

# Ionic liquids for promising ion-conducting polymer materials of electrochemical devices

*O.V. Chervakov, M.V. Burmistr, O.S. Sverdlikovs'ka, V.H. Shapka*

Ukrainian State Chemical Technology University  
Gagarina Ave. 8, Dnipropetrovs'k, 49005, Ukraine

*The review is devoted to analysis of synthesis methods development of ionic liquids based on quaternary ammonium salts and their application as components of the liquid and polymeric electrolytes for various electrochemical devices. The special attention is given to the properties analysis of ionic liquids depending on the structure of them cationic and anionic parts. The data on composition and properties of polymeric electrolytes that can be used in lithium batteries, capacitors, fuel cells, and dye-sensitized solar cells are shown.*

Historically, interest to quaternary ammonium salt increased during the search for electrolytes for highly performance electric double layer capacitors (EDLC). Organic electrolytes based on polar aprotic solvents and tetraalkylammonium perchlorates, tetrafluoroborates or hexafluorophosphates are widely used for EDLCs [1, 2]. They have a notable advantage over the aqueous electrolytes due to their much higher electrochemical stability resulting in a higher working voltage.

Another advantage of choosing polar aprotic solvents is a wider temperature range. Organic solvents, which are usually used in EDLCs, are liquids within a range of -60 to +240 °C. However, the solubility of the tetraalkylammonium salts mentioned above decreases rapidly with temperature so that, in practice, the lower temperature limit for the use of such electrolytes is usually -20 to -25 °C.

A number of other salts having a singly charged cation, such as different ammonium, phosphonium, pyridinium, imidazolium and other salts, have also been disclosed. Some of these have been used in EDLCs electrolytes, and include salts with doubly and triply charged cations.

Among these are flat aromatic heterocycles (fig. 1): pyridazine (I), pyrimidine (II), pyrazine (III) and also hexahydrotriazine (IV) alkyl derivatives [3] as shown below:

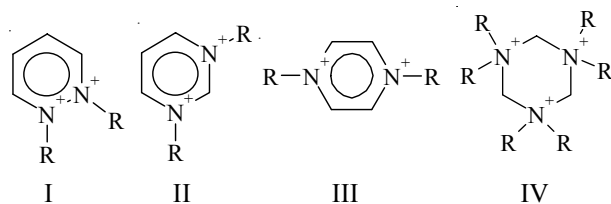
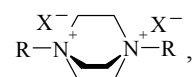


Fig. 1. Quaternary ammonium salts based on aromatic heterocycles

However, as experiments have shown, these cations are not electrochemically stable enough so that the organic electrolytes based on their salts cannot be used at voltages higher than 2,5–2,8 V. On the other hand, the idea of using doubly charged cations in the electrolytes for EDLC applications looks very attractive since an increase in the ion charge density would lead to a corresponding increase in the density of a counter-charge induced in an electrode, and as a result, the double layer capacitance would also increase.

In patent [4], have shown that new electrolytes, which contain electrochemically and chemically stable doubly charged cations and provide good performance (higher capacitance and higher working voltage) for EDLC. These are electrolytes for EDLC comprising doubly charged bicyclic cations of N,N-dialkyl-1,4-diazabicyclo[2.2.2]octanedium (DADACO):



where: R = an alkyl (C<sub>1</sub>–C<sub>4</sub>); X = BF<sub>4</sub><sup>-</sup> or PF<sub>6</sub><sup>-</sup>.

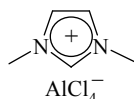
The DADACO cation surprisingly combines both the high chemical and electrochemical stability of bicyclic systems. Electrochemical double-layer capacitors based on these electrolytes, which include the salts DADACO<sup>+</sup>BF<sub>4</sub><sup>-</sup> and DADACO<sup>+</sup>PF<sub>6</sub><sup>-</sup> dissolved in aprotic polar solvents, can be used as back-up memory protection in personal computers, as pulse power sources for electric vehicle or spot welding application, for load leveling the battery in hybrid power supplies of various types, etc.

Over the past several years, electrolytes based on ionic liquids (ILs) technology for electrochemical capacitors and lithium batteries have been under development.

Ionic liquids (molten salts at room temperature) have been anticipated to act as novel ion conductive materials

owing to their unique characteristics such as non-volatility and excellent ionic conductivity. They show tremendous promise as replacements for harmful organic solvents currently in use.

The most commonly studied classes of room-temperature ionic liquids usually include a heterocyclic cation, such as a dialkyl imidazolium or an alkyropyridinium ion. These organic cations, which are relatively large and asymmetric compared with simple inorganic cations, account for the low melting points of the salts. A variety of anions can be utilized to form ionic liquids, including  $\text{BF}_4^-$ ,  $\text{PF}_6^-$ ,  $\text{AlCl}_4^-$  or other complex anion. The conventional formation of ionic liquids can be regarded as the complexation reactions of simple anionic species by neutral compounds. The most classic example is the formation of the ILs made of 1,3-dimethylimidazolium chloride ( $1,3\text{-DMI}^+\text{Cl}^-$ ) and aluminum chloride ( $\text{AlCl}_3$ ) [5]. When two solids are mixed stoichiometrically, the complexation of  $\text{Cl}^-$  by  $\text{AlCl}_3$  leads to formation IL composed  $1,3\text{-DMI}^+\text{AlCl}_4^-$ :



The reaction is thermodynamically favored, resulting in the release of heat.

Salts thus obtained exhibit high ionic conductivity, a wide electrochemical window, non-volatility, thermal stability and non-flammability. However, it should be noted that the chloroaluminate molten salts have quite high moisture sensitivity, and the decomposed product by hydrolysis ( $\text{HCl}$ ) is highly corrosive.

Recently, non-chloroaluminate ILs have been explored. It is known that certain combinations of imidazolium cations and bulky and soft anions form ionic liquids at or near room temperature [6–9].

Although extensive studies of ionic liquids have been performed, correlations between their structures and physico-chemical properties have not yet been summarized. In particular, information regarding the effect of anion structure is inadequate.

In order to achieve low melting points the imidazolium cation was made asymmetric by the introduction of a large alkyl group on one nitrogen, while keeping a small alkyl group (e.g. methyl) on the other nitrogen. In the case of 1,3-dialkylimidazolium tetrachloroaluminate ionic liquids the melting point decreased from  $75\text{ }^\circ\text{C}$  for  $1,3\text{-DMI}^+\text{AlCl}_4^-$ , to  $7\text{ }^\circ\text{C}$  for 1-ethyl-3-methylimidazolium tetrachloroaluminate ( $\text{EMI}^+\text{AlCl}_4^-$ ). For the corresponding tetrafluoroborate ionic liquids the melting point decreased from  $103,4\text{ }^\circ\text{C}$  for  $1,3\text{-DMI}^+\text{BF}_4^-$ , to about  $13\text{ }^\circ\text{C}$  for  $\text{EMI}^+\text{BF}_4^-$ . For one of the commonly used ionic liquids 1-butyl-3-methylimidazolium hexafluorophosphate, the melting point is  $10\text{ }^\circ\text{C}$  [10].

Authors [11] have prepared and studied the structures of a wide range of ionic liquids and related low-melting

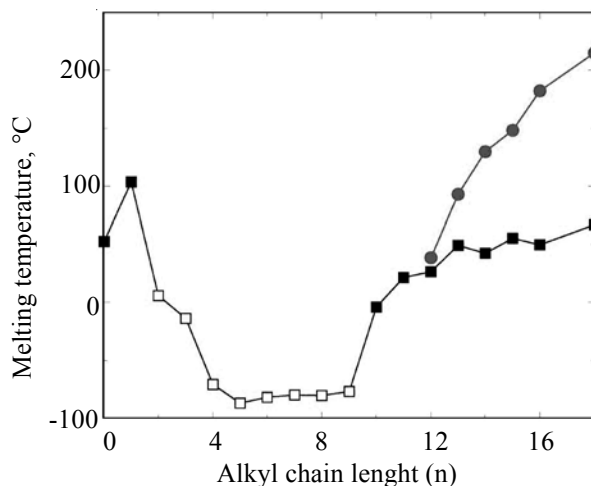
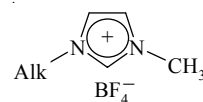


Fig. 2. Phase diagram of 1-alkyl-3-methylimidazolium tetrafluoroborate:



ionic liquids and ionic liquid crystals

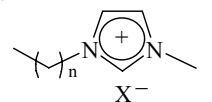
salts in order to study and develop a greater understanding of the liquid structure and interactions within room temperature alkyimidazolium ionic liquids and address these issues.

Phase diagrams have been prepared for homologous series of 1-alkyl-3-methylimidazolium ionic liquids with varying alkyl chains (fig. 2) and a range of anions ( $\text{Cl}^-$ ,  $\text{Br}^-$ ,  $\text{PF}_6^-$ ,  $\text{BF}_4^-$ ,  $\text{MX}_4^{2-}$ ) and show the wide liquid ranges and characteristic phase profile.

The most widely used room temperature ionic liquids (RTILs) are the asymmetric derivatives of N,N'-dialkylimidazolium salt [12]. The structures of some common RTILs that are based on substituted imidazolium cation are shown in fig. 3 and some of their properties are given in table 1. The synthesis of these ionic liquids is fairly straightforward.

However, the presence of a long chain alkyl group on the cation increases the viscosity and decreases the density of the IL. Further, the ionic liquid undergoes oxidation at lower potentials and becomes less thermally stable.

Ionic liquids based on the cation 1-ethyl-3-methylimidazolium are generally considered as green solvents



| where: $n =$                         | 1  | 2                            | 3  | 5                           |
|--------------------------------------|--|------------------------------|--|-----------------------------|
| $\text{X} = \text{BF}_4$             | $\text{EMI}^+\text{BF}_4^-$                        | $\text{PrMI}^+\text{BF}_4^-$ | $\text{BMI}^+\text{BF}_4^-$                        | –                           |
| $(\text{CF}_3\text{SO}_2)_2\text{N}$ | $\text{EMI}^+(\text{CF}_3\text{SO}_2)_2\text{N}^-$ | –                            | $\text{BMI}^+(\text{CF}_3\text{SO}_2)_2\text{N}^-$ | –                           |
| $\text{PF}_6$                        | $\text{EMI}^+\text{PF}_6^-$                        | –                            | $\text{BMI}^+\text{PF}_6^-$                        | $\text{HMI}^+\text{PF}_6^-$ |

Fig. 3. Structures of some imidazolium ionic liquids

Table 1. Some physical properties of RTILs

| RTIL  | $T_{mp}$ , °C | $T_d$ , °C | $h$ , cP | $\sigma$ , mS·cm <sup>-1</sup> | $E_T$ , (30) |
|---|---------------|------------|----------|--------------------------------|--------------|
| EMI <sup>+</sup> Cl <sup>-</sup>  | 86            | –          | s        | –                              | –            |
| EMI <sup>+</sup> Cl <sup>-</sup>  | 65            | –          | s        | –                              | –            |
| EMI <sup>+</sup> BF <sub>4</sub> <sup>-</sup>                                   | 6             | 447        | 66,5     | 13,0                           | 49,1         |
| PrMI <sup>+</sup> BF <sub>4</sub> <sup>-</sup>                                  | -17           | 435        | 103,0    | 5,9                            | –            |
| BMI <sup>+</sup> BF <sub>4</sub> <sup>-</sup>                                   | -81           | 435        | 154,0    | 3,5                            | 48,9         |
| EMI <sup>+</sup> PF <sub>6</sub> <sup>-</sup>                                   | 60            | –          | S        | 5,2                            | S            |
| BMI <sup>+</sup> PF <sub>6</sub> <sup>-</sup>                                   | -61           | –          | 371,0    | 1,5                            | 52,3         |
| EMI <sup>+</sup> (CF <sub>3</sub> SO <sub>2</sub> ) <sub>2</sub> N <sup>-</sup> | -3            | –          | 34,0     | 8,8                            | 47,7         |
| EMI <sup>+</sup> (CF <sub>3</sub> SO <sub>2</sub> ) <sub>2</sub> N <sup>-</sup> | -4            | >400       | 52,0     | 3,9                            | 47,2         |

$T_{mp}$  – melting point;  $T_d$  – decomposition temperature; s – solid;  $h$  – viscosity;  $\sigma$  – specific conductivity;  $E_T$  (30) – microscopic solvent polarity parameter.

mainly due their lack of vapor pressure. In fact, environmental and safety problems arising because of the volatility of organic solvents can be avoided by the use of these innovative liquids.


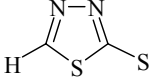
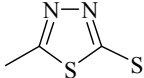
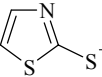
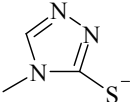
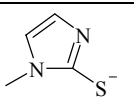


A number of publications are devoted to the applications imidazolium salts in the composition of capacitors [13] and lithium power sources [14, 15]. At the same time, despite the unique properties of ionic liquids and electrolyte systems based on them, work continues on their improvement. These efforts are connected to the growing requirement for ecological cleanliness, safety, and expansion of area of operation of these materials and the devices in which they are used. As a rule, work in this direction is connected with optimization of structure of both the anion and cation components of the ionic liquid.

Typical ionic liquids consist of halogen containing anion (such as AlCl<sub>4</sub><sup>-</sup>, PF<sub>6</sub><sup>-</sup>, BF<sub>4</sub><sup>-</sup>, CF<sub>3</sub>SO<sub>3</sub><sup>-</sup>, or (CF<sub>3</sub>SO<sub>2</sub>)<sub>2</sub>N<sup>-</sup>)

which restrict, to some extent, their “greenness”. The presence of halogen atoms may cause serious concerns if the hydrolysis stability of anion is poor (e.g. for AlCl<sub>4</sub><sup>-</sup> and PF<sub>6</sub><sup>-</sup>) or if a thermal treatment of spent ionic liquids is desired. In both cases additional effort is needed to avoid the liberation of toxic and highly corrosive HF or HCl into environment.

Since delocalization of charge considerably helps to lower the melting point ( $T_m$ ) of the salts,  $\pi$ -conjugated cations were frequently used. Similarly, introduction of halogens such as fluoride and chloride are used to lower the negative charge density. Therefore, most of general ionic liquids contain halogenated counter anions. Some halogen-free anions were also used to form salts with relatively low  $T_m$ , there were a few reports regarding ionic liquids based on these anions [16]. It is important to design halogen-free ionic liquids from the viewpoint of

Table 2.  $T_g$ ,  $T_d$ , and ionic conductivity of EMI-based ionic liquids containing sulfur-based anions

| Salt | Cation  | Anion   | $T_g$ , °C | $T_d$ , °C | $\sigma$ , mS·cm <sup>-1</sup><br>at 25 °C |
|------|---|---|------------|------------|--|
| a    |  |  | -69        | 212        | 4,60                                       |
| b    |   |  | -59        | 220        | 1,50                                       |
| c    |   |  | -64        | 215        | 0,52                                       |
| d    |   |  | -50        | 210        | 0,33                                       |
| e    |   |  | -43        | 192        | 0,32                                       |
| f    |   |  | -76        | 207        | 1,80                                       |
| g    |   |  | -89        | –          | 8,90                                       |

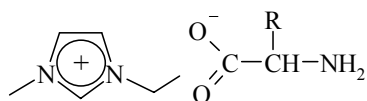


Fig. 4. Structure of amino acid ionic liquids

green chemistry.

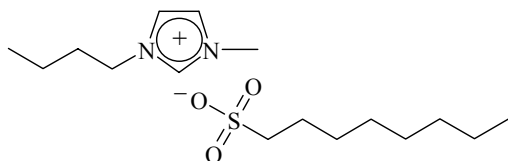
Ionic liquids have also been prepared by using sulfur-based anions such as thiol or dithiocarboxylic acid with the expectation of achieving a low surface charge density of sulfur [17]. For this purpose, new ionic liquids were composed of heterocycles having sulfur-based anions.

All salts in table 2 were obtained as liquids at room temperature. These ionic liquids showed only glass transition temperature ( $T_g$ ). They were totally amorphous having no  $T_m$ . As expected, the delocalization of negative charge of anion structure is effective in decreasing their  $T_g$  and increasing their ionic conductivity (owing to the weakened electrostatic interaction). To design excellent ionic liquid by using sulfur containing anions, it is necessary to use more acidic compounds to prepare counter ion. Salt f and g showed very low  $T_g$  similar to general ionic liquids containing TFSI anion. In particular, salt g shows the lowest  $T_g$  at  $-89^\circ\text{C}$  and displayed the best ionic conductivity  $-8,9 \cdot 10^{-3} \text{ S} \cdot \text{cm}^{-1}$  at  $25^\circ\text{C}$ . These results suggested that these azole type anions could be used effectively to prepare ionic liquids.

Ionic liquids based on combination of 1-ethyl-3-methylimidazolium cation with amino acid are investigated by K. Fukumoto and H. Ohno [18]. Structure of amino acid ionic liquids is shown in the fig. 4.

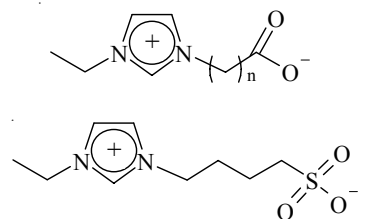
DSC analysis revealed that these amino acid ionic liquids exhibited no melting point but showed only glass transition temperature. Ionic conductivity of these ILs was in the range of  $10^{-4}$ – $10^{-9} \text{ S} \cdot \text{cm}^{-1}$  at  $25^\circ\text{C}$  reflecting the  $T_g$  of amino acid ionic liquids. Mostly, salts with lower  $T_g$  showed higher ionic conductivity at the same temperature.

The synthesis method halogen-free ionic liquid of the following structure is known [19]:



The resulting new ionic liquid systems are characterized by high performance ability (at relatively low cost) and their well documented toxicology thus making these systems highly interesting candidates for industrial bulk application.

The component ions of ionic liquid can migrate with target ions along a potential gradient. To improve this drawback, Japanese scientists [20] had proposed zwitterionic liquid (ZIL) as ionic liquid where cation and anion were tethered covalently by spacer [21, 22]. Although many of them are solid at room temperature, they turned



where:  $n = 1, 3, 4, 5, 6, 10$ .

Fig. 5. Structure of zwitterionic liquids

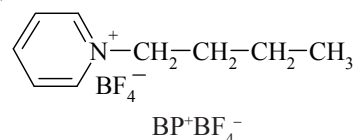
liquid by addition of LiTFSI at room temperature. There is an ionic liquid-like interaction between cation site of ZIL and TFSI anion (fig. 5).

These liquid have high ionic conductivity ( $10^{-4} \text{ S} \cdot \text{cm}^{-1}$ ). They also showed high thermal stability with a decomposition temperature of about  $400^\circ\text{C}$ . However, better design of ZIL is necessary to improve the ion conductive character.

Table 3 shows the difference between sulfonate and carboxylate zwitterions having N-ethylimidazolium cation and  $n=4$  spacer length. There is little difference in  $T_m$ . Sulfonate-type zwitterions have good thermal stability and high transference number of lithium cation. On the hand, carboxylate type zwitterions have good ionic conductivity and slow crystallization.

Quaternary ammonium salts (QAS) are attractive for use in ILs because they are easy to synthesize, relatively safe, and can have very low molecular weights, possibly leading to lower viscosity and high conductivity.

Comparative analysis of 1-ethyl-3-methylimidazolium tetrafluoroborate ( $\text{EMI}^+\text{BF}_4^-$ ) and 1-butylpyridinium tetrafluoroborate ( $\text{BP}^+\text{BF}_4^-$ ):



properties have been studied.  $\text{EMI}^+\text{BF}_4^-$  and  $\text{BP}^+\text{BF}_4^-$  exhibit melting points of approximately  $15^\circ\text{C}$  [21, 22]. The melting points are detected by DSC measurements only in heating processes from  $150$  to  $100^\circ\text{C}$  at  $10 \text{ K/min}$ , and cannot be detected in cooling processes (from  $100$  to  $150^\circ\text{C}$  at  $10 \text{ K/min}$ ), because of the slow crystallization rates. Both of salts form stable super cooled liquids down the glass transition temperature during the cooling processes.

Table 3. Comparison of thermal properties and ionic conductivity for ZILs with different anion species

| Properties                         | $-\text{SO}_3^-$ | $-\text{CO}_2^-$ |
|------------------------------------|------------------|------------------|
| $T_m$ (bulk, $^\circ\text{C}$ )    | 160              | 167              |
| $T_d$ (bulk, $^\circ\text{C}$ )    | 326              | 226              |
| $T_d$ (+LiTFSI, $^\circ\text{C}$ ) | 364              | 307              |
| Crystallization                    | fast             | very slow        |
| $t_{Li+}$                          | $>0,5$           | $0,1$            |

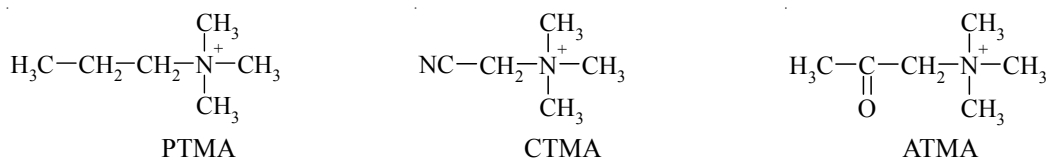


Fig. 6. Onium cations

Table 4. Conductivity data of materials based on onium cations ILs

| Ionic liquid | Pristine, $\text{mS}\cdot\text{cm}^{-1}$ | With 0,2 M of LiTFSI, $\text{mS}\cdot\text{cm}^{-1}$ |
|--------------|--|--|
| PTMA-TFSI    | 3,8                                      | 2,10   |
| CTMA-TFSI    | 0,5–0,7                                  | 0,53   |
| ATMA-TFSI    | 5,5                                      | -  |

$\text{EMI}^+\text{BF}_4^-$  and  $\text{BP}^+\text{BF}_4^-$  exhibit, respectively, a high conductivity of  $2,0\cdot 10^{-2} \text{ S}\cdot\text{cm}^{-1}$  and  $3,0\cdot 10^{-3} \text{ S}\cdot\text{cm}^{-1}$  at  $30^\circ\text{C}$ . The electrochemical window for  $\text{EMI}^+\text{BF}_4^-$  and  $\text{BP}^+\text{BF}_4^-$  are respectively, 4,0 V and 3,4 V. They can dissolve LiTFSI,  $\text{LiBF}_4$  and  $\text{LiPF}_6$  up to high concentration and form ionic liquids, which maintain high ionic conductivity.

Polymer electrolytes based on  $\text{BP}^+\text{BF}_4^-$  can be obtained by polymerization of vinyl monomers in the presence of molten salt. For example, in situ polymerization of 2-hydroxyethyl methacrylate in the presence of  $\text{BP}^+\text{BF}_4^-$  yields polymers that have an ionic conductivity of  $10^{-3} \text{ S}\cdot\text{cm}^{-1}$  at  $30^\circ\text{C}$ .

A series of ionic liquids containing tetraalkyl ammonium cations show higher cathodic stability than those containing imidazolium cations. The structural formulas of synthesized onium cations are shown in fig. 6:

The authors introduce several functional groups, such as cyano  $\text{CN}^-$  and acetyl  $\text{CH}_3\text{CO}^-$ , on tetraalkyl ammonium cation-based ionic liquid in order to improve the interfacial stability toward lithium [23, 24]. Authors first synthesized the iodides of these cations, and then exchanged their anions under an aqueous condition with LiTFSI. Such ionic liquids could not contain a large amount of lithium salts, their saturated contents being up to 0,5 M. Conductivity data of synthesized ILs and electrolytes based on them are shown in the table 4.

From the results obtained the, authors expect that

Table 5. Melting point of pyrazolium ILs

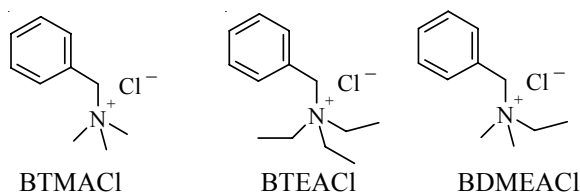
| Ionic liquid/Ionic liquid mixture  | Melting point, $^\circ\text{C}$ |
|--|---------------------------------|
| $\text{DMP}^+\text{BF}_4^-$  | 80,5 to 82,0                    |
| $\text{EMP}^+\text{BF}_4^-$  | 47,5 to 49,0                    |
| $\text{DMFP}^+\text{BF}_4^-$ *   | 54,0 to 55,5                    |
| $\text{EMI}^+\text{BF}_4^-$  | 12,3 to 13,1                    |
| 33,3 % $\text{DMP}^+\text{BF}_4^-$ – 66,7 % $\text{EMP}^+\text{BF}_4^-$ ** | 42,0 to 49,0                    |
| 60,0 % $\text{DMFP}^+\text{BF}_4^-$ – 40,0 % $\text{EMP}^+\text{BF}_4^-$   | 15,5 to 16,5                    |
| 50,0 % $\text{EMI}^+\text{BF}_4^-$ – 50,0 % $\text{EMP}^+\text{BF}_4^-$    | –18,0 to –14,0                  |
| 70,0 % $\text{EMI}^+\text{BF}_4^-$ – 30,0 % $\text{EMP}^+\text{BF}_4^-$    | –90,0 (glass transition)        |

\* 1,2-dimethyl-4-fluoropyrazolium tetrafluoroborate; \*\* composition in % mol.

CTMA-TFSI is available for electrolyte solvent, or at least additive to another ionic liquid, for advanced lithium batteries.

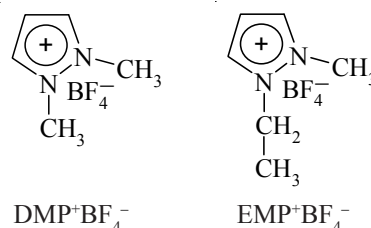
The following quaternary ammonium chloride salts were proposed for synthesis of ILs [25]:

- benzyltrimethylammonium chloride (BTMACl,  $T_m=55,6^\circ\text{C}$ );
- benzyltriethylammonium chloride (BTEACl,  $T_m=66,4^\circ\text{C}$ );
- benzyl dimethylthylammonium chloride (BDMEACl,  $T_m=13,4^\circ\text{C}$ ).



It was established that the asymmetric structure of BDMEACl (mixture of the methyl and ethyl groups from the other two) has a dramatic effect on its melting point compared BTMACl and BTEACl. It is believed that the higher symmetry of the quaternary ammonium salt permits easier crystallization resulting in a higher melting point.

Electrochemical System Inc. has developed pyrazolium cation based ionic liquids for application in lithium and lithium-ion batteries:

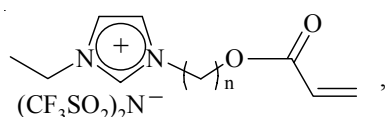


The melting point of the 1,2-dialkylpyrazolium ionic liquids decreased with increasing asymmetry of the cation (table 5).

Results obtained show that, while the melting points of single salts can be decreased by the increase of asymmetry of the cation, ionic liquid compositions with very low melting point can also be obtained by the use of mixtures of ionic liquids wherein the cations have significant differences in their structures [10].

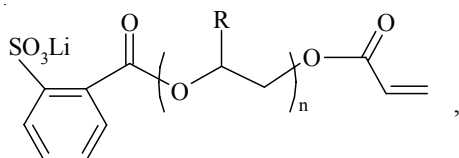
On the other hand, ionic liquid polymers in which ionic liquid component ions were tethered on the polymer main chain were also effective for obtaining target ion conduction. In particular, copolymerization of ionic liquids to provide target ion conductive polymer films were suggested [26]. The following structures can be used for synthesis of such polymers:

– cationic monomer that has hydrocarbon spacer between the polymerizable group and the ionic liquid moiety:



where:  $n = 0; 3; 6; 10$ .

– anionic monomer, having benzene sulfonic acid lithium salt on polyether chain end:

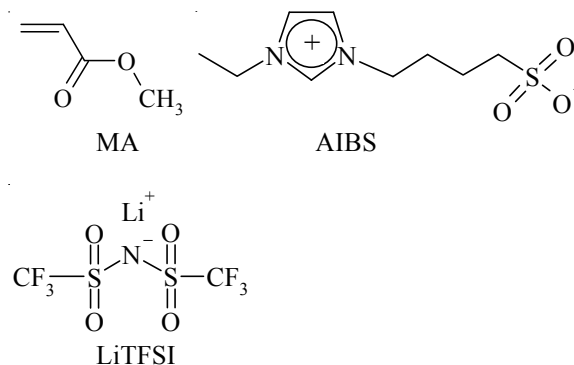


where:  $R=H, n=2; 8; R=Me, n=9$ .

These polymers were obtained as film-like solid. The electrostatic interaction between cationic and anionic side chains should be effective in improving mechanical properties. Conductivity of the obtained films depends from their  $T_g$ .  $T_g$  decreases with increasing cationic monomer content in the copolymer. On the other hand,  $t_{Li+}$  improved with increasing anionic monomer content (0,53 for 50 % mol. and 0,68 for 80 % mol.). This approach appears to be excellent for solid polymer electrolytes based on an ionic liquid moiety.

Thermally stable polymer-in-zwitterionic liquid electrolytes can be obtained by polymerization of

methyl-acrylate (MA) in the presence of 1-(1-alkyl-3-imidazolio)butane-4-sulfonate (AIBS) and LiTFSI [27]:



The electrolytes thus obtained are rubber-like polymers that have  $T_g = -15 \div -10$  °C and conductivity  $\sim 10^{-5} - 10^{-6}$  S·cm<sup>-1</sup> at room temperature, stable above 380 °C.

Ionic liquid-polymer gel electrolytes prepared by incorporation of hydrophilic EMI<sup>+</sup>BF<sub>4</sub><sup>-</sup> and EMI<sup>+</sup>CF<sub>3</sub>SO<sub>3</sub><sup>-</sup> and hydrophobic BMI<sup>+</sup>PF<sub>6</sub><sup>-</sup> (EMI<sup>+</sup> – 1-ethyl-3-methylimidazolium and BMI<sup>+</sup> – 1-(1-butyl)-3-methylimidazolium ionic liquids into a poly(vinylidene fluoride)-hexafluoropropylene copolymer (PVDF-HFP) matrix have higher ionic conductivity [28]. Conductivity at room temperature (22–23 °C) and at 100 °C for this family of compounds is shown in table 6.

Despite the successes in development of ionic liquids, they mainly are classified as room temperature ionic liquids.

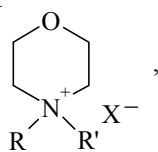
Recently increased interest is shown to development of synthesis methods of new type (no imidazolium derivatives) low-temperature ionic liquids capable of working in a range of temperatures from a minus 65 up to plus 65 °C. At the same time, the special attention is focused to decreasing of cost and ecological cleanliness of synthesized materials and opportunity of creation on their basis of polymeric materials with high ionic conductivity.

At Ukrainian State Chemical Technology University the synthesis methods of quaternary ammonium salts based on morpholine is develop [29]. The common structure of such compounds, which are ionic liquids at room

Table 6. Ionic conductivity of ILs and ionic liquid-polymer gel electrolytes

| Ionic liquid-polymer gel electrolytes  | Conductivity, mS·cm <sup>-1</sup> |        |
|--|-----------------------------------|--------|
|  | Room temperature                  | 100 °C |
| EMI <sup>+</sup> CF <sub>3</sub> SO <sub>3</sub> <sup>-</sup> : PVDF-HFP (2:1)     | 2,200                             | 22,9   |
| EMI <sup>+</sup> CF <sub>3</sub> SO <sub>3</sub> <sup>-</sup> : PVDF-HFP (1:1)     | 0,600                             | 9,1    |
| EMI <sup>+</sup> CF <sub>3</sub> SO <sub>3</sub> <sup>-</sup> : PVDF-HFP (0,4:1,0) | 0,006                             | 4,5    |
| EMI <sup>+</sup> BF <sub>4</sub> <sup>-</sup> : PVDF-HFP (2:1)                     | 3,200                             | 14,4   |
| EMI <sup>+</sup> BF <sub>4</sub> <sup>-</sup> : PVDF-HFP (1:1)                     | 1,400                             | 16,4   |
| EMI <sup>+</sup> BF <sub>4</sub> <sup>-</sup> : PVDF-HFP (0,5:1,0)                 | 0,100                             | 7,7    |
| BMI <sup>+</sup> PF <sub>6</sub> <sup>-</sup> : PVDF-HFP (1:1)                     | 0,100                             | 7,3    |
| Ionic liquids  |                                   |        |
| EMI <sup>+</sup> CF <sub>3</sub> SO <sub>3</sub> <sup>-</sup>                      | 9,300                             | 55,3   |
| EMI <sup>+</sup> BF <sub>4</sub> <sup>-</sup>                                      | 13,800                            | 59,0   |
| BMI <sup>+</sup> PF <sub>6</sub> <sup>-</sup>                                      | 1,800                             | 15,6   |

temperature, is given below:



where: X = Cl, Br; R, R' =  $-\text{CH}_2-\text{CH}_2-\text{OH}$ ;  $-\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{CH}_3$ .

These compounds are soluble in organic solvents (alcohols, aprotic solvents, methylene chloride), and compatible with many polymeric materials, in particular with cellulose triacetate [30]. These properties have allowed

their use as corrosion inhibitors [31] and developer's activator of the halogen-silver photo-materials display [32].

Anticipated benefits of using quaternary ammonium salt based on morpholine are simplicity of their synthesis using commercially produced starting materials. In our opinion, these compounds can be as model structures for obtaining wide range of low-temperature ionic liquids (at the expense of special selection of the radicals at quaternary nitrogen atom and anionic part) and new liquid and plasticized polymer electrolytes on their basis for new generation electrochemical devices, such as lithium power sources [33, 34], capacitors [35], fuel cells [36, 37], and dye-sensitized solar cells [38–40].

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## **Іонні рідини – перспективні йонопровідні полімерні матеріали для електрохімічних пристроїв**

**О.В. Черваков, М.В. Бурмістр, О.С. Свєрдліковська, В.Х. Шапка**

Український державний хіміко-технологічний університет  
8, бульв. Гагаріна, Дніпропетровськ, 49005, Україна

*Огляд присвячено аналізу розвитку методів синтезу йонних рідин на основі четвертинних амонієвих солей і їх застосування в якості компонент рідких і полімерних електролітів для різних електрохімічних пристроїв. Особлива увага надається аналізу залежності властивостей йонних рідин від структури їх катіонної та аніонної частин. Наведено дані складу і властивостей полімерних електролітів, які можуть використовуватися в літійових батареях, конденсаторах, сонячних батареях.*

## **Ионные жидкости – перспективные ионопроводящие полимерные материалы для электрохимических устройств**

**О.В. Черваков, М.В. Бурмистр, О.С. Свєрдликовская, В.Х. Шапка**

Украинский государственный химико-технологический университет  
8, бульв. Гагарина, Днепропетровск, 49005, Украина

*Обзор посвящен анализу развития методов синтеза ионных жидкостей на основе четвертичных аммониевых солей и их применения в качестве компонент жидких и полимерных электролитов для различных электрохимических устройств. Особое внимание уделяется анализу зависимости свойств ионных жидкостей от структуры их катионной и анионной частей. Представлены данные по составу и свойствам полимерных электролитов, которые могут использовать в литиевых батареях, конденсаторах, солнечных батареях.*