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Is the mixture of 1-ethyl-3-methylimidazolium tetrafluoroborate and 1-butyl-3-methylimidazolium tetrafluoroborate applicable as electrolyte in electrical double layer capacitors?

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ABSTRACT

The influence of small addition (from 0.005 to 1 M) of 1-butyl-3-methylimidazolium tetrafluoroborate ($BMImBF_4$) in 1-ethyl-3-methylimidazolium tetrafluoroborate ($EMImBF_4$) on the melting point, bulk conductivity and electrochemical properties of ionic liquid mixtures as electrolytes in electrical double layer capacitors (EDLCs) has been studied using cyclic voltammetry and electrochemical impedance spectroscopy methods. The melting point of $EMImBF_4$ can be reduced from 13.5 °C to 5.6 °C by adding small amount of $BMImBF_4$ (0.5 M) without noticeable decrease in capacitance (135 F g^{-1} at 3.2 V), energy (49 Wh kg^{-1}) and power (38 kW kg^{-1}) densities and minor increase in characteristic relaxation time (~16 s) for EDLCs studied. However, the EDLCs based on $EMImBF_4$ with 1 M addition of $BMImBF_4$ (melting point of mixture −6 °C) demonstrated noticeable decrease in capacitance (~122 F g^{-1} at 3.2 V), energy (43 Wh kg^{-1}) and power (30 kW kg^{-1}) densities and increase in characteristic relaxation time to 25 s.

1. Introduction

During recent years, the applicability of room-temperature ionic liquids (RTILs) as electrolytes for electrical double layer capacitors (EDLCs) and batteries has been widely discussed [1–12]. Compared to water and organic solvent based electrolytes, RTILs have lower conductivity, higher viscosity and narrower operation temperature range. To broaden the operation temperature range of RTIL based EDLCs, it has lately been proposed [1] to use eutectic mixture of two RTILs composed of different cations (1:1 by weight ratio of *N*-methyl-*N*-propylpiperidinium bis(fluorosulfonyl)imide ($PIP_{13}FSI$) and *N*-butyl-*N*-methylpyrrolidinium bis(fluorosulfonyl)imide ($PYR_{14}FSI$)). The mixing of $PIP_{13}FSI$ and $PYR_{14}TFSI$ led to the decrease in melting point respect to both ionic liquids and 1:1 $PIP_{13}FSI$:$PYR_{14}FSI$ mixture was suggested for use in EDLCs operating at temperatures from −50 °C to 100 °C. However, the bulk conductivity of 1:1 $PIP_{13}FSI$:$PYR_{14}FSI$ mixture was comparatively low ($\kappa = 4.9$ mS cm^{-1} at 20 °C) and electrochemical impedance spectra measured for 1:1 $PIP_{13}FSI$:$PYR_{14}FSI$ mixed RTIL based EDLCs with specially designed vertically aligned carbon nanotube array electrodes demonstrated very high series resistance, $R_s(f \to \infty) \cong 50 \ldots 100\ \Omega\ cm^2$, values (Supportive Information in ref [1]). Thus, relatively low power densities can be proposed for EDLCs discussed in Ref. [1].

In present article 1-ethyl-3-methylimidazolium tetrafluoroborate ($EMImBF_4$) was chosen due to high bulk conductivity ($\kappa = 14$ mS cm^{-1}) and wide region of electrochemical stability [2–7]. To reduce the melting point of $EMImBF_4$ (13.5 °C) but retain good ionic conductivity of mixture RTIL electrolyte the relatively low concentrations (from 0.005 M to 1 M) of 1-butyl-3-methylimidazolium tetrafluoroborate ($BMImBF_4$; concentration noted as c_{IL2}; melting point −71 °C; $\kappa =$ 1.7 mS cm^{-1}) were added. The electrochemical behavior of EDLCs filled with two component RTIL mixtures were characterized by cyclic voltammetry (CV) and electrochemical impedance spectroscopy (EIS) methods. The changes in bulk conductivity and melting point with the increase in the $BMImBF_4$ concentration were also analyzed.

2. Experimental

Two 775 μm thick microporous carbon cloth (MPCC, Institute of Problems in Materials Science, Ukrainian National Academy of Sciences, Ukraine) electrodes (2 cm^2, specific surface area $S_{BET} =$ 1560 m^2 g^{-1}) and 25 μm thick cellulose separator TF4425 (Nippon Kodoshi, Japan) were assembled at room temperature (22.0 ± 1 °C) in a clean and dry Ar atmosphere (99.9999%, AGA; O_2 and $H_2O < 0.1$ ppm) into a HS test-cell (Hohsen Corp., Japan) and filled with prepared $EMImBF_4$ (Fluka, assay ≥99.0%, $H_2O < 100$ ppm) and $BMImBF_4$ (Flucka, assay ≥98,5%, $H_2O < 100$ ppm) mixtures. The electrochemical behavior of EDLCs was tested applying CV and EIS methods. Impedance spectra were recorded over ac frequency range from 1×10^{-3} to 3×10^5 Hz with 5 mV modulation, using a 1252A Solartron FRA and SI1287 potentiostat.

The melting points of RTILs were determined from the differential scanning calorimetry (DSC) diagrams measured on a differential scanning

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calorimeter "Diamond DSC" (PerkinElmer, USA) in the region from −80 °C to 100 °C at the temperature ramp rate of 5 °C min^{-1}.

The conductivity of mixtures was obtained by recording the impedance spectra at 0 V using a self-made test-cell with platinum electrodes and filled with 1.5 ml of mixture at 22.0 ± 1 °C. The test-cell was calibrated by measuring the resistance for 0.001 M and 0.1 M KCl aqueous solutions. The intersection point of the Nyquist plot (where Z' is the real and Z'' is the imaginary part of the impedance) with Z' axis ($Z''=0$) was treated as the series resistance of the test-cell.

3. Results and discussion

The DSC measurements showed that the melting point, T_{mp}, (Fig. 1a) of $\text{EMImBF}_4 + \text{BMImBF}_4$ mixtures depends noticeably on the concentration of BMImBF_4 only at higher concentrations ($c_{\text{IL2}} \geq 0.5$ M) and is decreased from 13.5 °C (pure EMImBF_4) to −6 °C, when 1 M BMImBF_4 is added. The same tendency can be seen for the bulk conductivity of mixtures (Fig. 1a), where the conductivity is decreased 15% compared the conductivity of pure EMImBF_4 with the increase in concentration of BMImBF_4 to 1 M. The conductivity of $\text{EMImBF}_4 + 1$ M BMImBF_4 decreases with decrease in temperature (Fig. 1b) but still demonstrates relatively high conductivity values (7.9 mS cm^{-1}) even at temperatures as low as 0.8 °C. Only electrolytes demonstrating considerable change in melting point ($\text{EMImBF}_4 + 0.5$ M BMImBF_4 and $\text{EMImBF}_4 + 1$ M BMImBF_4) are discussed in the section of electrochemical behavior analysis of systems completed.

The CV data show that at applied potential scan rate $\nu = 1$ mV s^{-1} (Fig. 2a) the concentration of BMImBF_4 has only very small effect on the electrochemical characteristics of EDLCs, demonstrating slightly more visible distortion effects in the applied potential switch-over region for electrolyte with 1 M BMImBF_4 addition. At higher scan rates ($\nu \geq 10$ mV s^{-1}, Fig. 2b) the effect of BMImBF_4 concentration is more visible demonstrating well pronounced distortion effects for EDLCs with increase in concentration of BMImBF_4 in electrolyte. This can be explained with the lower conductivity of two component RTIL mixture at higher additions of BMImBF_4 and by increase in the importance of diffusion step rate of charged ions in porous electrode and separator matrix, when the scan rate is increased.

In Nyquist plots, measured at applied potentials $U \leq 2.7$ V, only the EDLC containing $\text{EMImBF}_4 + 1$ M BMImBF_4 deviates from the ideal capacitive behavior demonstrating phase angle values much higher than $\phi = -90°$. When the applied potential is increased, the differences between EMImBF_4, $\text{EMImBF}_4 + 0.5$ M BMImBF_4 and $\text{EMImBF}_4 + 1$ M BMImBF_4 based EDLCs become more pronounced and again the $\text{EMImBF}_4 + 1$ M BMImBF_4 based EDLC deviates more remarkably form the ideal capacitive behavior. From gravimetric series capacitance ($C_{\text{s}} = -1/(2\pi f Z'')$) vs. frequency, f, plot (Fig. 3b) it can be seen that C_{s} depends strongly on U and at lower applied potentials ($U \leq 2.7$ V) the series capacitance is nearly the same for pure EMmBF_4 and $\text{EMImBF}_4 + 0.5$ M BMImBF_4 based EDLCs, but the capacitance for $\text{EMImBF}_4 + 1$ M BMImBF_4 based EDLC is nearly 13% lower. At higher U the differences between pure EMImBF_4 and $\text{EMImBF}_4 + 0.5$ M BMImBF_4 based EDLCs becomes visible and can be explained by the lower surface coverage at/in the porous electrode|electrolyte interface at lower applied potentials ($U = 2.7$ V in Fig. 3b) [4–6]. The more proposed steric effects of larger cations increasing with the addition of BMImBF_4 influence the C_{s} only at 1 M BMImBF_4 addition. At higher U, the surface coverage for ions at/in the porous electrode|electrolyte interface is higher, the ions are more closely packed to the surface and compared to the pure EMImBF_4 based EDLCs, the C_{s} value is also reduced for EDLC based on $\text{EMImBF}_4 + 0.5$ M BMImBF_4 electrolyte.

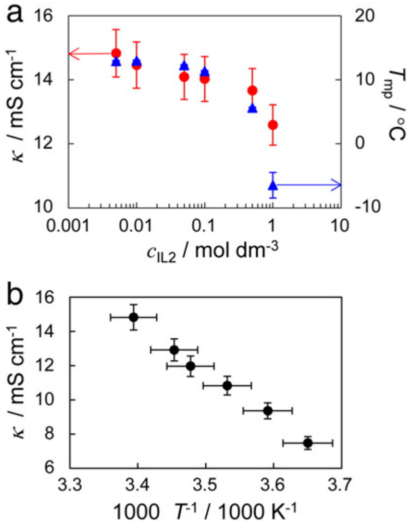

Fig. 1. The dependence of bulk conductivity (circles) and melting point (triangles) of EMImBF_4 on the addition of BMImBF_4 (a) and the dependence of bulk conductivity of $\text{EMImBF}_4 + 1$ M BMImBF_4 mixture on the temperature (b).

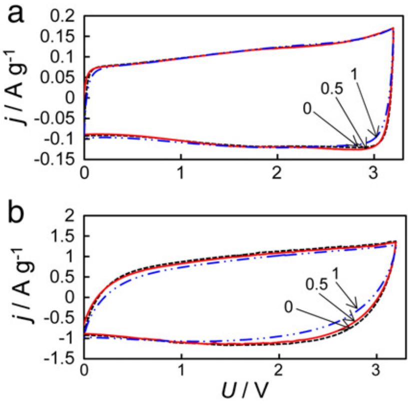

Fig. 2. The cyclic voltammograms measured with scan rates of applied potential $\nu = 1$ mV s^{-1} (a) and $\nu = 10$ mV s^{-1} (b) for EDLCs filled with $\text{EMImBF}_4 + x$ M BMImBF_4.

The complex power of a system calculated from EIS data can be expressed as

$$S(\omega) = P(\omega) + jQ(\omega) \tag{1}$$

where the real part of the power is

$$P(\omega) = \frac{Z'(\omega)}{|Z(\omega)|^2} |\Delta U_{\text{rms}}|^2 \tag{2}$$

and the imaginary part of power is

$$Q(\omega) = \frac{Z''(\omega)}{|Z(\omega)|^2} |\Delta U_{\text{rms}}|^2 \tag{3}$$

with $|\Delta U_{\text{rms}}|^2 = \Delta U_{\max}/\sqrt{2}$ ($\Delta U_{\max}$ is the maximum amplitude of ac potential) [4–9]. The EDLCs balance between two limiting states: resistive at high frequencies and capacitive at low frequencies. Between these two states EDLC behaves like a resistive–capacitive transmission line circuit [9,10,13]. In Fig. 4 the normalized real part of complex power ($|P(\omega)|/|S(\omega)|$) and imaginary part of complex power ($|Q(\omega)|/|S(\omega)|$) vs. f-plot intersect at the characteristic frequency, f_{int}, giving the so-called relaxation time $\tau_{\text{R}} = 1/(2\pi f_{\text{int}})$ (inset in Fig. 4). The obtained τ_{R} corresponds to the time required to release half of the energy stored in EDLC [9]. It can be seen, that τ_{R} does not depend strongly on the concentration of BMImBF_4, when $c_{\text{IL2}} \leq 0.5$ M, suggesting that the melting point of EMImBF_4 through adding BMImBF_4 can be brought down to −5.6 °C without changes in rate capability of EDLC. At higher concentrations of BMImBF_4 ($c_{\text{IL2}} = 1$ M) in the mixed RTIL electrolyte,