large surface area (S_{BET} of 1347 m² g⁻¹) and large pore diameters (**Figure 1d**) compared to AC. However, here the surface is not as open as in MWCNT and RGO, and the tortuosity of this mesoporous network impacts the diffusion of the large IL ions. As a consequence, although less than in cells containing AC, the resistance of EDLC based on MES is considerable and has a great impact on rate capability and power density (**Figure 3**). Besides, the shape of the N₂ isotherm indicates that the MES has a significant contribution of microporosity (457 m² g⁻¹) that cannot be neglected.

Attending to the details of the galvanostatic curves (**Figure 7b, c**) it is noticeable that the similarities in C_{cell} for both cells tested with EMIBF₄ and EMITFSI (**Figure 3a, b**) are obtained following quite different routes in the positive and negative electrodes. In EMITFSI, the capacitance of the positive electrode (93.3 F g⁻¹) is lower than the capacitance of the negative one (123.2 F g⁻¹), but in EMIBF₄ is the positive one which presents higher capacitance (120.7 F g⁻¹) than the negative (93.1 F g⁻¹). The values of resistance in each electrode can provide some clues about the reasons for this behavior. The ion that seems to have the easiest interaction with the MES is BF₄⁻. The positive electrode in the cell with EMIBF₄ yields not only a good value of capacitance but also the lowest electrical resistance (3.80 Ω). On the contrary, the interaction of TFSI⁻ with MES seems to be more difficult, with a very high electrical resistance (13.3 Ω, four folds larger than BF₄⁻). Therefore, it is the positive electrode that limits the MES|EMITFSI|MES cell, generating high values of the cell resistance (EMITFSI: 21.4 Ω; EMIBF₄: 10.2 Ω) and worsening in rate capability.

Figure 7. (a) Schematic representation of the porous structure of MES. (b, c) Evolution of the potentials of the electrodes at different current densities (50 and 500 $mA g^{-1}$) and (d) the specific electrode capacitances calculated from these galvanostatic curves. (e) Equivalent series resistances for cells and electrodes.

Attending to the negative electrode, the same carbon material and the same ion (EMI^+) to form the electric double layer yield quite different results. The electrical resistances are similar in both cases, but both capacitances are quite different. In EMITFSI, the cation EMI^+ yields high capacitance ($123.2 F g^{-1}$) which indicates an easy-going process of electrosorption on MES. On the contrary, the same cation on the same surface (but with EMIBF₄ as electrolyte) produces lower capacitance ($93.1 F g^{-1}$). In addition, it is important to note that the behavior of the electrodes for MES (EMITFSI: $C_+ < C_-$; EMIBF₄: $C_+ > C_-$) is the opposite of that observed for ACs (EMITFSI: $C_+ > C_-$; EMIBF₄: $C_+ < C_-$). This

demonstrates that ion adsorption/desorption on the electrode surface plays a fundamental role in the double layer formation. In addition to the porous structures being different, MES structure is much less graphitic and has less content of functional groups compared with AC, as evidenced by resistivity measurements and elemental composition. In this particular case, the interaction and diffusion of BF_4^- in MES is favored, justifying the higher capacitance (120.7 F g^{-1}) and lower resistance (3.80Ω) of the positive electrode in the cell containing EMIBF₄. This lower resistance also justifies the higher capacitance retention of this electrode at the higher current density (82.5 F g^{-1}). On the other hand, the strong adsorption of BF_4^- may limit the formation of the double layer of EMI^+ , which justifies the higher C. values in EMITFSI (123.2 F g^{-1}) in relation to EMIBF₄ (93.1 F g^{-1}) at 50 mA g^{-1} .

CONCLUSION

The use of galvanostatic methods which explore the electrochemical behavior at the cell and electrode levels, simultaneously, allow inferring about the mechanism of charge accumulation, ion-electrode compatibility, and their consequences for the performance of the global cell. After exploring cells with different carbon electrodes operating with imidazolium ILs, it is remarkable that the simple consideration between the compatibility of the pore size with the diameter of the ions is not enough to choose a suitable carbon as an active material of the supercapacitor electrode. For these ILs, the electrochemical results reveal that mesoporous materials with high surface areas are desirable to ensure high capacitance and energy density, but the best performance in power densities are obtained with materials containing more open surfaces (MWCNT and RGO). In addition, we conclude that ions interact in a specific way with the carbon surface, which can limit the performance of an electrode. In carbon materials with a higher pore volume and a higher micropore content (AC and MES), the resistances and specific capacitances are more influenced by the breakdown of strong ion-ion interactions of ILs and by the desorption of co-ions present in the pores. Structures with small diameter micropores are very resistive to an IL and limits the charge accumulation at higher charge rates.

Analyzing the differences in specific capacitance and resistance of the electrodes in each cell, it is possible to infer about the particularities of each system. The sp^2 structures of MWCNT and RGO, which are richer in free π -electrons, favors the interactions with positive charges of cations, specifically

with a rather planar structure of the EMI^+ . MES presents an excellent interaction with BF_4^- that yields very low resistance, and high capacitance in the positive electrode. The anion TFSI^- shows a complex interaction with the RGO surface that leads to unexpected high resistances and low capacitances. On the other hand, AC is the only material that presents a better interaction with anions especially TFSI^- . Finally, this simple electrochemical approach allows to optimize future EDLCs selecting for each electrode the materials with the best compatibility with a specific counterion.

Supporting Information. Description and calculation of electrochemical parameters; Galvanostatic curves for EDLCs constructed with different carbon materials and ionic liquids at 3.0 V and at different current densities.

Corresponding authors

E-mail: pauloortega@cefetmg.br (Paulo F. R. Ortega), rodrigo.lavall@qui.ufmg.br (Rodrigo L. Lavall), riqui@incar.csic.es (Ricardo Santamaría).

ACKNOWLEDGMENTS

The authors would like to thank the Conselho Nacional de Desenvolvimento Científico e Tecnológico (CNPq) – Brazil for the financial support (PVE 2014, process number 400714/2014-0), the Spanish Government and European Union (AEI/FEDER,EU; project MAT2016-77114-R), N. Quintanal predoctoral contract (BES2017-082038), and Principado de Asturias (FEDER: IDI/2018/000121). The work was partially supported by the Brazilian Institute of Science and Technology (INCT) in Carbon Nanomaterials. P.F.R. Ortega acknowledges the Fundação de Amparo à Pesquisa do Estado de Minas Gerais (FAPEMIG) - Brazil (DOF nº. 2720262/2018). P.F.R. Ortega and G. A. dos Santos Junior also acknowledge the scholarships received from CNPq. R.L. Lavall is a recipient of a fellowship from CNPq (grant number 313304/2017-3). P.F.R. Ortega, G.G. Silva, and R.L. Lavall are members of the Rede Mineira de Química (RQ-MG) – Brazil.

REFERENCES

1. Gonzalez, A.; Goikolea, E.; Barrena, J. A.; Mysyk, R. Review on Supercapacitors: Technologies and Materials. *Renew. Sustain. Energy Rev.* **2016**, *58*, 1189-1206.
2. Conway, B. E. *Electrochemical Supercapacitors: Scientific Fundamentals and Technological Applications*; Kluwer Academic/Plenum Publishers: New York, 1999.
3. Béguin, F.; Presser, V.; Balducci, A.; Frackowiak, E. Carbons and Electrolytes for Advanced Supercapacitors. *Adv. Mater.* **2014**, *26*, 2219-2251.
4. Simon, P.; Brousse, T.; Favier, F. *Supercapacitors Based on Carbon or Pseudocapacitive Materials*; Wiley: UK 2017; Vol. 3.
5. Roldan, S.; Barreda, D.; Granda, M.; Menendez, R.; Santamaria, R.; Blanco, C. An Approach to Classification and Capacitance Expressions in Electrochemical Capacitors Technology. *Phys. Chem. Chem. Phys.* **2015**, *17*, 1084-1092.
6. Santos, M. C. G.; da Silva, D. R.; Pinto, P. S.; Ferlauto, A. S.; Lacerda, R. G.; Jesus, W. P.; da Cunha, T. H. R.; Ortega, P. F. R.; Lavall, R. L. Buckypapers of Carbon Nanotubes and Cellulose Nanofibrils: Foldable and Flexible Electrodes for Redox Supercapacitors. *Electrochim. Acta* **2020**, *349*, 136241-136249.
7. Xue, D.; Zhu, D.; Duan, H.; Wang, Z.; Lv, Y.; Xiong, W.; Li, L.; Liu, M.; Gan, L., Deep-Eutectic-Solvent Synthesis of N/O Self-Doped Hollow Carbon Nanorods for Efficient Energy Storage. *Chem. Comm.* **2019**, *55*, 11219-11222.
8. Zhong, C.; Deng, Y. D.; Hu, W. B.; Qiao, J. L.; Zhang, L.; Zhang, J. J. A Review of Electrolyte Materials and Compositions for Electrochemical Supercapacitors. *Chem. Soc. Rev.* **2015**, *44*, 7484-7539.
9. Santos, M. C. G.; Silva, G. G.; Santamaría, R.; Ortega, P. F. R.; Lavall, R. L. Discussion on Operational Voltage and Efficiencies of Ionic-Liquid-Based Electrochemical Capacitors. *J. Phys. Chem. C* **2019**, *123*, 8541-8549.
10. Fedorov, M. V.; Kornyshev, A. A. Ionic Liquids at Electrified Interfaces. *Chem. Rev.* **2014**, *114*, 2978-3036.

11. Ivaništšev, V.; Fedorov, M. V.; Lynden-Bell, R. M. Screening of Ion–Graphene Electrode Interactions by Ionic Liquids: The Effects of Liquid Structure. *J. Phys. Chem. C* **2014**, *118*, 5841-5847.
12. Hayes, R.; Warr, G. G.; Atkin, R. Structure and Nanostructure in Ionic Liquids. *Chem. Rev.* **2015**, *115*, 6357-6426.
13. Largeot, C.; Portet, C.; Chmiola, J.; Taberna, P. L.; Gogotsi, Y.; Simon, P. Relation between the Ion Size and Pore Size for an Electric Double-Layer Capacitor. *J. Am. Chem. Soc.* **2008**, *130*, 2730-2731.
14. Embs, J. P.; Burankova, T.; Reichert, E.; Hempelmann, R. Cation Dynamics in the Pyridinium Based Ionic Liquid 1-N-Butylpyridinium Bis((Trifluoromethyl)Sulfonyl) as Seen by Quasielastic Neutron Scattering. *J. Phys. Chem. B* **2012**, *116*, 13265-13271.
15. Pak, A. J.; Hwang, G. S. Charging Rate Dependence of Ion Migration and Stagnation in Ionic-Liquid-Filled Carbon Nanopores. *J. Phys. Chem. C* **2016**, *120*, 24560-24567.
16. Fang, A.; Smolyanitsky, A. Simulation Study of the Capacitance and Charging Mechanisms of Ionic Liquid Mixtures near Carbon Electrodes. *J. Phys. Chem. C* **2019**, *123*, 1610-1618.
17. Breitsprecher, K.; Szuttor, K.; Holm, C. Electrode Models for Ionic Liquid-Based Capacitors. *The J. Phys. Chem. C* **2015**, *119*, 22445-22451.
18. Chen, J.; Yao, B. W.; Li, C.; Shi, G. Q. An Improved Hummers Method for Eco-Friendly Synthesis of Graphene Oxide. *Carbon* **2013**, *64*, 225-229.
19. dos Santos Junior, G. A.; Fortunato, V. D. S.; Silva, G. G.; Ortega, P. F. R.; Lavall, R. L., High-Performance Li-Ion Hybrid Supercapacitor Based on LiMn_2O_4 in Ionic Liquid Electrolyte. *Electrochim. Acta* **2019**, *325*, 134900-134908.
20. Fuertes, A. B., Synthesis of Ordered Nanoporous Carbons of Tunable Mesopore Size by Templating Sba-15 Silica Materials. *Micropor. Mesopor. Mat.* **2004**, *67*, 273-281.
21. Thommes, M.; Kaneko, K.; Neimark, A. V.; Olivier, J. P.; Rodriguez-Reinoso, F.; Rouquerol, J.; Sing, K. S. W. Physisorption of Gases, with Special Reference to the Evaluation of Surface Area and Pore Size Distribution (Iupac Technical Report). *Pure Appl. Chem.* **2015**, *87*, 1051-1069.

22. Gomes Ferreira de Paula, F.; Campello-Gómez, I.; Ortega, P. F. R.; Rodríguez-Reinoso, F.; Martínez-Escandell, M.; Silvestre-Albero, J. Structural Flexibility in Activated Carbon Materials Prepared under Harsh Activation Conditions. *Materials (Basel)* **2019**, *12*, 1988-1999.
23. Richey, F. W.; Tran, C.; Kalra, V.; Elabd, Y. A. Ionic Liquid Dynamics in Nanoporous Carbon Nanofibers in Supercapacitors Measured with in Operando Infrared Spectroelectrochemistry. *J. Phys. Chem. C* **2014**, *118*, 21846-21855.
24. Osti, N. C.; Gallegos, A.; Dyatkin, B.; Wu, J.; Gogotsi, Y.; Mamontov, E. Mixed Ionic Liquid Improves Electrolyte Dynamics in Supercapacitors. *J. Phys. Chem. C* **2018**, *122*, 10476-10481.
25. Zhang, S. L., X.; Zhou, Q.; Li, X.; Zhang, X.; Li, S. *Ionic Liquids Physicochemical Properties*, First ed.; Elsevier: Oxford, 2009.
26. Laheaar, A.; Przygocki, P.; Abbas, Q.; Beguin, F. Appropriate Methods for Evaluating the Efficiency and Capacitive Behavior of Different Types of Supercapacitors. *Electrochem. Commun.* **2015**, *60*, 21-25.
27. Chmiola, J.; Yushin, G.; Gogotsi, Y.; Portet, C.; Simon, P.; Taberna, P. L. Anomalous Increase in Carbon Capacitance at Pore Sizes Less Than 1 Nanometer. *Science* **2006**, *313*, 1760-1763.
28. Ortega, P. F. R.; González, Z.; Blanco, C.; Silva, G. G.; Lavall, R. L.; Santamaría, R. Biliquid Supercapacitors: A Simple and New Strategy to Enhance Energy Density in Asymmetric/Hybrid Devices. *Electrochim. Acta* **2017**, *254*, 384-392.
29. Roobottom, H. K.; Jenkins, H. D. B.; Passmore, J.; Glasser, L. Thermochemical Radii of Complex Ions. *J. Chem. Educ.* **1999**, *76*, 1570-1573.
30. Masterton, W. L.; Bolocofsky, D.; Lee, T. P. Ionic Radii from Scaled Particle Theory of Salt Effect. *J. Phys. Chem.* **1971**, *75*, 2809-2815.
31. Forse, A. C.; Merlet, C.; Griffin, J. M.; Grey, C. P. New Perspectives on the Charging Mechanisms of Supercapacitors. *J. Am. Chem. Soc.* **2016**, *138*, 5731-5744.
32. Shakourian-Fard, M.; Jamshidi, Z.; Bayat, A.; Kamath, G. Meta-Hybrid Density Functional Theory Study of Adsorption of Imidazolium- and Ammonium-Based Ionic Liquids on Graphene Sheet. *J. Phys. Chem. C* **2015**, *119*, 7095-7108.

33. Zhou, Z.; Miao, L.; Duan, H.; Wang, Z.; Lv, Y.; Xiong, W.; Zhu, D.; Li, L.; Liu, M.; Gan, L. Highly Active N, O-Doped Hierarchical Porous Carbons for High-Energy Supercapacitors. *Chin. Chem. Lett.* **2020**, *31*, 1226-1230.
34. Dubal, D. P.; Ayyad, O.; Ruiz, V.; Gomez-Romero, P. Hybrid Energy Storage: The Merging of Battery and Supercapacitor Chemistries. *Chem. Soc. Rev.* **2015**, *44*, 1777-1790.
35. Costentin, C.; Savéant, J.-M. Energy Storage: Pseudocapacitance in Prospect. *Chem. Sci.* **2019**, *10*, 5656-5666.
36. Yang, M.; Zhou, Z. Recent Breakthroughs in Supercapacitors Boosted by Nitrogen-Rich Porous Carbon Materials. *Adv. Sci.* **2017**, *4*, 1600408-1600417.
37. Miao, L.; Duan, H.; Wang, Z.; Lv, Y.; Xiong, W.; Zhu, D.; Gan, L.; Li, L.; Liu, M. Improving the Pore-Ion Size Compatibility between Poly(Ionic Liquid)-Derived Carbons and High-Voltage Electrolytes for High Energy-Power Supercapacitors. *Chem. Eng. J.* **2020**, *382*, 122945-122954.

TOC graphic