Polish J. Chem., **78**, 1371–1378 (2004)

Polymer Electrolyte Based on Ionic Liquid $(EMIm)_3PO_4$ as an Electrolyte for Electrochemical Capacitors[*]

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(Received March 22nd, 2004; revised manuscript May 18th, 2004)

A series of polymer electrolytes, based on ionic liquid $(EMIm)_3PO_4$, and the polymers PAN, PVdF, PVdF-HFP, PVA and PEO were prepared as thin-foils, using the casting technique. The composite electrolytes showed conductivity at a level of *ca*. 10 mS/cm, apart from the system PEO-$(EMIm)_3PO_4$. The electrochemical stability window of the electrolytes based on PAN, PVdF and PVdF-HFP, as determined at the glassy carbon, was at a level of *ca.* 4V. The solid electrolytes polymer-$(EMIm)_3PO_4$ were applied in a series of double-layer capacitors. The specific capacity expressed *versus* the active carbon mass was at a very high level of 230 F/g (for an activated carbon powder with a specific surface area of *ca*. 2600 m^2/g). Good specific conductivity, a broad electrochemical stability window and very high specific capacity suggest that the polymer-$(EMIm)_3PO_4$ composites are good candidates for application in double layer capacitors.

Key words: polymer electrolyte, ionic liquid, electrochemical capacitor

Electrochemical double-layer capacitors (EDLC), based on the capacity of the double layer formed at the carbon/electrolyte interface, have received considerable attention. While classical batteries have high energy density, they suffer from low power density and low cyclability, double-layer capacitors offer an order of magnitude higher power density and much higher number of charge-discharge cycles. However, the energy density of electrochemical capacitors is of an order of magnitude lower in comparison to that characteristic for batteries. Both main components of EDLCs, namely carbon materials as well as electrolytes, have been developed in various systems [1,2]. Many aqueous and organic liquid solutions of electrolytes [1], as well as a number of polymer electrolytes [1–13] have been applied in EDLCs. In such systems the liquid electrolyte solutions were obtained by dissolving a salt (electrolytes) in a molecular solvent. Polymer electrolytes are systems that can be generally described as salts dissolved in polymers.

However room temperature ionic liquids (RTIL or shorter IL), being molten salts, can dissolve polymers. As a result an ion conducting composite (polymer-IL) is formed. The first polymer electrolytes incorporating ionic liquids were based on

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[*] Dedicated to Prof. Dr. Z. Galus on the occasion of his 70th birthday.

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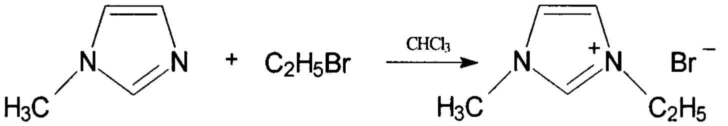
1-butylpyridinium halides (chloride or bromide) and aluminium chloride [14]. Ion-conducting solid composites, based on nonchloroaluminate ionic liquids have also been prepared. Membranes made of poly(vinylidene fluoride-hexafluoropropylene) (PVdF-HFP) [15,16] as well as NAFION [17] were impregnated with room temperature, non-chloroaluminate ionic liquids. The best room temperature conductivity of the PVdF-HFP-IL composite was *ca.* 3 mS/cm. Polymeric conducting systems were also prepared by *in situ* polymerization of vinyl monomers in ionic liquids [18]; the resulting composites showed conductivity of *ca.* 1 mS/cm. Recently, we prepared polymer electrolytes in the form of thin foils, by incorporating ionic liquids in a polymer matrix [19–22].

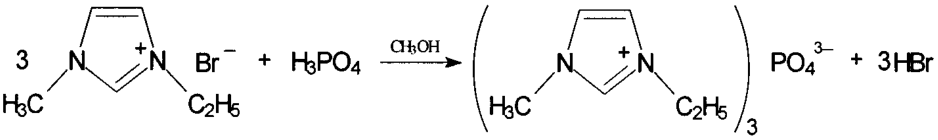
This paper reports on some of the properties of a novel class of electrochemical capacitors based on the polymer-IL solid electrolyte, based on 1-ethyl-3-methyl-imidazolium phosphate, $(EMIm)_3PO_4$.

EXPERIMENTAL

Materials. Poly(acrylonitrile), PAN (MW = 150 000, Aldrich), poly(vinylidenefluoride), PVdF (M_W = 534 000, Fluka), poly(vinylidenefluoride)-co-hexafluoropropane, PVdF-HFP (M_W = 400 000, Aldrich), poly(ethyleneoxide), PEO (M_W = 900 000, Aldrich), poly(vinylalcohol), PVA (M_W = 100 000, Aldrich) were used as received. N,N-Dimethylformamide, DMF (Merck), 1-methyl-2-pyrolidone, NMP (Merck, >99%) were purified by distillation under reduced pressure. Acetonitrile, AN, (Merck, for analysis) and bromoethane (Aldrich) were purified by distillation under atmospheric pressure. 1-Ethyl-3-methylimidazolium bromide (EMImBr) was prepared by reacting 1-methylimidazole (Fluka), dissolved in chloroform (P.O.Ch. Gliwice), with freshly distilled bromoethane [23].



Ionic liquid $(EMI)_3PO_4$ was obtained by reacting EMImBr solution in methanol with anhydrous orthophosphoric acid (H_3PO_4, 99%, Fluka) for 48 hours at 50°C [24]. Hydrogen chloride and traces of water were removed by evaporation at 50°C for 1 week (yield 88%).



Activated carbon powders (ACP), purchased in Fluka (determined specific surface area 830 m^2/g, moisture content 4%) and Kansai (specific surface area 2600 m^2/g), were dried at 130°C under reduced pressure for 8 hours. Acetylene black (AB) was purchased in Fluka.

Polymer electrolytes. The polymer-IL polymer electrolytes were prepared by the casting technique. The polymer was swollen in a solvent (PAN in DMF at 50°C, both PVdF and PVdF-HFP in NMP at 50°C, PEO in AN, PVA in water) for 24 hours and then mixed with ionic liquid. The viscous solution of polymer in a mixture of the solvent and the IL was cast onto a glass plate. After weighing, the plate was transferred into a desiccator where the solvent was slowly evaporated under a stream of dry nitrogen. After evaporation of the solvent, the plate with the polymer-IL foil was weighed again and the composition of the electrolyte was determined from the mass balance.

Electrodes. Electrodes for capacitors (polymer-IL-ACP-CB) were prepared as thin foils by the casting technique, in the same way as electrolytes, but carbon materials (ACP and CB) were mixed with the polymer, in a dry form, before preparation of the final solution.

Capacitors. Capacitors were prepared by sandwiching the polymer electrolyte (polymer-IL foil) between two electrodes (polymer-IL-ACP-AB foil) and pressing across the system. The devices had a coin-like shape (diameter: 12 mm). For measurements, capacitors were sandwiched between two gold electrodes. All operations were performed in a glove box in a nitrogen atmosphere.

Measurements. The specific conductivity of electrolytes was deduced from impedance spectroscopy. The impedance technique was also employed for the capacitor characterization. The spectrum was measured over a frequency range from 0.01 Hz to 99 kHz with an *ac* potential amplitude of 10 mV (Atlas-Sollich system, Poland). Electrolyte foils or capacitors were sandwiched between two gold electrodes. The cyclic voltammetry measurements were obtained with an electrochemical system μAutolab (EcoChemie, the Netherlands). Electrolytes were placed between a gold counter electrode with a central hole for a reference electrode, as well as a working glassy carbon electrode with a surface of 0.286 cm^2. A silver/silver(I) couple in dimethylsulphoxide (Ag/Ag$^+$ 0.01 mol dm^{-3} in DMSO) was used as the reference electrode. The galvanostatic charging and discharging of capacitors was performed using ZT-980-4 system (Unitra, Poland).

RESULTS AND DISCUSSION

Polymer electrolyte. The ionic liquid (EMIm)$_3$PO$_4$ showed a specific conductivity at a level of 3.2 mS/cm. The literature [25] reports a cosiderably higher level of conductivity: *ca*. 22 mS/cm. The discrepancy between these two results is unknow, but it is possible that remaining HBr after the IL preparation could increase the conductivity level.

The polymer-(EMIm)$_3$PO$_4$ electrolytes were obtained as transparent foils with a thickness in the range of 0.1–0.15 mm. The *dc* resistance of the electrolytes was detected from *ac* impedance experiments. The bulk resistance, R_b, obtained from the curve fitting procedure was converted into electrolyte specific conductance: $\sigma = d/R_b$, (d is the foil thickness). The typical conductivities of the polymer electrolytes consisting of different polymers are shown in Table 1. As can be seen from the table the conductivity reaches a high level of *ca*. 13.5 mS/cm for the PAN-(EMIm)$_3$PO$_4$ composite. For the composites PVdF-(EMIm)$_3$PO$_4$, PVdF-HFP-(EMIm)$_3$PO$_4$ and PVA-(EMIm)$_3$PO$_4$, the conductivity also reaches a level of 10 mS/cm (10.4, 9.0 and 8.2 mS/cm, respectively). In the case of the PEO-(EMIm)$_3$PO$_4$ composite, the conductivity is considerably lower ($\geq$ 0.7 mS/cm).

A high increase in the conductivity, in comparison to that characteristic for the neat ionic liquid, can be observed after its dilution with electrically neutral polymers such as PVdF, PVdF-HFP and PVA. There are a number of studies on RTILs specific conductivity, as well as on their solutions in molecular solvents and composites with polymers [26–37]. Generally, the conductivity of a system IL+ML increases with the increasing amount of IL, goes through a maximum and goes down to the specific conductivity of the neat IL. This is not unusual, as the IL + ML mixtures are simply solutions of salts in molecular solvents. The polymer-IL system is similar to the IL + ML systems, where the low molecular weight solvent (ML) has been replaced by the high molecular weight component (the polymer).

Table 1. Specific conductivity and stability window of polymer-$(EMIm)_3PO_4$ solid electrolytes.

	wt. %		σ	stability window [V]	
polymer	polymer	$(EMIm)_3PO4$	[mS/cm]	cathodic	anodic
PAN	61.5	38.5	3.4	–2.0	2.3
PAN	40.5	59.5	4.0	–2.0	2.3
PAN	30.0	70.0	13.5	–2.0	2.3
PVdF	44.8	55.2	2.3	–1.9	2.1
PVdF	30.1	69.9	10.4	–1.9	2.1
PVdF-HFP	55.6	44.4	0.1	–1.9	2.0
PVdF-HFP	54.6	45.4	0.3	–1.9	2.1
PVdF-HFP	44.3	55.7	5.6	–1.9	2.1
PVdF-HFP	30.0	70.0	9.0	–1.9	2.1
PVA	29.3	70.7	8.2	–1.0	1.8
PEO	52.3	47.7	0.4	–0.5	2.0
PEO	43.4	56.6	0.4	–0.6	2.0
PEO	29.9	70.1	0.7	–0.6	2.0

One of the most important factors is that the electrolyte should not undergo electrochemical degradation at possibly high voltages applied. The energy E which can be stored in the device is proportional to the voltage U in the second power: $E = ½CU^2$. Figure 1 shows a typical cyclic voltammogram of the polymer-$(EMIm)_3PO_4$ composite (PAN-$(EMIm)_3PO_4$). As can be seen, the electrochemical stability window is quite broad, > 4.0 V. A comparable stability window was detected in the case of the composites based on PVdF and PVdF-HFP polymers. However, the polymer electrolytes composed of PVA and PEO show a considerably lower range of stability, limited from the cathodic side. Broad electrochemical stability windows are typical of many ionic liquids. However, a voltage that can be applied to a capacitor is practically considerably lower. This is due to the fact that the capacitor electrodes are formed from different kinds of activated carbons, possessing functional groups, while the stability window is usually determined at glassy carbon.

Capacitor. Figure 2 shows an example of a typical cyclic voltammogram of a capacitor containing the composite PAN-$(EMIm)_3PO_4$ as an electrolyte. In addition, it can be seen from Figure 3, that the cyclic voltammetry shows a rectangular shape at a broad voltage range (up to 3 V). However, with increasing voltage applied to the device an increasing peak at the potential sweep reversal can be seen. This is probably due to faradaic processes which occur at higher voltages. The device shown in Figure 2 consisted of two electrodes with a mass of *ca.* 12.3 and 15.8 mg, and based on acti-

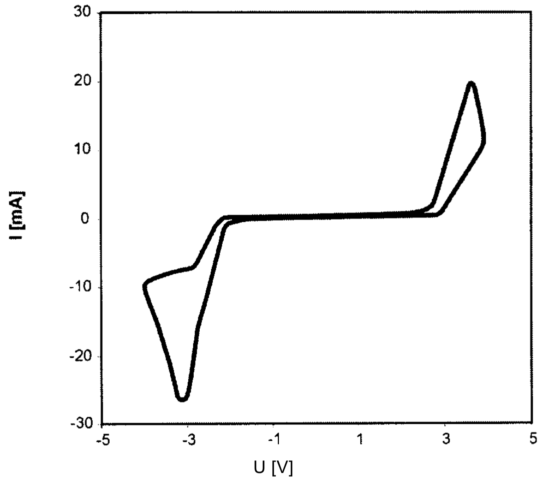


Figure 1. Cyclic voltammetry for the system C|PAN (30.0 wt.%), (EMIm)$_3$PO$_4$ (70.0 wt.%)| Au. Sweep rate 5 mV/s.

vated carbon with a specific surface area of *ca.* 2600 m^2/g. The current flowing through the device at a sweep rate of 2mV/s was *ca.* 0.5 mA. Hence, the capacity of the device was $C = I/(dU/dt) = (0.5\ \text{mA})/(2\text{mV/s}) = 0.25$ F. This leads to a specific capacity of the carbon material of *ca.* 236 F/g. Capacitors based on activated carbons of a lower specific surface area (870 m^2/g) showed a capacity at the level of *ca.* 90 F/g. The specific capacity expressed *versus* total surface of carbon material was within the range of 9–10 μF/cm^2. The same values of specific capacity were obtained from galvanostatic charging-discharging (an example shown in Figure 4). These results can be compared with the literature data on capacitors based on RTILs. Capacitors made of high-surface carbon with PVdF-co-HFP as a binder and filled with neat ionic liquids, without any molecular solvent, show high specific capacity, of up to 180 F/g [38]. Similar or even better capacity was obtained in systems with polymer electrolytes based on ILs. Room temperature ionic liquids such as EMImBF$_4$, BMPyN(tf)$_2$ and BMImPF$_6$ served both as sources of ions as well as polymer plasticisers; in some cases sulpholane was added as an additional plasticiser. Specific capacity was up to 200 F/g expressed *versus* the mass of carbon material materials.

The charged capacitor is in a state of higher energy with respect to the discharged device, which induces a driving force for a spontaneous self-discharge of the device kept at the open circuit conditions. The capacitors studied here, loaded to the potential difference of *ca.* 1.5 V, showed the voltage drop by about 150 mV (to *ca.* 1.35 V) after 20 min. An ideally polarizable electrode could not undergo a self-discharge, and therefore, the voltage drop is due to the Faradaic processes which can occur at the carbon/electrolyte interface (reduction or oxidation involving functionalities present at the carbon electrode surface or electrolyte and all possible impurities).

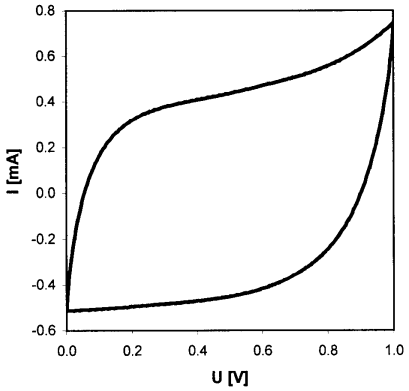


Figure 2. Cyclic voltammetry of a capacitor consisting of two electrodes of the mass 12.3 mg and 15.8 mg, of the composition (1) electrolyte: PAN (27.7 wt.%), $(EMIm)_3PO_4$ (72.3 wt.%), (2) electrodes: PAN (8.8 wt.%), $(EMIm)_3PO_4$ (68.4 wt.%), ACP (2600 m^2/g, 17.2 wt.%), AB (5.6 wt. %). Sweep rate 2 mV/s.

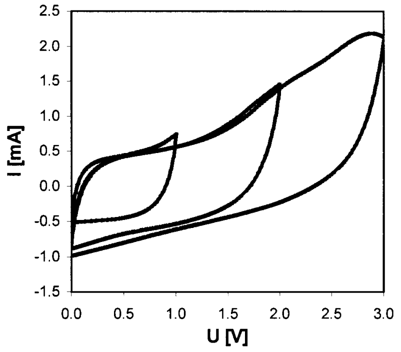


Figure 3. Cyclic voltammetry, at different potential ranges, of a capacitor consisting of two electrodes of the mass 12.3 mg and 15.8 mg, of the composition (1) electrolyte: PAN (27.7 wt.%), $(EMIm)_3PO_4$ (68.4 wt.%), (2) electrodes: PAN (8.8 wt.%), $(EMIm)_3PO_4$ (72.3 wt.%), ACP (2600 m^2/g, 17.2 wt.%), AB (5.6 wt. %).

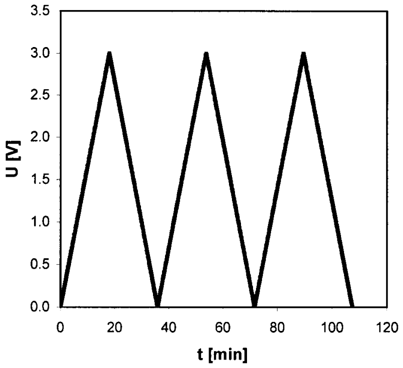


Figure 4. Galvanostatic charging-discharging characteristic of a capacitor consisting of two electrodes of the mass 13.7 mg and 14.3 mg, of the composition (1) electrolyte: PAN (27.7 wt.%), $(EMIm)_3PO_4$ (72.3 wt.%), (2) electrodes: PAN (9.2 wt.%), $(EMIm)_3PO_4$ (66.6 wt.%), ACP (830 m^2/g, 18.3 wt.%), AB (5.9 wt. %). Current = 2 mA.

CONCLUSIONS

1. Ionic liquid (EMIm)$_3$PO$_4$ forms with polymers: PAN, PVdF, PVdF-HFP, PVA and PEO solid electrolytes showing conductivity at the level of *ca.* 10 mS/cm, apart from the composite PEO-(EMIm)$_3$PO$_4$.
2. Electrochemical stability window of the composite electrolytes based on PAN, PVdF and PVdF-HFP, as determined at the glassy carbon is at a level of *ca.* 4 V.
3. Solid electrolytes polymer-(EMIm)$_3$PO$_4$ may be applied in double-layer capacitors. The specific capacity expressed *versus* the active carbon mass is at a high level of 230 F/g.
4. Good specific conductivity, a broad electrochemical stability window and very high specific capacity suggest that the polymer-(EMIm)$_3$PO$_4$ composites are good candidates for application in double layer capacitors.

Acknowledgment

This work was supported by grant TB31-074/2004DS.

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