Electric properties of composite materials based on porous ceramics and low temperature ionic liquids


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Composite materials were obtained by saturation of pores of a monolithic porous ceramic matrix with low temperature ionic liquids. Tetrafluoroborates, hexafluorophosphates, and triflates (trifluoromethanesulfonates) of 1-alkyl-3-methylimidazolium (alkyl=butyl, hexyl, octyl or decyl) were studied. The above ionic liquids have a broad electrochemical window (up to 5.5 V), and the electrochemical window of the composite materials is even broader. The conductivity of the ionic liquids is approximately proportional to their reciprocal viscosity. The composites (porous material with porosity of 27 %) show a conductivity only slightly lower than the corresponding ionic liquid with a few exceptions.

1. INTRODUCTION

The low temperature ionic liquids (also known as ambient temperature ionic liquids or room temperature ionic liquids) show many advantageous properties with respect to their possible electrochemical applications [1]. Their vapor pressure is negligibly low, thus they are inflammable and their acute toxicity is relatively low [2]. Unlike water they have a broad electrochemical window, and unlike molecular organic solvents they conduct electricity and they easily dissolve salts. Therefore the electric properties of low temperature ionic liquids have been extensively studied. Mantz and Trulove [3,4] reviewed the conductivities and molar conductivities of a few dozens of ionic liquids. The later range from $7 \times 10^{-6}$ to $8 \times 10^{-4}$ Sm$^{-1}$mol$^{-1}$, and they are substantially lower than
the molar conductivities of aqueous solutions of 1-1 electrolytes, which often exceed $10^{-2}$ Sm$^2$mol$^{-1}$. The conductivities reported in various studies for the same ionic liquid are not always consistent, e.g., two sources report conductivities of EMI bis(trifluoromethylsulfonate)imide, which differ by a factor of almost two. Consequently, the molar conductivities also substantially differ, while the viscosities reported in various papers for the same ionic liquid are rather consistent. Apparently there is a factor other than the viscosity, which affects the measured conductivity, and which is difficult to control. However, the differences in the conductivity between various ionic liquids is chiefly due to the difference in the viscosity, which ranges from $8 \times 10^{-3}$ to $6 \times 10^{-1}$ Pa s in the ionic liquids studied in ref. [3] while in dilute aqueous solution it is as low as $8.92 \times 10^{-4}$ Pa s (all values for 298 K).

The conductivity and viscosity are temperature-dependent, and this is another factor, which contributes to the scatter of results. The effect of temperature is often presented in form of the following Vogel-Tamman-Fulchher equations [5]:

$$
\eta = \eta_0 \exp \left[ \frac{B}{T - T_0} \right]
$$

(1)

$$
\kappa = A T^{-1/2} \exp \left[ -\frac{B}{T - T_0} \right]
$$

(2)

where A, B, $\eta_0$ and $T_0$ are empirical constants. For given ionic liquid, B and $T_0$ in Eq. (1) and (2) assume similar, although not necessarily equal values. Over a narrow temperature range (a few K), $\eta$ and $\kappa$ are linear functions of $T$. A few examples of temperature coefficients of viscosity, calculated from data of Seddon et al. [4] are summarized in Table 1.

| Tab. 1. Temperature coefficients (in %) of viscosity of low temperature ionic liquids at 25 °C |
|-----------------|---------|---------|---------|
| 0.01 K$^{-1}$   | BF$_4$  | PF$_6$  | triflate|
| EMI             | 4.5     | 3.2     |
| BMI             | 5.3     | 6.2     | 4.4     |
| HMI             | 5.9     | 6.6     |
| MOI             | 6.2     | 6.7     | 6       |
| DMI             | 7.4     | 6.7     |

The temperature coefficients of viscosity in ionic liquids are higher than that in water (2.3 %). Table 1 shows a clear trend, namely the temperature coefficient increases with the chain length, and the anion series is PF$_6$ > BF$_4$ > triflate.
In order to normalize the molar conductivity in various ionic liquids, Mantz and Trulove [3] calculated the Walden products ($\lambda\eta$), which range from $3 \times 10^{-6}$ to almost $10^{-5}$ N s S mol$^{-1}$ for the ionic liquids, and the maximum value of Walden product in ionic liquids is only slightly lower than the typical values observed in aqueous solutions (e.g., $1.15 \times 10^{-5}$ N s S mol$^{-1}$ for 0.1 mol dm$^{-3}$ KCl). The Walden products of imidazolium derivatives reported in ref. [4] are limited to short-chain substituents (up to C$_4$). In their recent study, Hayamizu et al. [5] obtained a Walden product of EMI BF$_4$ of $1.01 \times 10^{-5}$ N s S mol$^{-1}$ (calculated from Eqs.(1) and (2) with parameters from Tables 2 and 3 in ref. [5]), which is even closer to that in aqueous solutions. The temperature coefficients of reciprocal viscosity and of conductivity of EMI BF$_4$ are equal [5], thus the Walden product is rather insensitive to the temperature. On the other hand the value reported in ref. [5] (2.7 %) is substantially lower than the value reported in Table 1.

Consistent values of Walden product in aqueous solutions and in ionic liquids suggest a similar mechanism of the conductivity. It should be emphasized that the Walden product in aqueous solutions depends on the nature of the salt, and for most Na and Li salts it is substantially lower than for KCl. The Walden product of 1-1 salts in most organic solvents (alcohols, formamide) is lower than in water [7], but in ethylene glycol it is higher than in water. The Walden product for aqueous solutions of most inorganic salts decreases when the temperature increases. Interpretation of the Walden products of solutions of salts in molecular solvents is discussed in detail elsewhere [7].

Trulove and Mantz [4] reviewed the electrochemical windows of ionic liquids. They range from 3.6 to 5.7 V for various non-haloaluminate ionic liquids, and the results reported by different authors are rather consistent. The electrochemical windows of chloroaluminate ionic liquids are not that broad (2.2 - 4.6 V), but still significantly broader than the electrochemical window of water (1.23 V).

Kosmulski et al. [8] reviewed a few values of the permittivity of ionic liquids reported in the literature. These values were based on the correlations between the permittivity and various solvent scales, thus they have rather speculative character. The present authors are not aware of any published paper reporting directly measured permittivities of low temperature ionic liquids.

In the present study we report electric properties of low temperature ionic liquids and of composite materials based on porous ceramics and low temperature ionic liquids. The immobilization of ionic liquids in porous ceramics was studied in view of potential electrochemical applications of the ionic liquids [9]. In our opinion, immobilization of the ionic liquids in a ceramic matrix is advantageous over immobilization in a polymer matrix, which was widely discussed in the literature [10,11,12].
2. EXPERIMENTAL

The synthesis of the ionic liquids is described elsewhere [8]. In the first step, 1-alkyl-3-methylimidazolium chlorides (alkyl=butyl, hexyl, octyl or decyl) were obtained from 1-methylimidazole (Fluka) and n-alkyl chlorides (Sigma-Aldrich). In the second step, metathesis reaction between 1-alkyl-3-methylimidazolium chlorides and ammonium salts of tetrafluoroboric and hexafluorophosphoric acids (or silver triflate) was carried out in acetonitrile medium. The metathesis reaction was not complete, and BMI, HMI, MOI, and DMI tetrafluoroborates obtained in the present study contained 0.202, 0.136, 0.355, and 0.117 (mass fraction) of corresponding chlorides. The other ionic liquids used in the present study, namely, BMIPF$_6$, HMIPF$_6$, MOIPF$_6$, DMIPF$_6$, BMI triflate, and DMI triflate contained less than 0.61% of chlorine by mass. Chlorine and other impurities substantially affect the conductivity of the ionic liquids, and they may be the reason for discrepancies discussed in the Introduction, and in many studies, especially those carried out with commercially available ionic liquids the problem of the impurities is ignored. For example, in our recent study [13] we found a substantial amount of silver in a high-purity reagent-grade ionic liquid.

Ceramic matrix was obtained from Al6SG aluminum oxide powder (Alcoa), average particle diameter 0.5 μm. A paste composed of alumina and aqueous solution of dextrin (0.04 mass fraction) was pressed at 10 MPa at room temperature, dried at 60 °C for 1 day, and sintered at 1150 °C for 2 hours. This procedure resulted in cylindrical specimens, 1 cm in height and in diameter, of average pore diameter of 0.1 μm, and open porosity (water) of 27%. More details on the properties of the ceramic matrix can be found elsewhere [14].

In order to immobilize ionic liquid in a ceramic matrix, the ceramic material and the ionic liquid were evacuated, the ceramic specimen was dropped into the liquid and the vacuum was maintained for 4 more hours. We successfully tested also other procedures to obtain composite materials, but in the present study only the above method was used.

The fraction of pore volume filled with the ionic liquid was estimated as the quotient of the volume of the ionic liquid to the volume of water (2-hours equilibration at 100 °C) absorbed in the ceramic matrix.

The electrochemical window of ionic liquids was determined from the course of voltammetric curves obtained by means of ATLAS-91 (Poland) in a 3-electrode system. The working electrode and the counter electrode (1 cm$^2$ each) were made of sheet platinum, and platinum wire 0.5 mm in diameter served as a reference electrode. The potentiodynamic method (1 V/min) was used. Cyclic voltammetric curves in the range from −5 to +5 V against the platinum reference electrode were recorded. The ionic liquid was insulated from
the atmospheric moisture during and before the measurement. The temperature was 20 °C.

The electrochemical window of composite materials was measured in a 2-electrode system. Platinum electrodes were pressed against the bases of a cylindrical specimen by means of a spring clamp. The other conditions of the measurement as for ionic liquids.

The conductivity of the ionic liquids was measured at 22 °C by means of CDM 3 (Radiometer) conductivity meter at 10 kHz. The measurement cell had electrodes made of smooth platinum. The ionic liquid was insulated from the atmospheric moisture during and before the measurement.

The conductivity of composite materials was measured at 20 °C by means of Hioki 3532 Hitester LRC bridge. The bases of cylindrical specimens were covered by conductive materials (graphite, pulverized silver, electroconductive glue CW 2400 (Circuit Works). The voltage was always 3 V, and the frequency ranged from 100 Hz to 100 kHz.

3. RESULTS AND DISCUSSION

3.1. Ionic liquids

The widths of electrochemical window of ionic liquids are summarized in Table 2.

Tab. 2. The electrochemical windows [5] of ionic liquids

<table>
<thead>
<tr>
<th></th>
<th>BF₄/Cl</th>
<th>PF₆</th>
<th>triflate</th>
</tr>
</thead>
<tbody>
<tr>
<td>BMI</td>
<td>4.3</td>
<td>4.5</td>
<td>4.5</td>
</tr>
<tr>
<td>HMI</td>
<td>4.3</td>
<td>4.8</td>
<td>3.8</td>
</tr>
<tr>
<td>MOI</td>
<td>4.5</td>
<td>4.5</td>
<td></td>
</tr>
<tr>
<td>DMI</td>
<td>2.9</td>
<td>4.3</td>
<td>4.5</td>
</tr>
</tbody>
</table>

The results shown in Table 2 are similar as electrochemical windows reported in the literature, and there is no regular dependence of the electrochemical windows on the nature of the anion or of the cation.

The conductivities, viscosities and Walden products of ionic liquids are summarized in Table 3.
Tab. 3 The Walden product in ionic liquids (22 °C)

<table>
<thead>
<tr>
<th></th>
<th>$\kappa$ / S/m</th>
<th>$\lambda$ / Sm²mol⁻¹</th>
<th>$\eta$ / Pa s</th>
<th>Walden product N s S mol⁻¹</th>
</tr>
</thead>
<tbody>
<tr>
<td>BMI BF₄/Cl</td>
<td>0.205</td>
<td>3.6×10⁻⁵</td>
<td>0.274</td>
<td>9.9×10⁻⁶</td>
</tr>
<tr>
<td>BMI PF₆</td>
<td>0.13</td>
<td>2.8×10⁻⁵</td>
<td>0.32</td>
<td>8.8×10⁻⁶</td>
</tr>
<tr>
<td>HMI BF₄/Cl</td>
<td>0.082</td>
<td>1.8×10⁻⁵</td>
<td>0.315</td>
<td>5.6×10⁻⁶</td>
</tr>
<tr>
<td>MOI BF₄/Cl</td>
<td>0.02</td>
<td>4.9×10⁻⁶</td>
<td>1.07</td>
<td>5.2×10⁻⁶</td>
</tr>
<tr>
<td>MOI PF₆</td>
<td>0.026</td>
<td>7.3×10⁻⁶</td>
<td>0.721</td>
<td>5.3×10⁻⁶</td>
</tr>
</tbody>
</table>

The Walden products summarized in Table 3 are on the same order as the results reported in the literature [4], and they decrease when the chain length in the substituent in the imidazolium ring increases. This result suggests association of ions, which may be due to ion-pairing or to chain-chain interactions between the cations.

We attempted to determine the static permittivity of the ionic liquids, and we found that the dielectric spectra of the ionic liquids are very different from those of water or of the other common molecular liquids. In the later, the dielectric dispersion ($\varepsilon'$) is practically constant and the dielectric loss ($\varepsilon''$) is negligible at frequencies below 1 GHz. This type of behavior can be quantitatively described by single Cole-Cole equation. The dielectric spectra in low temperature ionic liquids are more complex, and $\varepsilon'$ is frequency dependent and $\varepsilon''$ is substantial at frequencies as low as 50 kHz. Our preliminary results show that Havriliak-Negami model [15], which combines the Debye and Cole-Cole relaxations with a low frequency dispersion can be useful to interpret the dielectric spectra of the ionic liquids. We plan additional measurements at even lower frequencies (below 1 Hz).

3.2. Composite materials

The procedure described in the Experimental part resulted in practically 100 % saturation of pores of ceramic matrix with ionic liquids.

The voltammetric curves of a composite material is shown in Figure 1, which also shows the effect of aging in moist air. The potential range, in which the current is negligibly low, practically does not depend on the aging. On the other hand, the current outside the electrochemical window increases on aging, although the effect of aging (up to 90 days) is not dramatic. Interestingly the reduction current even decreases on a 30-days aging. This effect is rather
surprising since the presence of moisture induces a substantial decrease in the viscosity of the ionic liquids, thus increase in the current is expected.

![Voltammetric curves of a composite material, fresh aged in air.](image)

Conductivities of ionic liquids and of composite materials (bases covered with conductive glue) are summarized in Table 4.

<table>
<thead>
<tr>
<th>Ionic liquid</th>
<th>composite</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>f = 10 kHz</td>
</tr>
<tr>
<td>BMIBF$_4$/Cl</td>
<td>2050</td>
</tr>
<tr>
<td>BMIPF$_6$</td>
<td>1300</td>
</tr>
<tr>
<td>HMIBF$_4$/Cl</td>
<td>820</td>
</tr>
<tr>
<td>MOIPF$_6$</td>
<td>260</td>
</tr>
</tbody>
</table>

The effect of frequency on the conductivity of composite is rather insignificant, and there is no apparent regular trend. For BMIBF$_4$/Cl and MOIPF$_6$ the ratios of the conductivities of the composite and of the ionic liquid match the volume fraction of the ionic liquid in the composite (27 %), while for the other two ionic liquids, the ratio is surprisingly high.

The high conductivity of the composites studied in this paper makes them promising materials for electrochemical applications.
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REFERENCES


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Marek Kosmulski is professor at the Department of Electrical Engineering of the Technical University of Lublin, Poland. His research interest covers electric double layer at solid-liquid interface and low temperature ionic liquids.