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The use of ionic liquids as solvent-free green electrolytes for hybrid supercapacitors

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ABSTRACT The aim of this paper is to demonstrate that the use of ionic liquids (ILs) in activated carbon (AC)//poly(3-methyl-thiophene) (pMeT) hybrid supercapacitors is a very promising strategy to develop high voltage supercapacitors operating above room temperature with solvent-free green electrolytes. The ILs used were 1-butyl-3-methyl-imidazolium tetrafluoroborate, 1-butyl-3-methyl-imidazolium hexafluorophosphate, N-butyl-N-methylpyrrolidinium bis(trifluoromethanesulfonyl)-imide. We report and discuss the performance of AC and pMeT electrodes in such ILs compared to that in propylene carbonate-based electrolytes, in order to give indications for further research effort in IL-based hybrid supercapacitors.

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1   Introduction

Electrochemical energy conversion and storage devices are playing a crucial role in the development of a new energy economy capable of substituting that based on fossil fuels [1]. Among such devices, supercapacitors of high specific power and energy are gaining even more importance as an intermittent power supply, load levelling, and energy storage in fields ranging from distributed energy networks to domestic and transport applications [2–7]. For high-performance supercapacitors, the components of these devices should be appropriately designed for envisioned use. For transportation, supercapacitors are expected to be coupled with fuel cells or batteries to provide the required power peaks during acceleration as well as for energy recovery during braking of electric vehicles. For such application, supercapacitors typically operate above room temperature and electrode and electrolyte materials should be selected to guarantee long cycle-life and high specific power and energy at such temperatures, with attention to low cost and non-toxicity for industrial viability. The latest generation of supercapacitors on the market are double-layer carbon supercapacitors (DLCSs) with electrolytic solutions based on aprotic organic solvents, typically acetonitrile (ACN), which allow operating voltages as high as 2.5 V at room temperature; devices based on propylene

carbonate (PC), a safe and environmentally compatible solvent, are also available. It is known that the electrochemical stability windows of organic electrolytes decrease with increasing temperature [8], and accelerated tests have demonstrated that the increase of cell voltage with such electrolytes significantly reduces their cycle-life, an effect even more marked by increasing the temperature from room temperature to 65 °C [9].

Hence, because of their very low vapor pressure, high chemical and thermal stability [10–12], wide electrochemical stability window [13, 14] and good conductivity [15] at the temperatures required for supercapacitor coupling with PEM fuel cells in electric vehicle, ionic liquids (ILs) are attracting attention as solvent-free "green" electrolytes for high voltage supercapacitors [16–23].

The electrochemical properties of the ILs, which are room temperature molten salts, depend on the type of cation and anion; the cation limits the negative potential window while the anion affects the positive potential window as well as the melting point, which in turn affects the temperature range for high conductivity of ILs. The cation and anion chemistry also affects the IL/water miscibility which depends on cation substituents and increases for anions in the order PF_6^-, $(CF_3SO_2)_2N^-$ (hydrophobic) $> BF_4^-$, $CF_3SO_3^- > CH_3CO_2^-$, $CF_3CO_2^-$ (hydrophilic) [24–26]. When ILs are used as electrolytes in supercapacitors, their electrochemical stability window has to match the potential range of the charge–discharge process of the two electrode materials so as to allow their deep charge–discharge. Furthermore, for long supercapacitor cycle life, the IL should be hydrophobic in order to display a low content of water and of water-soluble byproducts deriving from preparation procedures.

Research into electrode materials for supercapacitors is focusing on capacitive materials which store the charge electrostatically, such as activated carbons (ACs), carbon nanotubes and carbon aerogels with morphology and porosity designed for easy electrolyte access to double-layer surface, and on pseudocapacitive materials which store charge via fast and reversible Faradic processes at defined electrode potentials [2], such as inorganic oxides and electronically conducting polymers (ECPs).

In the last few years, the concept of asymmetric supercapacitors, in which the two electrode materials are charged–discharged with different modes – electrostatic and Faradic

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– has proven to be powerful because it enables separate electrode design in view of the required operating conditions [2, 4, 27, 28]. Different asymmetric devices operating at room temperature with organic electrolyte have already been developed by coupling electrodes based on ACs and ECPs [29–31], ACs and lithium inorganic oxides [32, 33], and lithium inorganic oxides and ECPs [34, 35]. We developed an AC/PC-Et_4NBF_4/poly(3-methyl-thiophene) (pMeT, electrochemically prepared) hybrid supercapacitor with a voltage of 3 V which delivers at room temperature 40 Wh kg^{-1} maximum specific energy (E_{max}) and 9 kW kg^{-1} maximum specific power (P_{max}) [29].

In order to develop AC//pMeT hybrid supercapacitors operating at 60 °C with cell voltage higher than 3 V, we pursued the strategy of using 1-butyl-3-methyl-imidazolium tetrafluoroborate, 1-butyl-3-methyl-imidazolium hexafluorophosphate (BMIMX, X = BF_4^-, PF_6^-) and N-butyl-N-methyl-pyrrolidinium bis(trifluoromethanesulfonyl)imide (PYR$_{14}$TFSI) ILs (1) [22, 23] and we demonstrated the long-term viability over 16 000 cycles of a device featuring PYR$_{14}$TFSI as electrolyte with a V_{max} of 3.43 V [23].

In this paper, we report and discuss the main features of BMIMX and PYR$_{14}$TFSI ILs and the performance of AC and pMeT electrode materials in these ILs at 60 °C compared to that in PC-based electrolytes, with the aim to highlight in which direction research should be focused to further enhance the performance of hybrid supercapacitors with ILs operating at high voltage above room temperature.

$$X^- = BF_4^-, PF_6^- \qquad N(SO_3CF_3)_2^- \qquad (1)$$
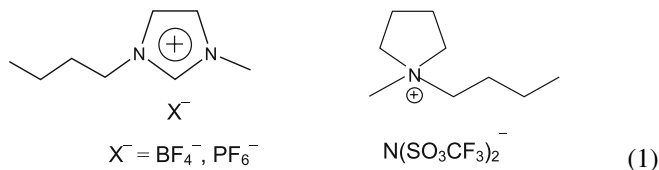
2   Experimental

The ILs BMIMX and PYR$_{14}$TFSI were prepared as in [36, 37]; the electrolyte PC-Et_4NBF_4 1 M (Mitsubishi) was used as received, PC-LiTFSI 1 M was prepared from PC (Fluka) twice-distilled under vacuum and dried LiTFSI (3 M). The water content in the electrolytes, which were stored and handled in dry box (MBraun Labmaster 130, H_2O and O_2 < 1 ppm), was checked by Karl Fisher titration (684 KF Coulometer Metrohm). Conductivity measurements were carried out with an AMEL mod.160 conductivity-meter by equilibrating the cell at each temperature in a Haake thermocryostat.

Evaluation of the electrochemical stability window was carried out with a linear sweep voltammetry (LSV) at 20 mV s^{-1} in dry box with a carbon coated Al grid (Al/C, Lamart) working electrode, carbon paper counter electrode (Spectracarb 2050, Spectracorp), and Ag quasi-reference electrode whose potential was measured by adding the highly reversible redox couple ferrocene/ferrocinium (Fc/Fc$^+$) to the medium (at 60 °C, $E_{1/2,Fc/Fc^+}$ = 432 mV vs. saturated calomel electrode SCE, E_{Ag} = −220 mV vs. $E_{1/2,Fc/Fc^+}$ in PYR$_{14}$TFSI).

The composite positive polymer electrode (pMeT$_{chem}$) was prepared with 80% w/w pMeT (Polyscience, chemically

prepared), 15% w/w acetylene black (AB, Hoechst) and 5% w/w polytetrafluoroethylene binder (PTFE, Du-Pont). For the negative carbon electrode (AC), 95% w/w activated carbon (PICACTIF Supercap BP) and 5% PTFE were mixed. The current collectors were carbon coated aluminum or copper grids (Lamart). Electrodes with pMeT electropolymerized on Pt (pMeT/Pt) were prepared galvanostatically at 10 mA cm^{-2} in a three-compartment cell with SCE reference electrode and Pt counterelectrode in ACN (distilled, Fluka)-0.5 M Et_4NBF_4 (Fluka, dried at 80 °C under dynamic vacuum over night)-0.1 MeT (distilled, Aldrich).

Electrochemical characterization of AC and pMeT-based electrodes was carried out by cyclic voltammetry (CV) at 20 mV s^{-1}, in dry box, using Ag quasi-reference electrode and double-layer carbon counter-electrodes with charge storage capability at least double that of the AC or pMeT working electrodes.

Hybrid supercapacitors were assembled in dry box as in [22, 23]. The electrochemical tests were performed with a Perkin–Elmer VMP multichannel potentiostat/galvanostat; the electrodes and supercapacitors were kept at the controlled temperature of 60 ± 2 °C by a Thermoblock (FALC).

3   Results and discussion

For high power performance AC/IL/pMeT super-capacitors, a low ESR is required; thus, the IL ionic conductivity has to be at least as high as that of the conventional organic electrolytes. Figure 1, which reports the Arrhenius conductivity plots in the temperature range 20–80 °C of the ILs BMIMX and PYR$_{14}$TFSI and of the two organic electrolyte solutions PC-Et_4NBF_4 and PC-LiTFSI, shows that the conductivity values (σ) of the ILs are comparable to those of the two conventional organic electrolytes at temperatures of at least 60 °C.

For high cell-voltage and, hence, high E_{max} AC//pMeT hybrid supercapacitors, the electrochemical stability window of the electrolyte should be as wide as possible at the envisioned operating temperature. Figure 2 shows the LSVs of carbon-coated aluminum grids (Al/C) in PYR$_{14}$TFSI at 60 °C and 30 °C and in PC-LiTFSI at 60 °C. These data demonstrate the advantage of using IL, which at 60 °C allows cell voltage up to 1 V wider than that provided by conventional organic electrolyte at room- and, more importantly, at the highest temperature.
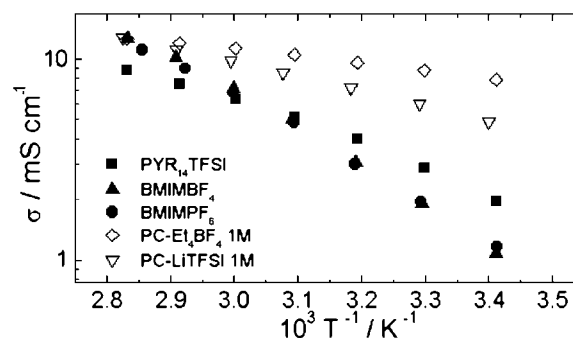

FIGURE 1   Arrhenius conductivity plots from 20 °C to 80 °C of the ILs BMIMX and PYR$_{14}$TFSI and of PC-Et_4NBF_4 1 M and PC-LiTFSI 1 M
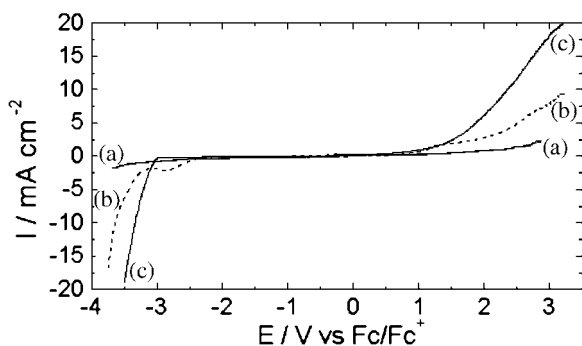
FIGURE 2 Linear sweep voltammetry at $20\,\text{mV s}^{-1}$ and $60\,^{\circ}\text{C}$ in PYR$_{14}$TFSI (a) and in PC-LiTFSI 1 M at $30\,^{\circ}\text{C}$ (b) and $60\,^{\circ}\text{C}$ (c) of the Al/C current collector

FIGURE 3 Capacitance values per gram of composite electrode material (C_{ecm}) of AC electrodes from cyclic voltammetry at $20\,\text{mV s}^{-1}$ and $60\,^{\circ}\text{C}$ in PYR$_{14}$TFSI (*full line*, composite electrode weight $= 8\,\text{mg cm}^{-2}$) and in PC-Et$_4$NBF$_4$ 1 M (*dashed line*, composite electrode weight $= 11\,\text{mg cm}^{-2}$)

The performance of the electrodes for AC/IL/pMeT hybrid supercapacitors was evaluated at $60\,^{\circ}\text{C}$, in terms of negative ($V_{\text{max},-}$) and positive ($V_{\text{max},+}$) potential limits that ensure Coulombic efficiencies ($\eta\%$) of their charge–discharge processes higher than 95%, and in terms of their specific capacitances in these electrode potential ranges. As an example, Fig. 3 shows the values of capacitance per gram of composite material (C_{ecm}) of an AC negative electrode obtained by cyclic voltammetry at $60\,^{\circ}\text{C}$, with $\eta\% > 95\%$, in PYR$_{14}$TFSI and in PC-Et$_4$NBF$_4$ 1 M. The data show that in PYR$_{14}$TFSI the charge–discharge process of the AC can be extended over a wider potential range than in PC-Et$_4$NBF$_4$, but the capacitive response in the former electrolyte is lower than that in the latter. This may be because pore size distribution in the AC is not adequate for the IL or because of the presence of hydrophilic moieties on the carbon surface that prevent easy interaction with the hydrophobic PYR$_{14}$TFSI.

Table 1 shows the $V_{\text{max},-}$, $\eta\%$ and C_{ecm} data, the latter estimated from the integrated charge (upon discharge) vs. electrode potential by cyclic voltammetry of the AC negative electrode at $60\,^{\circ}\text{C}$ in BMIMX, PYR$_{14}$TFSI, and PC-Et$_4$NBF$_4$ 1 M. All the ILs displayed more negative $V_{\text{max},-}$ than that of the conventional organic electrolyte; the fact that BMIMBF$_4$, with same cation as BMIMPF$_6$, displayed a less negative $V_{\text{max},-}$ was ascribed to the presence of water-soluble impurities derived from its preparation, and difficult to remove because of the higher affinity for water of the first IL with respect to the latter [24–26]. Table 1 reports the water content in the
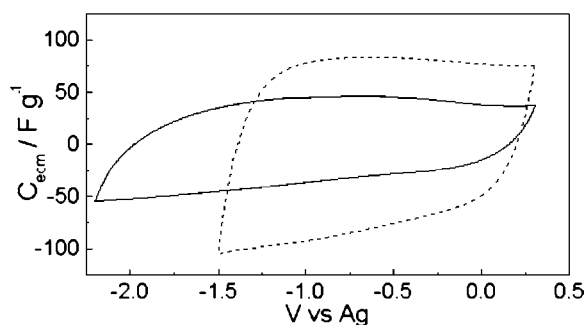
ILs and PC-Et$_4$NBF$_4$ 1 M and shows that, while PYR$_{14}$TFSI and the conventional organic electrolyte were very dry systems, the BMIMX, and mainly BMIMBF$_4$, displayed a significant amount of dissolved H$_2$O. Indeed, a high purity of the ILs is of paramount importance for a high reversibility of the electrode charge–discharge processes, as evinced by the data in the table for PYR$_{14}$TFSI (obtained at a high level of purity [12, 23]), which despite the low capacitance values of the AC electrode provides the highest Coulombic efficiency and the most negative $V_{\text{max},-}$. Optimization of the preparation procedure of BMIMX, and particularly of BMIMBF$_4$, may improve $\eta\%$ of the AC negative electrodes with these ILs, whereas optimization of the affinity of the AC towards PYR$_{14}$TFSI by increasing its mesoporosity and removing hydrophilic surface groups, may increase the surface available for the double-layer charging process, thus enhancing its specific capacitance in such an IL. Carbon aerogels, whose porosity and tendency to adsorb water can be tailored to their envisioned use [38, 39], are promising carbonaceous electrode materials for IL-based supercapacitors.

Table 1 also shows the $V_{\text{max},+}$, $\eta\%$ and C_{ecm} data in the ILs and PC-Et$_4$NBF$_4$ 1 M for pMeT$_{chem}$ positive composite electrodes; data for a positive electrode obtained by electropolymerization of pMeT on Pt (pMeT/Pt) and tested in PYR$_{14}$TFSI are also reported. These data indicate that at $60\,^{\circ}\text{C}$ the potential range useful for the *p*-doping/undoping of the pMeT$_{chem}$ electrode widens in ILs with a Coulombic

Electrolyte	H$_2$O (ppm)	negative electrode AC			positive electrode pMeT$_{chem}$			AC//pMeT			
		$V_{\text{max},-}$ (V vs. Ag)	$\eta\%$	C_{ecm} (F g^{-1})	$V_{\text{max},+}$ (V vs. Ag)	$\eta\%$	C_{ecm} (F g^{-1})	V_{max} (V)	$R_{ecm,+/-}$	C_{tcm} (F g^{-1})	E_{max} (Wh kg^{-1})
BMIMPF$_6$	170	−2.40	95	110	1.50	95	90	3.90	2.8	20	42
BMIMBF$_4$	1500	−1.75	97	110	-	-	-	- -	- -	- -	-
PYR$_{14}$TFSI	20	−2.20	99	45	1.40	99	80	3.60	1.3	14	25
					1.40[a]	97[a]	135[a]	3.60[a]	0.8[a]	18[a]	32[a]
PC-Et$_4$NBF$_4$	5	−1.50	96	80	1.20	90	75	2.70	2.1	17	17

[a] data for pMeT/Pt electrode obtained by pMeT electropolymerization on Pt.

TABLE 1 Water content in the IL, negative ($V_{\text{max},-}$) and positive ($V_{\text{max},+}$) potential limits, Coulombic efficiency values ($\eta\%$) of the charge–discharge processes of AC negative and pMeT$_{chem}$ positive composite electrodes and capacitance values per gram of composite electrode materials (C_{ecm}) by cyclic voltammetry at $60\,^{\circ}\text{C}$ and $20\,\text{mV s}^{-1}$ in BMIMX, PYR$_{14}$TFSI, and PC-Et$_4$NBF$_4$ 1 M. Feasible values of maximum cell voltage (V_{max}), positive to negative composite electrode mass ratio ($R_{ecm,+/-}$), device specific capacitance (C_{tcm}) and maximum specific energy (E_{max}) for AC//pMeT hybrid supercapacitors with the different electrolytes
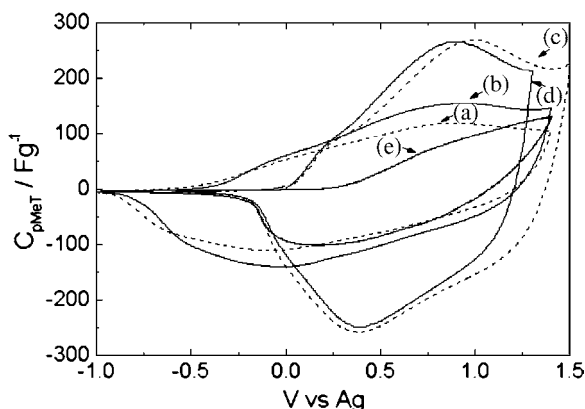
FIGURE 4 Capacitance values per gram of pMeT (C_{pMeT}) from cyclic voltammetry at $20\,\mathrm{mV\,s^{-1}}$ of the electrodes pMeT/Pt in PYR$_{14}$TFSI at 30 °C (a) and 60 °C (b) and in PC-LiTFSI 1 M at 30 °C (c) and 60 °C (d), and of a pMeT$_{chem}$ composite polymer electrode at 60 °C in PYR$_{14}$TFSI (e) with $3\,\mathrm{mg\,cm^{-2}}$ of polymer

efficiency higher than 95% and, particularly in the presence of BMIMPF$_6$ the specific capacitance increases. However, the specific capacitance of the polymer is 35% lower than that displayed in the same experimental conditions by the electrochemically prepared pMeT/Pt electrode and ca. 50% lower than that obtained in PC-Et$_4$NBF$_4$ at room temperature with a composite electrode with electrochemically prepared pMeT [29].

Figure 4 compares the capacitance values per gram of pMeT, C_{pMeT}, of the pMeT/Pt electrode from cyclic voltammetry at 30 °C and 60 °C in PYR$_{14}$TFSI and PC-LiTFSI 1 M and of a pMeT$_{chem}$ composite electrode with the same pMeT content of $3\,\mathrm{mg\,cm^{-2}}$ tested at 60 °C in PYR$_{14}$TFSI. The pMeT/Pt electrode shows a better capacitance than the pMeT$_{chem}$ composite electrode in PYR$_{14}$TFSI at 60 °C, and at the two temperatures it displays significantly higher values in the conventional organic electrolyte than in the IL. However, with the temperature increase, in PC-LiTFSI the pseudocapacitance of pMeT/Pt decreases and the $V_{max,+}$ is less positive, whereas in the IL the pseudocapacitance increases, maintaining a high Coulombic efficiency within the same potential limit. Table 2, which reports the $V_{max,+}, \eta\%$, capacity and specific capacitance data of the pMeT/Pt electrode in PYR$_{14}$TFSI and PC-LiTFSI at 30, 60 and 80 °C, confirms this trend up to 80 °C. These data indicate that the preparation procedure of the polymer composite electrode has to be improved and that the electrochemical approach can yield a polymer with high performance in the IL. Work is in progress in our laboratory to optimize electropolymerization even using IL in

the polymerization bath. Furthermore, in the pMeT$_{chem}$ composite electrode, a carbon-conducting additive and a binder are present. These components have to be carefully selected with respect to their affinity for the ILs in order to increase the polymer permeability to these electrolytes.

In hybrid supercapacitors, the electrode material mass balancing is an important issue, affecting the specific properties as well as cycle-life. The optimum positive to negative composite material weight ratio ($R_{ecm,+/-}$) can be evaluated on the basis of the different capacitances of the two electrode materials and of the different potential ranges for their different charge processes, using the equation $R_{ecm,+/-} = (V_{max,-} - V_{discharge,-})C_{ecm,-}/(V_{max,+} - V_{discharge,+})C_{ecm,+}$ (2), in which $V_{discharge,-}$ and $V_{discharge,+}$ are the potentials of the negative and positive electrodes in the discharged state. Given the experimental data at 60 °C summarized in Table 1, we evaluated the optimum $R_{ecm,+/-}$ values for AC//pMeT hybrid supercapacitors with the ILs and PC-Et$_4$NBF$_4$ electrolyte operating at 60 °C (a typical value of 0.3 V vs. Ag was considered for $V_{discharge,-}$ and $V_{discharge,+}$). The data are reported in Table 1 with the estimated feasible values of cell maximum operating voltage (V_{max}), device specific capacitance (C_{tcm}) and E_{max} of the different AC//pMeT supercapacitors with the corresponding $R_{ecm,+/-}$ values; the C_{tcm} data were calculated by the formula $C_{tcm} = [(C_{ecm,+}R_{ecm,+/-})^{-1} + C_{ecm,-}^{-1}]^{-1}/(R_{ecm,+/-} + 1)$ (3). The V$_{max}$ and E$_{max}$ data clearly show the great advantage provided by the use of ILs, which may enable a cell voltage as high as 3.9 V and 3.6 V in the case of BMIMPF$_6$ and PYR$_{14}$TFSI, respectively. Furthermore, despite the lower specific capacitance of AC in PYR$_{14}$TFSI than in PC-Et$_4$NBF$_4$, using a suitable $R_{ecm.,+/-}$ ratio makes it possible to assemble a AC/PYR$_{14}$TFSI/pMeT device with a slightly lower specific capacitance than that of a supercapacitor with the PC-based electrolyte, but with a maximum specific energy significantly higher because the cell voltage is higher by 0.9 V. The BMIMPF$_6$ provides the highest expected device capacitance and voltage and, hence, the highest maximum specific energy of $42\,\mathrm{Wh\,kg^{-1}}$.

In previous work [22, 23] we assembled and tested AC/BMIMPF$_6$/pMeT$_{chem}$ and AC/PYR$_{14}$TFSI/pMeT$_{chem}$ hybrid supercapacitors with $12\,\mathrm{mg\,cm^{-2}}$ of total composite electrode materials and $R_{ecm,+/-}$ of 1.6 and 0.5, respectively. Figure 5 reports their cell voltage profiles at the 105th galvanostatic cycle and 60 °C. The AC/BMIMPF$_6$/pMeT$_{chem}$ and AC/PYR$_{14}$TFSI/pMeT$_{chem}$ supercapacitors displayed $30\,\mathrm{Wh\,kg^{-1}}$ and $28\,\mathrm{Wh\,kg^{-1}}$ E_{max} and $10\,\mathrm{kW\,kg^{-1}}$ and $17\,\mathrm{kW\,kg^{-1}}$ P_{max} with a V_{max} of 3.4 V. The main drawback in such supercapacitors is the high ESR of $25\,\Omega\,\mathrm{cm^2}$

T	PYR$_{14}$TFSI				PC-LiTFSI			
(°C)	$V_{max,+}$ (V vs Ag)	$\eta\%$	Q_{pMeT} (mAh g^{-1})	C_{pMeT} (F g^{-1})	$V_{max,+}$ (V vs. Ag)	$\eta\%$	Q_{pMeT} (mAh g^{-1})	C_{pMeT} (F g^{-1})
30	1.4	98.8	43	105	1.4	96.6	67	240
60	1.4	96.7	54	134	1.3	96.1	64	225
80	1.4	95.7	60	150	1.2	95.5	55	210

TABLE 2 Positive potential limit ($V_{max,+}$) and Coulombic efficiency ($\eta\%$) data of the p-doping/undoping processes of pMeT/Pt electrodes (electrochemically prepared) and values of capacity (Q_{pMeT}) and capacitance (C_{pMeT}) per gram of polymer. The latter is estimated from the integrated charge vs. electrode potential from cyclic voltammetry at 60 °C and $20\,\mathrm{mV\,s^{-1}}$ in PYR$_{14}$TFSI, and PC-LiTFSI 1 M
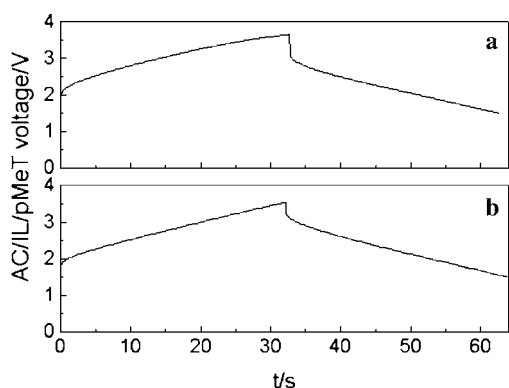
FIGURE 5   Voltage profiles of the AC/IL/pMeT$_{chem}$ hybrid supercapacitors with (**a**) BMIMPF$_6$ and (**b**) PYR$_{14}$TFSI during the 105th galvanostatic cycle at $10\,mA\,cm^{-2}$ and $60\,°C$

and $14\,\Omega\,cm^2$, respectively, as evaluated from the Ohmic drop of the reported cell voltage profiles. These high values arise from electrode charging resistance and electrolyte bulk resistance and may be lowered with optimized electrode materials and with a suitable separator. Indeed, the AC/PYR$_{14}$TFSI/pMeT$_{chem}$ supercapacitor, with the lowest ESR, was assembled without a separator and by keeping the electrodes sufficiently distant (ca 0.5 mm) for not causing a short circuit. With a suitable separator, an ESR value of $10\,\Omega\,cm^2$ is feasible, so that the P_{max} would become $25\,kW\,kg^{-1}$ for both hybrid supercapacitors with the commercial electrode materials.

The cycling stability of hybrid supercapacitors operating with ILs was also demonstrated by using PYR$_{14}$TFSI: the supercapacitor displayed specific energy and power of practical interest over 16 000 charge–discharge cycles at $60\,°C$ and at the 16 000th cycle the E_{max} and P_{max} were $12\,Wh\,kg^{-1}$ and $6\,kW\,kg^{-1}$, respectively [23]. This is an important result obtained with still not optimized materials and $R_{ecm,+/-}$, which demonstrates the long-term viability of ILs in hybrid supercapacitors.

4   Conclusions

The results of our studies demonstrate that ILs can be used as "green" electrolytes for enhancing the performance of AC//pMeT hybrid supercapacitors in terms of high voltage and long cycle life at the high temperatures required for application in fuel-cell-powered electric vehicles. The AC/BMIMPF$_6$/pMeT$_{chem}$ and AC/PYR$_{14}$TFSI/pMeT$_{chem}$ hybrid supercapacitors, though still not optimized for material "affinity" towards the ILs and for positive to negative electrode mass balancing, delivered at $60\,°C$ high specific energy and power that can be further enhanced by optimizing the entire system. The components of the composite electrodes, i.e., binder, carbon-conducting additive, pMeT and, particularly, AC, have to be selected with attention to a higher affinity for the hydrophobic ILs and to their morphology for easy IL access to the electrode's active surface; alternative negative electrode materials such as carbon aerogels can also be considered. For the polymer, electrochemical preparation directly on the current collector provides electrode materials of higher capacitance in IL than that of composite electrodes

with chemically prepared pMeT. This may be due to different morphology of electrochemically and chemically prepared pMeT as well to the presence of binder and carbon-conducting additive in the pMeT composite electrodes. Finally, a suitable separator should reduce the ESR, with a positive effect on the delivered specific power, while optimization of the electrodes mass balancing should enhance the overall performance of the system. It is noteworthy that the preparation of ILs, and particularly of BMIMX, should be carried out with a high level of purity in order to increase the cycling stability of the electrode materials, to broaden the potential range for their charge–discharge process and, hence, to increase the supercapacitor cell voltage.

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