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Ionogel-based solid-state supercapacitor operating over a wide range of temperature

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ABSTRACT

An inorganic gel polymer electrolyte based on the confinement of an ionic liquid mixture (1:1 by weight or molar ratio) of N-methyl-N-propylpiperidinium bis(fluorosulfonyl)imide (PIP13FSI) and N-butyl-N-methylpyrrolidinium bis(fluorosulfonyl)imide (PYR14FSI) into a SiO₂ matrix prepared from a sol-gel method was prepared and further used as electrolyte in an all solid-state supercapacitor. The synthesized ionogel exhibits a high ionic conductivity over a wide temperature range (from 0.2 mS cm⁻¹ at -40 °C up to 10 mS cm⁻¹ at 60 °C). The ionogel-based supercapacitor using two activated carbon electrodes can be operated over 3 V cell voltage window. Moreover this all solid-supercapacitor shows a capacitance up to 90 F g⁻¹ at room temperature. These encouraging results show the interest of developing such devices, including non-toxic and safer electrolytes, packaging issues and flexible devices development.

1. Introduction

Electrochemical double layer capacitors (EDLCs), also known as supercapacitors, store energy by ion electrosorption on porous electrodes, mostly activated carbons [1]. The key feature of EDLCs compared to Li-ion batteries is their high power delivery (full charge or discharged can be achieved within few seconds or tens of seconds) and high cyclability. Despite abounding research on pseudocapacitive materials with promising performance [2–4], conventional EDLCs using high surface area carbon electrodes and non-aqueous liquid electrolytes represent the state of the art [5]. However, the current liquid electrolytes used in supercapacitor devices suffer from several drawbacks. Conventional supercapacitors employ the use of solvent-based electrolytes which allow ion conduction at sub-zero temperatures, e.g. NEt₄BF₄ in propylene carbonate (PC) or acetonitrile (AN). Nevertheless, these organic solvents reduce the voltage window of the device and AN can pose security issues due to its flammability and low flash point of 2 °C. Electrolyte leaks, which can occur because of internal gas release, is also an important concern. Since the maximum specific energy increases with squared of the voltage window ($E_{\max}(\text{in Wh}) = \frac{1}{2} \cdot C(\text{in F}) \cdot \Delta V_{\max}^2(\text{in V})$ [1]), the type of electrolyte used is important in determining the energy density and safety of a device. A strategy to tackle these issues is to replace liquid by solid

– or gelified – electrolytes. Several materials have been utilized as solid polymer electrolytes, such as Nafion [6], poly(etheretherketone) [7], polybenzimidazole [8], poly(methyl methacrylate) [9] and poly(ethylene oxide) [10] are promising candidates offering as well easy assembly, low cost, and flexible packaging. However, the operating voltage is limited to less than 2 V because of the use of proton or proton-like conducting polymers [11]. More recently, ionogels, which are solid or quasi-solid electrolytes based on the trapping of room temperature ionic liquids (RTILs) in a silica matrix have been proposed [12–14] because they can reach high voltage, up to 4 V [15]. However, based on ionic liquid salt, the ionic conductivity at low temperature is still an issue for developing solid-state supercapacitors operating with a wide range of temperature.

In this paper, we propose to develop a solid-state electrolyte based on a ionic liquid mixture trapped into an inorganic silica network. Following previous work [16], we used a mixture composed of (1:1 by weight or molar ratio) N-methyl-N-propylpiperidinium bis(fluorosulfonyl) imide (PIP13-FSI) and N-butyl-N-methylpyrrolidinium bis(fluorosulfonyl) imide (PYR14-FSI). In these mixtures, cations have the same molecular weight and the same number of atoms of the same nature, with the only difference being their cation molecular structure: a five-member (piperidinium) or six-member (pyrrolidinium) heterocycle. As a result, the increasing disorder and asymmetry among the cations hinders lattice formation, thus to lowering the melting point while maintaining good miscibility and conductivity [17]. The liquid state of this IL mixture can be maintained at temperatures several tens

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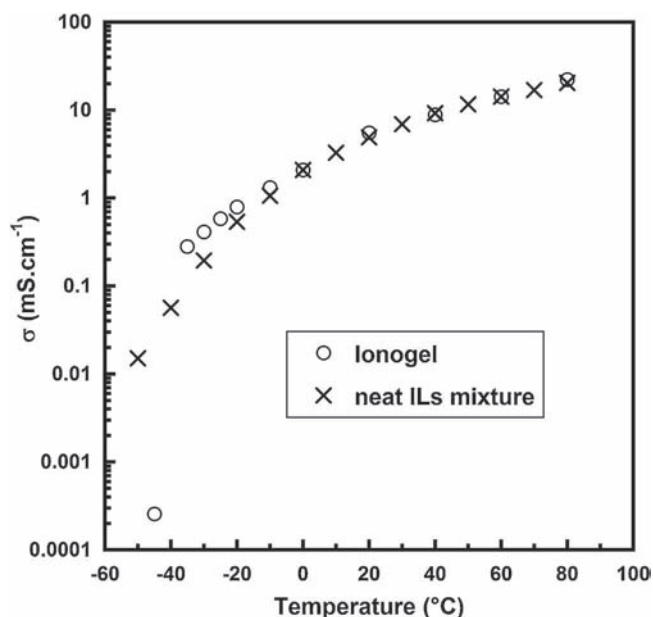


Fig. 1. Conductivity variation versus temperature of neat ILs mixture (PIP13-PYR14/FSI) and ionogel between -50°C and 80°C . Conductivities were calculated from high frequency intercept with real axis of the Nyquist plots obtained from Electrochemical Impedance Spectroscopy (EIS) measurements.

of degrees lower than the individual ILs. Ionic liquid mixture-based ionogel have been designed for enlarging the operating temperature range of these solid state electrolytes, thus offering new opportunities for solid-state supercapacitors.

2. Experimental

Ionogel synthesis procedure was described elsewhere [14]. Basically, a solid ionogel-based electrolyte was synthesized using two different sol-gel agents: TMOS (TetraMethyl Ortho Silicate 98%, from Sigma-Aldrich) and TEOS (TetraEthyl OrthoSilicate 98%, from Sigma-Aldrich) under acidic conditions (Methanoic acid 98%, from VWR). The TEOS:TMOS:MA volumetric ratio was 2:2:5. All reactants were mixed together under moderate stirring (300 rpm) at 40°C during 18 min. The second step was the addition of 60% by volume of ionic liquid mixture (PIP13-FSI):(PYR14-FSI):50:50 in weight. Compared to our previous work using 1-ethyl-3-methyl imidazolium bis(trifluoromethanesulfonylimide) EMITFSI-based ionogel [14], IL content was decreased from 70% down to 60%vol to improve the mechanical properties of the gel. Then, the resulting solution was casted in sealed cylindrical containers and kept for 24 hours at room temperature for gelation and then dried at 50°C during 4 days. All the cells used for conductivity measurement were assembled in a

MBraun glove box operating under argon atmosphere (O_2 and H_2O contents lower than 0.1 ppm) to avoid any contamination. Samples prepared for further mechanical characterizations were injected into stainless steel molds, which ensured good reproducibility of measurements.

2.1. Supercapacitor cell assembly

Active material was made of 95 wt% of PICAFTIF SC, a standard high specific surface area activated carbon ($2300\text{ m}^2\text{ g}^{-1}$) [18], and 5 wt% of PTFE (60 wt% PTFE in water DuPont Nemours, France) [19]. Carbon electrodes were dried out in a vacuum oven during 2 hours then 250 μL of silane-IL mixture was spread onto an electrode which was laid in an appropriate mould, then another electrode

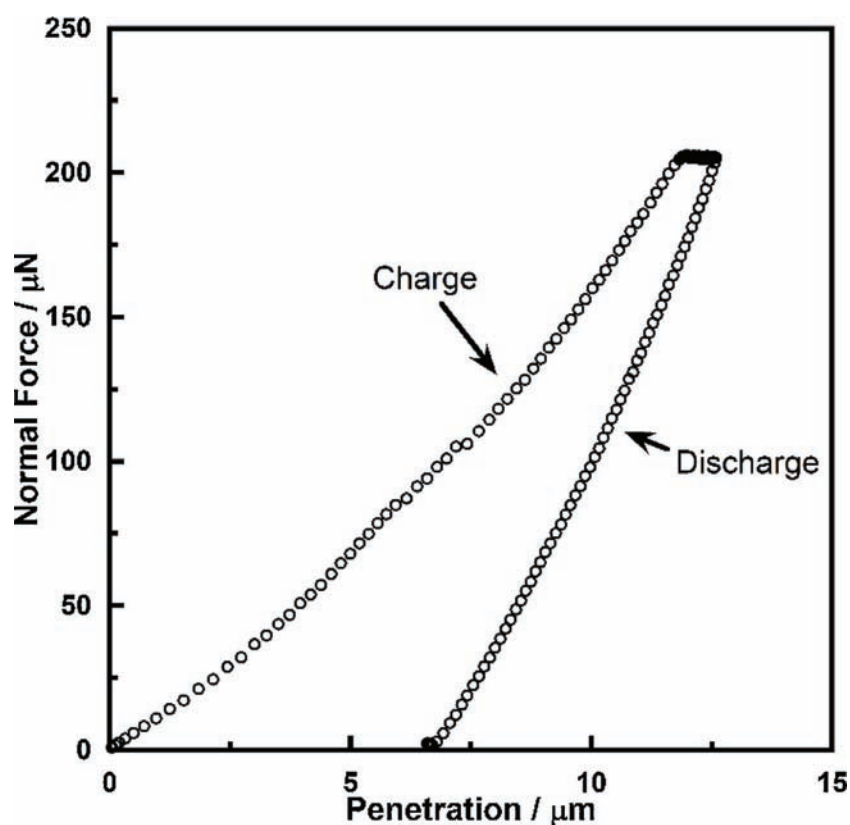


Fig. 2. Ionogel charge-discharge curve obtained with nano-indentation technique.

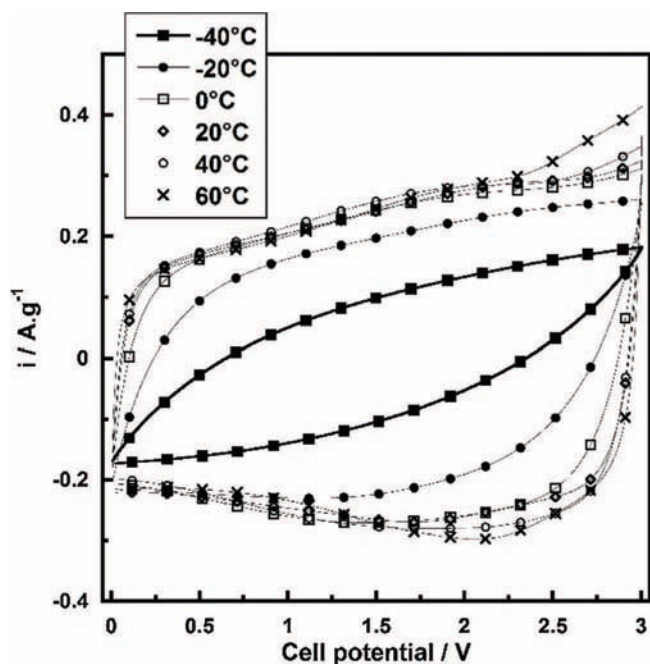


Fig. 3. Cyclic Voltammetry of an ionogel-based supercapacitor using activated carbon electrodes, at 5 mV s^{-1} at various temperatures (from -40 to 60°C).

Table 1

Gravimetric and areal capacitance calculated from the 5 mV s^{-1} CVs during the discharge at different temperatures.

Temperature	-40°C	-20°C	0°C	20°C	40°C	60°C
Gravimetric capacitance (F g^{-1})	34	68	89	91	94	96
Areal capacitance (mF cm^{-2})	89	178	233	238	247	250

was deposited onto the surface of the liquid Silane-ILs mixture. The gel formation was obtained following procedure previously described. The resulting Carbon-Ionogel-Carbon sandwich was placed between two gold current collectors in a RHD cell for further electrochemical tests. This technique offers a way to work

with a large amount of active material (from few mg up to 15 mg cm^{-2}).

Electrochemical tests were carried out using an Autolab PG-STAT128 N (Metrohm, Switzerland). A RHD Cell (RHD, Germany) was used for precise control of the cell temperature from -40°C to $+60^\circ\text{C}$. Prior any measurement, the cell was maintained at the set temperature for 2 h until equilibration. After sandwiching the samples between two gold current collectors, ionic conductivity measurements of the ionogel were performed by Electrochemical Impedance Spectroscopy (EIS) for each temperature; a bias cell voltage of 0 V with a frequency range from 25 kHz down to 0.01 Hz were applied. Conductivities were calculated from high frequency intercept with the real axis of the Nyquist Plots. All electrochemical tests of the supercapacitors were performed with an electrode mass loading of 5 mg cm^{-2} .

Mechanical characterizations of the ionogel were conducted using an UltraNanoHardness Tester from CSM Instruments (Switzerland). Young's modulus E and hardness H and percentage of elastic recovery were measured with a modified Berkovich three-sided pyramid diamond indenter. The maximal normal force was $200 \mu\text{N}$; the maximum force was kept during 60 s before discharge. The loading rate was $400 \mu\text{N min}^{-1}$ and the maximum penetration depth was $12 \mu\text{m}$ (value lower than the tenth of the sample thickness (1.5 mm) thus the mechanical answer of the substrate was neglected). The Poisson ratio of the hybrid coatings was taken at a medium value of $\nu = 0.3$ (value between the Poisson ratio of amorphous silica (0.17) and that of conventional polymeric materials (0.5)). Experiments were performed at ambient temperature. In all CSM nano-indentation tests, a total of three indents were averaged to determine the mean Young's modulus and nano-hardness. The analysis procedure suggested by Oliver and Pharr [20] were used to calculate the hardness and elastic modulus.

3. Results and discussions

3.1. Ionogel conductivity

Fig. 1 shows the change of the ionogel and neat ILs mixture conductivities with temperature (Arrhenius plot) between 80°C and -50°C . As can be seen in Fig. 1, the ionogel conductivity is close to that of the neat IL mixture in the -20°C $+60^\circ\text{C}$ temperature

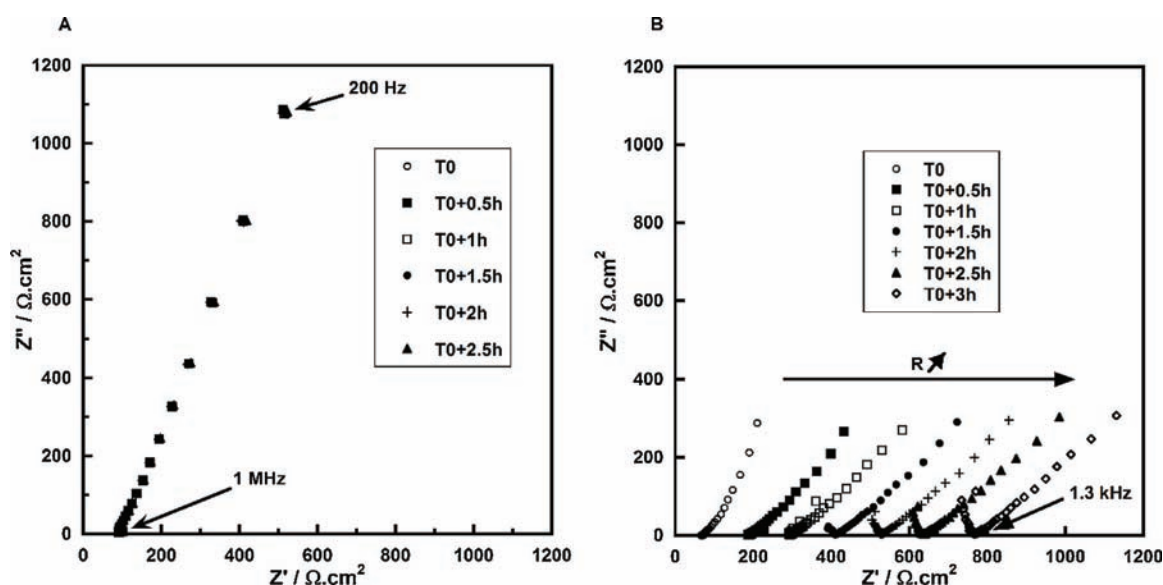


Fig. 4. EIS plot of (A) supercapacitor using two carbon glass electrodes and an ionogel soaked separator between 1 MHz and 200 Hz (B) supercapacitor using two activated carbon electrodes and an ionogel soaked separator between 1 MHz and 0.1 Hz. Bias Voltage: 0 V. Signal amplitude: 5 mV RMS.

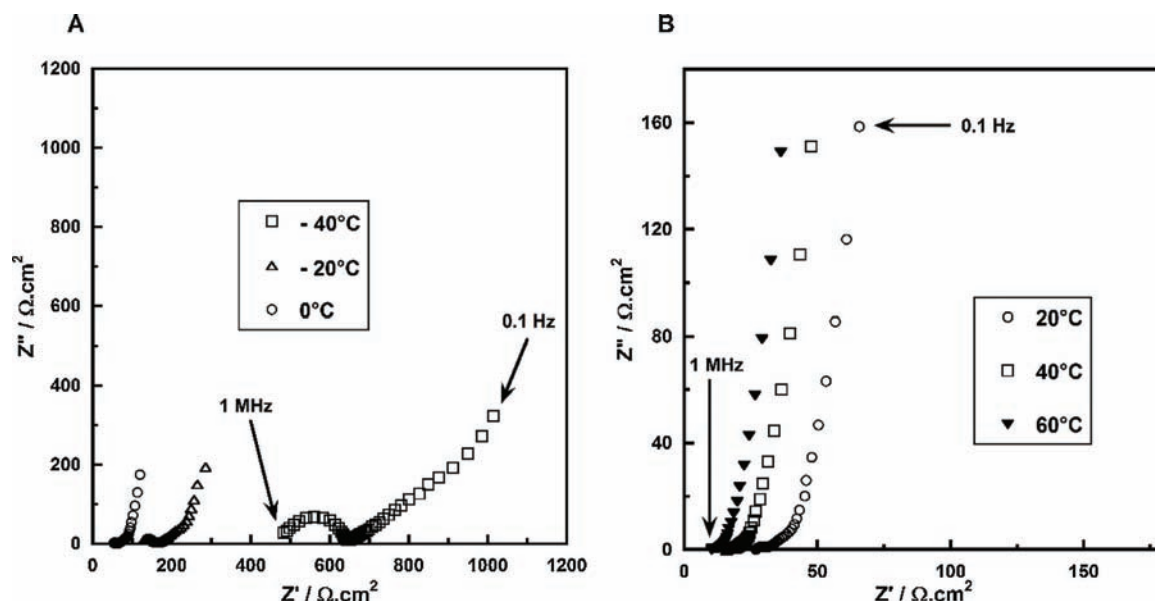


Fig. 5. EIS Plot of iongel-based supercapacitor at different temperature (a) -40°C , -20°C and 0°C (b) 20°C , 40°C and 60°C . Bias voltage: 0 V. Signal amplitude: 150 mV RMS.

range, which evidences a small impact of the presence of the silica matrix. The room temperature conductivity (20°C) was measured at $5.5 \text{ mS} \cdot \text{cm}^{-1}$ for both the neat IL mixture and the iongel, which is comparable to conventional propylene carbonate-based liquid electrolytes [21] and matches with the standards needed for use as electrolyte in supercapacitor devices. However, for temperature below -20°C , the limited mobility of the electrolyte due to the confinement effect inside the silica matrix is assumed to limit the conductivity. A conductivity up to $0.2 \text{ mS} \cdot \text{cm}^{-1}$ was still maintained at -40°C . Such high conductivity values at such low temperature, to our knowledge, have never been reported in the literature for iongel electrolyte. Nevertheless, these kind of electrolytes have been intended to suit to mechanical stress experience since a good mechanical stability has to be. Mechanical

tests were carried out using a nano-indentation technique to assess the mechanical properties of as made iongels.

3.2. Mechanical characterizations

Mechanical properties of iongels were measured by nano-indentation. Fig. 2 shows the load as a function of the penetration depth plot for a 1.5 mm-thick iongel pellet using a Berkovich indenter. Ionogels exhibit rather low values of both Vickers Hardness ($0.11 \pm 0.02 \text{ MPa}$) and elastic modulus ($0.935 \pm 0.114 \text{ MPa}$) as compared to other gel electrolytes: 26 MPa for PMMA [22] and 35–50 MPa for PVdF-based polymer [23]. The elastic contribution to the loading can be obtained from Fig. 2, by subtracting the plastic displacement to the total displacement normalized to the total

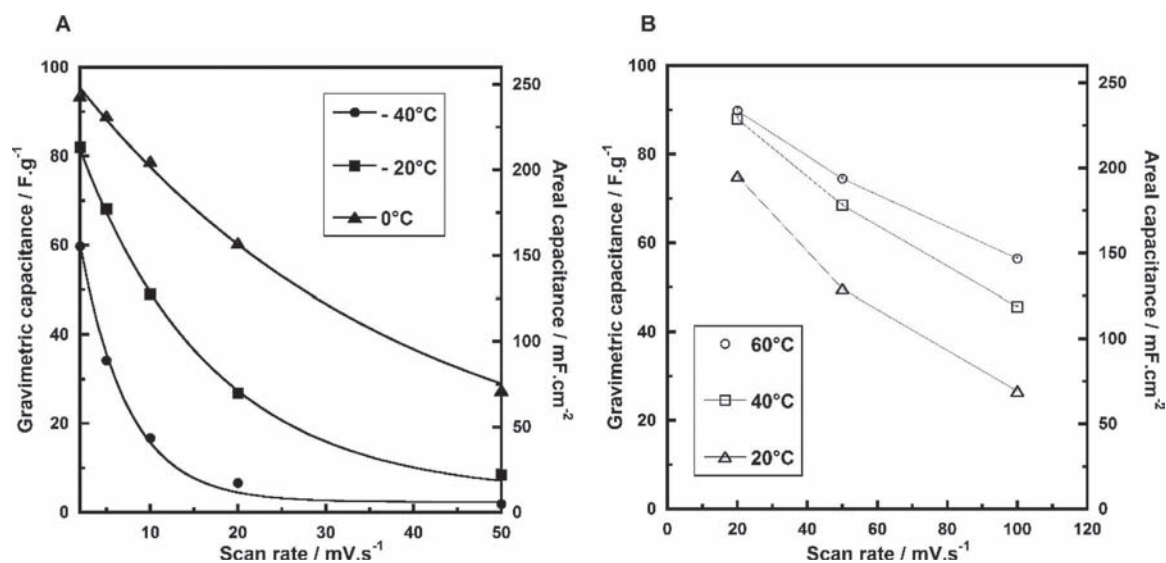


Fig. 6. Evolution of capacitance versus potential scan rate of iongel-based supercapacitor within 3 V at different temperatures (A) -40°C , -20°C and 0°C (B) 20°C , 40°C and 60°C .

displacement. An elastic recovery of 45% was measured, that has to be compared to 14% for pure TEOS and TMOS silica gel. The trapped ionic liquid is acting as a plasticizer in the resulting ionogel.

3.3. Ionogel as solid-state electrolyte for supercapacitor

An all-solid supercapacitor was assembled using porous PICTACTIF activated carbon based electrodes stacked with the ionogel as electrolyte (see experimental). In Fig. 3 are presented Cyclic Voltammograms obtained (CV) at 5 mVs^{-1} between 0 and 3 V at various temperatures (from -40 to 60°C). Down to -20°C the electrochemical signatures are quite decent since a rectangular-shape characteristic was achieved which was expected for a capacitive behaviour based on charging/discharging of the electrical double layer.

A specific capacitance of 91 F g^{-1} (per gram of activated carbon) have been obtained at 20°C with a cell voltage of 3 V, which is very similar to that was measured in conventional organic liquid electrolyte [19]. Table 1 summarizes gravimetric and areal capacitances calculated from the CVs at a potential scan rate of 5 mVs^{-1} between 0 and 3 V from -40 to 60°C .

As observed in this table, the capacitive behaviour is kept down to temperature as low as -20°C ; with only 25% capacitance loss at -20°C . These results are consistent with Fig. 1 that showed that ionogel ionic conductivity was still decent (0.2 mS cm^{-1}) at such low temperature. At -40°C , the crystallization of the IL confined in pores of the carbon structure is assumed to occur. Despite an electrochemical kinetics mainly controlled by ohmic drop, 40% of the capacitance obtained at 20°C was preserved. Interestingly the electrochemical behaviour of all-solid supercapacitor was found to be very close to liquid-based supercapacitors. Such performance could be explained by a wetting carbon micropore by the IL that can move freely with the silicium network. To check the hypothesis, we carried out to design an additional experiment using a non-porous carbon (carbon glass) for comparison purpose.

In the experiment, an (EMITFSI)-based ionogel soaked separator was used to observe the carbon/ionogel interface; EIS measurements were made each 30 min between 1 MHz–200 Hz to measure the change of the impedance with time. Fig. 4A shows the soaked separator between two carbon glass electrodes. Same experiment was conducted with two activated carbon electrode placed between the same separator soaked with ionogel (Fig. 4B).

While the impedance is kept constant for the non porous electrode (Fig. 4B), the real part of the impedance increases with time when using porous carbon electrode. This is assumed to be linked to the hydrophobicity of the carbon which attracts ionic liquid (hydrophobic) from the silica host network (which is hydrophilic) into the carbon pores; besides, capillarity force can also contribute to attract IL in the pores. This behaviour allows a (partial) filling of the carbon microporous structure with ions leading to such high capacitance.

In Fig. 5 are presented the Nyquist plots of a carbon-carbon ((PIP13-FSI)0.5(PYR14-FSI)0.5) ionogel based supercapacitor at a bias cell voltage of 0 V.

In the $20^\circ\text{C} - 60^\circ\text{C}$ temperature range (Fig. 5A), the high frequency series resistance, which is the ionic bulk resistance, was measured at $20 \Omega \text{ cm}^2$ for the whole cell at room temperature (20°C), which is comparable to our previous work [14]. As expected, when the temperature increases from 0°C up to 60°C , the high frequency resistance decreases from 52 to $9.2 \Omega \text{ cm}^2$. The sharp increase of the imaginary part of the impedance at low frequencies is characteristic of the system capacitive behaviour. Even for sub-zero temperatures, EIS measurements still show a capacitive behaviour, despite the presence of a growing semi-circle at high frequency, attributed to the onset of gelation that is related

to decreased mobility of the electrolyte ions at such low temperatures.

Fig. 6 shows the change of the areal and gravimetric capacitance (derived from the slope of the Q-V curve during cell discharge) of the activated carbon electrodes versus the potential scan rate at various temperatures. The capacitance of the ionogel-based supercapacitor decreases with increasing scan rate, since the ohmic drop increases with the scan rate. Temperature plays an important role, since already mentioned series resistance increase at low temperature while a fast decrease of the capacitance is observed at higher scan rate.

In here, it was expected since capacitance limitation is purely due to ohmic drop. The effective accessible surface is strongly dependent on the scan rate [17].

4. Conclusion

The present paper presents some results obtained with a carbon-carbon solid-state supercapacitor using ((PIP13-FSI)0.5(PYR14-FSI)0.5)-based ionogel as both electrolyte and separator. Thanks to high ionic conductivity of the ionogel, ions from the gel are able to fulfil porosity of the carbon electrodes leading to such high capacitance (95 F g^{-1} at room temperature). An all solid supercapacitor with attractive areal capacitance up to 100 mF cm^{-2} per electrode at -40°C for 5 mVs^{-1} scan rate up to 3 V cell voltage could be assembled. Such devices could efficiently match multiple criteria (high capacitance, good power density and high cell potential window) needed for solid supercapacitor applications.

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