

Short communication

N-Methyl-*N*-propylpiperidinium bis(trifluoromethanesulphonyl)imide as an electrolyte for carbon-based double-layer capacitors

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Abstract

N-Methyl-*N*-propylpiperidinium bis(trifluoromethanesulphonyl)imide (MePrPipNTf₂), as well as its mixture with a molecular liquid acetonitrile (MeCN) were tested as electrolytes for carbon-double-layer capacitors. The conductivity of the MePrPipNTf₂ neat ionic liquid is at the level of 1.5 mS cm⁻¹, while the corresponding value for the mixture (48 wt.% MePrPipNTf₂ + 52 wt.% of MeCN) is *ca.* 40 mS cm⁻¹ (both recorded at 25 °C). The electrochemical stability of the electrolyte (both neat ionic liquid, as well as its mixture with acetonitrile), detected at the glassy carbon electrode, was as broad as 5.7 V. However, the tested capacitors with activated carbon as the active electrode material show considerable lower stability, reduced to *ca.* 3.7 V. The specific capacity estimated from both cyclic voltammetry and charging/discharging experiments was *ca.* 140 F g⁻¹, and after *ca.* 700 cycles, decreased to *ca.* 100 F g⁻¹. The effect of the loss of the part of initial specific capacity is probably due to the loss of Faradaic pseudo-capacity. The specific energy of the activated carbon in the tested devices was at the level of 240 kJ kg⁻¹ while the specific power density was *ca.* 25 kW kg⁻¹.

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1. Introduction

The electric capacity of the electrode/electrolyte double layer is usually of the order of tens of μF cm⁻² for classical aqueous and nonaqueous electrolyte solutions [1]. In the case of solvent free fused salts the specific capacity of the double layer seems to be somewhat lower, but may approach values of a few to 10 μF cm⁻² [2–4]. Electrodes prepared from high-specific-surface area carbons (*ca.* 2000 m² g⁻¹), and filled with an electrolyte, may produce high capacity of the order of 100 F g⁻¹ of carbon. Such a capacitor, consisting of two carbon electrodes, separated by a separator, and filled with an electrolyte, usually called electrochemical double-layer capacitor (EDLC), may be used as an energy storage device. The EDLC charging and discharging is the effect of charge separation, theoretically without any Faradaic reactions, and hence, should be characterised by relatively high power density, in comparison to primary or secondary bat-

teries. Capacitors are also characterised by a much higher number of possible charging/discharging cycles (even 100,000) in comparison to secondary batteries (typically *ca.* 1000). Aqueous and organic solutions of electrolytes [1], as well as a number of polymer electrolytes [5–15] have been applied in EDLCs.

Classical liquid, both aqueous as well as nonaqueous (organic) solutions of electrolytes are prepared by dissolution of salts in molecular solvents, and consist of solvated ions separated by solvent molecules. On the other hand, salts of low melting point, called molten salts, room temperature ionic liquid (RTIL), or simply ionic liquids (IL), are free of any molecular solvent. Ionic liquids show a broad electrochemical stability window of *ca.* 4 V or broader [16], and hence, they have been applied in EDLCs as neat ionic liquids or as solutions in molecular solvents [17–26]. Ionic liquids are able to dissolve polymers, with the formation of ion conducting composites (polymer-IL), and such electrolytes were tested in EDLCs [27–37].

The general aim of the present work was to study the properties of *N*-methyl-*N*-propylpiperidinium bis(trifluoromethanesulphonyl)imide as a component of carbon-based double-layer capacitors. The salt was chosen as a potential electrolyte

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due to its exceptionally broad electrochemical stability determined at a solid electrode [16].

2. Experimental

2.1. Materials

Activated carbon fabric ACC-507-25 ($2500 \text{ m}^2 \text{ g}^{-1}$, thickness 0.4 mm) was obtained from Nippon Kynol INC, graphite SL-20 from Superior Graphite (USA) and carbon black (CB) from Fluka. Cryptand 222 (4,7,13,16,21,24-hexaoxa-1,10-diazabicyclo[8.8.8]hexacosane) was from Merck. *N*-Methyl-2-pyrrolidone (NMP, Fluka) and acetonitrile (Fluka, >99.9%) were distilled through a Vigreux column and stored over A3 molecular sieves. The activated carbon cloth was dried before use in 180°C for 24 h. *N*-Methyl-*N*-propyl-piperidinium bromide (MePrPipBr) was synthesised from *N*-methyl piperidine (Aldrich) and bromopropane (Aldrich) in chloroform. MePrPipBr was purified by crystallisation in 2-propanol (P.O.Ch., Poland); after addition of tetrahydrofurane (P.O.Ch., Poland) white crystals of MePrPipBr were precipitated. *N*-Methyl-*N*-propyl-piperidinium bis(trifluoromethanesulphonyl)imide (MePrPipNTf₂) was obtained from MePrPipBr by metathesis with lithium bis(trifluoromethanesulphonyl)imide (Fluka) in aqueous solution. The ionic liquid was dried in a vacuum at 50°C for 10 h and finally kept over A3 molecular sieves. The water content determined with the Karl Fisher method was below the detection limit.

2.2. Capacitors

Carbon electrodes were prepared by pressing a slurry of carbon black and graphite in NMP into the activated carbon fabric. After evaporation of the solvent, the final electrode had a composition of 8 wt.% of CB + 15 wt.% of G + 77 wt.% of AC. Capacitors were assembled from two carbon electrodes, of comparable mass, separated by a glass micro-fibre GF/A separator (thickness 0.3 mm, Whatmann), all filled with the electrolyte, and placed in an adapted 0.5 in. Swagelok[®] connecting tube. All operations were done in a dry argon atmosphere in a glove box. One carbon electrode with a thickness of 0.4 mm and a radius of 10.6 mm, contained AC of the mass of *ca.* 7.0–7.4 mg.

2.3. Measurements

The charging/discharging measurements were done using the ATLAS 0461 MBI multi-channel electrochemical system (Atlas-Sollich, Poland) and cyclic voltammetry experiments with μ AutoLab Electrochemical System (EcoChemie, the Netherlands). The conductivity of MePrPipNTf₂ and its mixtures with acetonitrile was obtained from impedance spectroscopy performed in a cell Pt|electrolyte|Pt, over a frequency range from 0.01 Hz to 99 kHz, with an ac potential amplitude of 10 mV, applying the Atlas-Sollich 98 E II system. The cell contained two parallel platinum rods, each with a 1.22 mm diameter and thermostated through a water jacket ($25.0 \pm 0.1^\circ\text{C}$).

The cell constant was obtained from measurements at 25.0°C with KCl 0.01 M and 0.1 M solutions. Cyclic voltammetry curves were recorded in the three electrode configuration against the ‘cryptate reference’ electrode, consisting of a silver wire immersed in a solution of Ag⁺ 0.01 M and cryptand 222 0.1 M in dimethylsulphoxide (Ag/(Ag⁺ 0.01 M, 222 0.1 M in DMSO)). The solution was contained in a glass tube with a glass frit at the end.

3. Results and discussion

3.1. Electrolyte conductivity

The conductivity of the MePrPipNTf₂ neat ionic liquid, was detected from the impedance measurements at the level of 1.5 mS cm^{-1} at 25°C , which agrees very well with the literature data [16]. The relatively low specific conductivity of the ionic liquid is probably due to its high viscosity (*ca.* 117 cP [16] at 25°C). With increasing temperature, the conductivity increases according to the Arrhenius law (Fig. 1). The activation energy detected from the $\log(\sigma) = f(1/T)$ straight line is 27.6 kJ mol^{-1} . Increasing the IL temperature for example to 80°C results in a conductivity increase by a factor 5.8, only to *ca.* 8.7 mS cm^{-1} . Mixing of ionic liquid with a molecular liquid, characterised by low viscosity, is an effective way of conductivity increase [38]. One of the solvents characterised by both broad electrochemical stability as well as low viscosity (0.345 cP at 25°C) is acetonitrile (MeCN). Fig. 2 shows the dependence of the conductivity of the MePrPipNTf₂ mixtures with MeCN as a function of composition. The conductivity increases significantly with the increasing content of acetonitrile, up to *ca.* 40 mS cm^{-1} (maximum at MeCN wt.% of *ca.* 50–55) and then decreases.

3.2. Stability of the glassy carbon–electrolyte interface

A typical curve showing the electrochemical stability window of the electrolytes (MePrPipNTf₂ or MePrPipNTf₂ + MeCN)

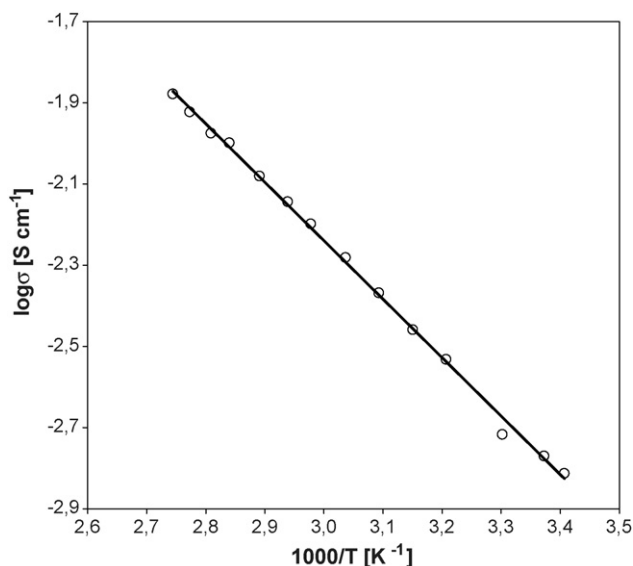


Fig. 1. Arrhenius plot for the conductivity of the neat ionic liquid MePrPipNTf₂.

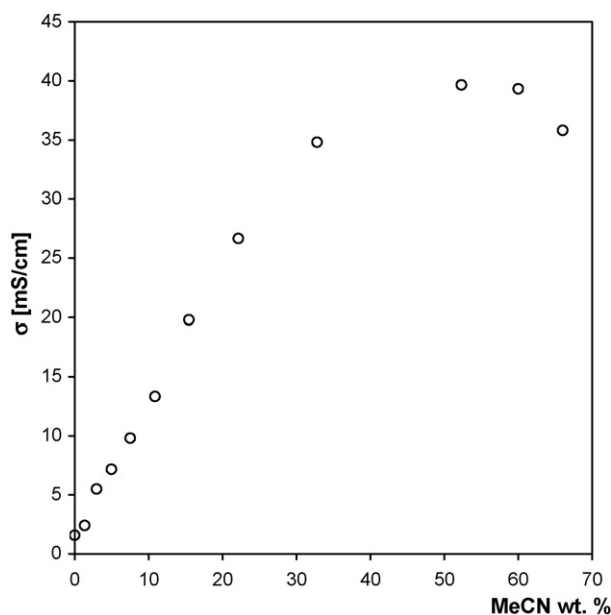


Fig. 2. Conductance of the MePrPipNTf₂ + MeCN mixtures as a function of the composition. Temperature: 25.0 °C.

at the glassy carbon electrode is shown in Fig. 3. The anodic limit is *ca.* +2.9 V and the cathodic limit is *ca.* -2.8 V (both expressed versus the Ag/(Ag⁺ 0.01 M, 222 0.1 M, in DMSO) reference), which leads to a very broad theoretical stability range of *ca.* 5.7 V. This value may be compared to those characteristic for some other popular ionic liquids. The cathodic limit of the electrochemical stability window of the ionic liquids based on the EtMeIm⁺ cation at the glassy carbon electrode is -2.1 V (measured against the Ag/Ag⁺ (0.01 M in DMSO) reference) [19]. The electrochemical stability window of *ca.* 4.5 V was determined for the EtMeImTf with the cathodic limit of *ca.* -2.1 V and anodic limit at *ca.* 2.4 V [36]. The BuMePy⁺ cation is reduced at the glassy carbon at a more positive potential of *ca.* -1.0 V. The anodic oxidation of the tetrafluoroborate anion (BF₄⁻) takes place at the potential of *ca.* 2.1 V, while the hexafluorophosphate (PF₆⁻) and imide (N(CF₃SO₂)₂⁻) anions are oxidised at the potential of *ca.* 2.0 V. Therefore, the EtMeImTf

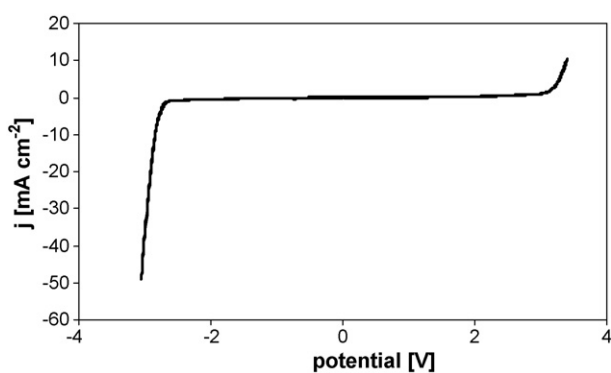


Fig. 3. Cyclic voltammety of the electrolyte: 47.7 wt.% MePrPipNTf₂ + 52.3 wt.% at the glassy carbon electrode (surface 0.0707 cm²). Potential recorded against the Ag/(Ag⁺ 0.01 M, 222 0.1 M in DMSO) reference. Scan rate: 10 mV s⁻¹.

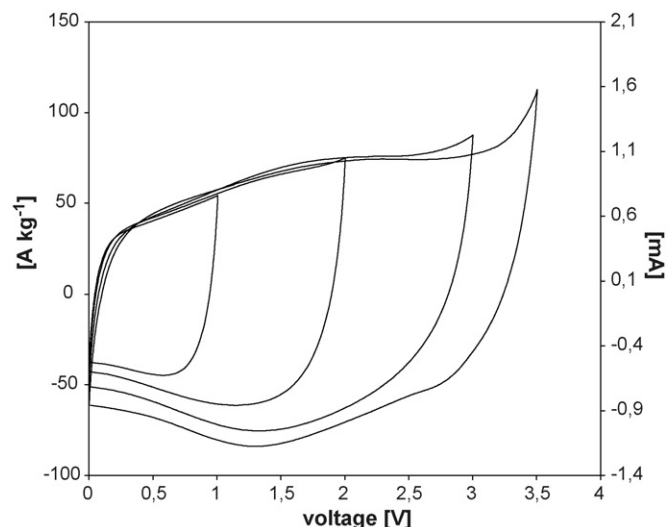


Fig. 4. Cyclic voltammety of the tested capacitor (7.1 mg of Kynol 2500 m² g⁻¹ in one electrode). Electrolyte: neat ionic liquid MePrPipNTf₂. Scan rate: 2 mV s⁻¹.

is more stable in comparison to EtMeImPF₆ or EtMeImN(Tf)₂, due to the higher oxidation potential of the triflate anion. However, the MePrPipNTf₂ ionic liquid is much more stable due to both a more negative cathodic reduction limit as well as a more positive anodic oxidation limit.

3.3. Cyclic voltammety of the capacitor

Fig. 4 shows a typical cyclic voltammety of a capacitor with neat ionic liquid as an electrolyte. As can be seen in figure, the curve has a rectangular shape, typical of capacitive behaviour, at all potential ranges (up to 3.5 V). The current flowing through the device at a polarization rate of 2 mV s⁻¹ was *ca.* 1 mA. The double layer capacitance may be estimated approximating the system by a simply equivalent circuit consisting of two capacitors (of an equal capacitance) and an equivalent series resistance R_s (Fig. 5). The capacity of the device was *ca.* $C = 1 \text{ mA} / (2 \text{ mV s}^{-1}) = 0.5 \text{ F}$, and hence, the capacity of a single electrode was twice higher (*ca.* 1 F). Taking into account the mass of AC in one electrode (*ca.* 7 mg), the specific capacity of the activated carbon was *ca.* $C_S = 1 \text{ F} / 0.007 \text{ g} \approx 140 \text{ F g}^{-1}$ (expressed versus the mass of AC in one electrode). Taking into account the specific surface of the activated carbon (2500 m² g⁻¹), the capacity may be expressed against the electrode surface: $C_S = (140 \text{ F g}^{-1}) / (2500 \text{ m}^2 \text{ g}^{-1}) \approx 5.6 \mu\text{F cm}^{-2}$.

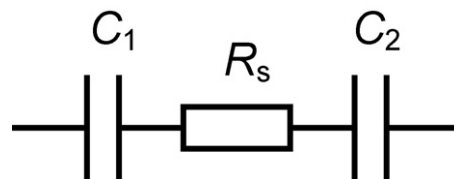


Fig. 5. Equivalent circuit used for the AC/IL capacity calculation. Both electrodes have the same mass and geometry ($C_1 = C_2$). The resistor R_s represents the equivalent series resistance.

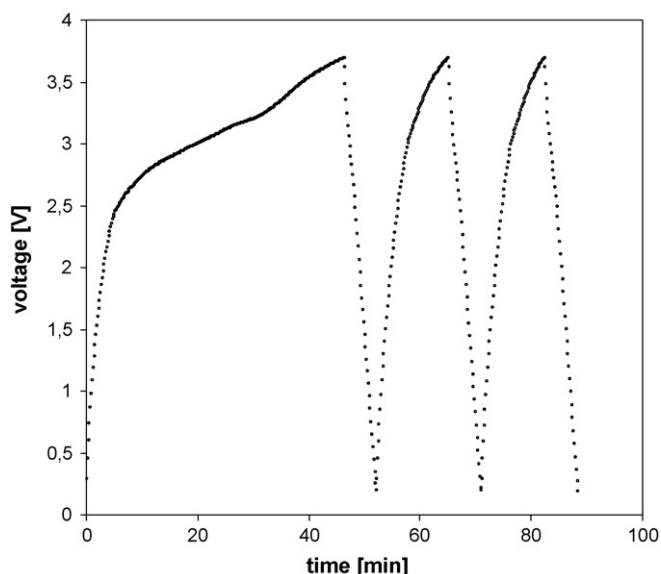


Fig. 6. Initial galvanostatic charging/discharging of the tested capacitor (7.0 mg of Kynol $2500 \text{ m}^2 \text{ g}^{-1}$ in one electrode). Electrolyte: 48.0 wt.% MePrPipNTf₂ + 52.0 wt.% of MeCN. Current: 5 mA.

3.4. Galvanostatic charging/discharging

Galvanostatic charging/discharging experiments were performed for neat ionic liquid as the electrolyte, as well as for the mixture of the ionic liquid with acetonitrile (MePrPipNTf₂ (ca. 48 wt.%) + MeCN (ca. 52 wt.%)). The current flowing through the tested capacitors was established at levels of 1 mA, 3 mA, 5 mA or 10 mA. Taking into account the activated carbon mass of ca. 7.0 mg in one electrode, and ca. 14 mg in the capacitor, the current densities, expressed versus the AC mass in the device, were 71 A kg^{-1} , 214 A kg^{-1} , 357 A kg^{-1} and 710 A kg^{-1} . After assembling the capacitor showed a non-typical charging–discharging behaviour (Fig. 6)—it required some kind of ‘formation’ during the first cycle, after which it was characterised by the usual charging–discharging $E=f(t)$ curves (Fig. 7). The sharp change of the potential during the switching from charging into discharging, is due to the ohmic loss which arises from the internal series resistance of the device. The capacity of the device calculated from the current (I) and the slope (dU/dt) of the charging/discharging curves, according to the formula $C=I/(dU/dt)$, was ca. 0.51 F for the initial cycles, which leads to the same specific capacity as that estimated from the cyclic voltammetry (ca. 140 F g^{-1}). However, during the next 300 cycles the specific capacity increased to ca. 160 F g^{-1} , and then decreased (after ca. 700 cycles) to a constant value of ca. 100 F g^{-1} (Fig. 8). This value is characteristic for the system at the next cycles (at least 15,000 cycles measured). The effect of the loss of the part of the initial specific capacity is probably due to the loss of Faradaic pseudo-capacity after ca. 700 cycles. Although the cyclic voltammetry at the glassy carbon electrode suggests a very broad stability range of ca. 5.7 V, the practical devices with activated carbon as the active electrode material show considerable lower stability, reduced to ca. 3.7 V. Carbon materials are in general chemically and electrochemi-

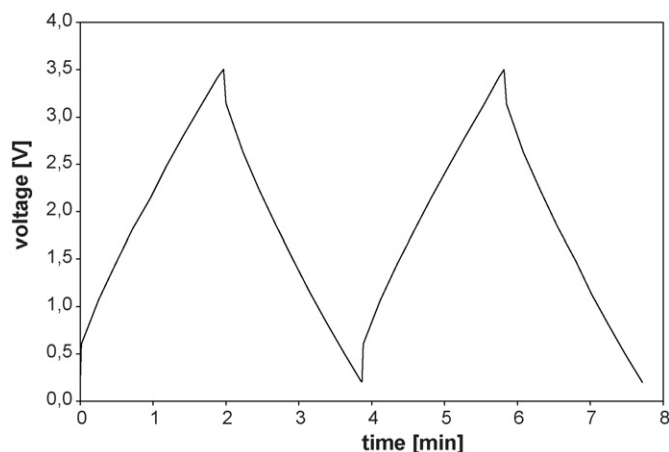


Fig. 7. Galvanostatic charging/discharging of the tested capacitor (7.2 mg of Kynol $2500 \text{ m}^2 \text{ g}^{-1}$ in one electrode). Electrolyte: 47.7 wt.% MePrPipNTf₂ + 52.3 wt.% of MeCN. Current: 10 mA, current density 694 A kg^{-1} of AC. Cycle 915 and 916.

cally unstable [39,40]. In contact with atmospheric oxygen the carbon surface is oxidized with formation of oxygen containing functionalities, such as carboxyl, hydroxyl or carbonyl, with the oxygen to carbon ratio even 0.2 [41]. These functionalities may undergo faradaic red-ox reactions, which results in lowered electrochemical stability of the carbon. In addition, both glassy carbons as well as activated carbons are prepared under different conditions from different precursors, which results in a variety of final products showing different electrochemical stabilities. The possible functionalities may not only reduce the electrochemical stability range, but may also be responsible for the loss of the pseudo-capacity after several 100 cycles. At higher potentials applied to the capacitor, at a current density of ca. 200 A kg^{-1} of AC, a decrease of the capacity was detected after approximately 1000 cycles. At higher final voltages (4.0 V) and currents (710 A kg^{-1} of AC) the decrease of the capacity was observed even after 100 cycles.

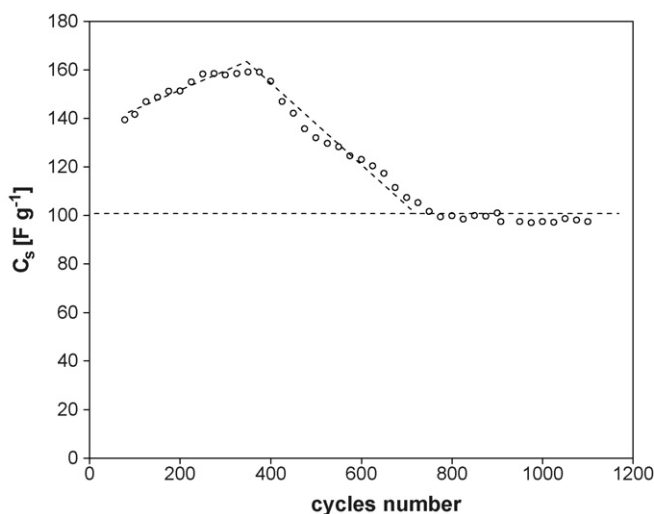


Fig. 8. Dependence of the specific capacity of the activated carbon on the cycle number. Mass of Kynol $2500 \text{ m}^2 \text{ g}^{-1}$ in one electrode was 7.1 mg. Electrolyte: 47.7 wt.% MePrPipNTf₂ + 52.3 wt.% of MeCN. Current: 10 mA.

3.5. Specific energy and power densities

Energy E stored in a capacitor is proportional to its capacity, C , as well as to the voltage U in the second power: $E = CU^2/2$, while the maximum power P is independent of the capacity: $P = E/t = U^2/4R_s$. The series resistance R_s which appears in Eq. (2) is due to the resistance of the electrolyte contained in the separator as well as that in the pores, and the connection resistance between solid parts of the electrode. Electrodes made of activated carbons of very high porosity, possess a high volume fraction which is occupied by the electrolyte. The resistance of a capacitor composed of flat electrodes is solely the resistance of the electrolyte layer between the electrodes. However, in the case of the porous electrodes, the resistance of the electrolyte in the pores is much higher [39]. Therefore, from the point of view of the high power of the device, the thickness of the carbon electrode, containing electrolyte in the pores, as well as the separator, should be as low as possible. On the other hand, the activated carbon content in the device, and hence the energy density, decreases with decreasing electrode thickness. The specific capacity of devices tested (electrode thickness 0.4 mm, separator thickness 0.3 mm, surface 0.882 cm², AC mass of *ca.* 2 × 7 mg, capacity *ca.* 0.5 F) was at the level of $C_{sp}^d \approx (0.5 \text{ F})/(2 \times 7 \text{ mg AC}) \approx 35.7 \text{ kF kg}^{-1}$ of AC. Note that the specific capacity expressed versus the total mass of the activated carbon in the device must be four times lower than that characteristic for the single electrode (*ca.* 140 kF kg⁻¹). Finally, the specific energy, expressed versus the activated carbon mass in the device, was: $E = (1/2)35.7 \text{ kF kg}^{-1} 3.7^2 \text{ V}^2 \approx 240 \text{ kJ kg}^{-1}$. The specific power density depends on the carbon electrode surface. The tested capacitor containing 14 mg of activated carbon (the surface of 0.882 cm²) showed a resistance of *ca.* 10 Ω. Consequently, the surface of a device containing 1 kg of activated carbon is 71,430 times higher (1000 g/0.014 g) and the resulting resistance drops to *ca.* 0.14 mΩ. The specific power is $P = (1/4)(3.7^2 \text{ V}^2)/(0.14 \text{ mΩ}) \approx 25 \text{ kW kg}^{-1}$.

4. Conclusions

- The conductivity of the MePrPipNTf₂ neat ionic liquid, is at the level of 1.5 mS cm⁻¹, while the corresponding value for the mixture (48 wt.% MePrPipNTf₂ + 52 wt.% of MeCN) is *ca.* 40 mS cm⁻¹ (both recorded at 25 °C).
- The stability of the electrolyte (both neat ionic liquid, as well as its mixture with acetonitrile), detected at the glassy carbon electrode, is as broad as 5.7 V. However, the tested capacitors with the activated carbon as the active electrode material show considerable lower stability, reduced to *ca.* 3.7 V.
- The specific capacity estimated from both cyclic voltammetry and charging/discharging experiments was *ca.* 140 F g⁻¹. However, during the next 300 cycles the specific capacity increased to *ca.* 160 F g⁻¹, and then decreased to a value of *ca.* 100 F g⁻¹, constant for at least the next 15,000 cycles. The effect of the loss of the part of the initial specific capacity is probably due to the loss of Faradaic pseudo-capacity.
- The specific energy of the activated carbon in the tested devices was at the level of 240 kJ kg⁻¹, while the specific power density was *ca.* 25 kW kg⁻¹.
- The energy capacity of 10² kJ kg⁻¹ is at the level characteristic for the lead-acid battery, with much better cyclability and specific power, therefore, the system AC/MePrPipNTf₂ seems to be a good candidate for a high-power energy storage device.

Acknowledgement

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