

# Ionic Liquids as Electrolyte in Lithium-ion Batteries: Imidazolium and Pyrazolium Tetrafluoroborate in $\text{LiMn}_2\text{O}_4$ /Metal Oxide Cells

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This paper describes the application of ionic liquids, 1-ethyl-3-methylimidazolium tetrafluoroborate ( $\text{EMIBF}_4$ ) and 1-ethyl-2-methylpyrazolium tetrafluoroborate ( $\text{EMPBF}_4$ ) as electrolytes in lithium-ion cells. Lithium-ion cells employed  $\text{LiMn}_2\text{O}_4$  as the cathode and metal oxide ( $\text{MoO}_2$ ,  $\text{Li}_4\text{Ti}_5\text{O}_{12}$ ) as the anode. The physicochemical properties of ionic liquids, such as: melting point, thermal stability, conductivity, and electrochemical stability, were determined. Melting point for  $\text{EMPBF}_4$  was 47.5 °C to 49 °C and for 0.8 molal  $\text{LiAsF}_6$  in  $\text{EMPBF}_4$  21 °C to 26 °C.  $\text{EMPBF}_4$  is thermally stable to 300 °C. Conductivity of neat ionic liquids as well as ionic liquids containing dissolved lithium salts ( $\text{LiBF}_4$ ,  $\text{LiAsF}_6$ ) was determined. The conductivity is much lower for the latter than for the neat ionic liquids; in addition, it decreases with an increase in the lithium salt concentration. Electrochemical window was > 4.3V for all examined ionic liquid compositions except for neat  $\text{EMIBF}_4$  which was slightly lower (4.2V). Reduction and oxidation potential vs. lithium was lower for  $\text{EMIBF}_4$  containing ionic liquids than for the  $\text{EMPBF}_4$  ones. The cells were cycled at several temperatures. It was observed that the cells using  $\text{EMPBF}_4$  were less affected by increase in temperature. Both  $\text{MoO}_2/\text{LiMn}_2\text{O}_4$  and  $\text{Li}_4\text{Ti}_5\text{O}_{12}/\text{LiMn}_2\text{O}_4$  cells demonstrated stable capacity with cycling at room temperature and remained stable to 60 °C for the cell employing  $\text{EMIBF}_4$  ionic liquid. The cells employing  $\text{EMPBF}_4$  showed stable capacity with cycling to 80 °C. Coulombic efficiency showed similar behavior. It was 96% for both type of cells at room temperature. It decreased to 90 % at 80 °C for the cells employing  $\text{EMPBF}_4$  while the cells using  $\text{EMIBF}_4$  achieved coulombic efficiency of ~90 % at 60 °C or below.

Keywords: *Ionic liquids, low temperature molten salts, lithium-ion batteries, nonflammable solvents,  $\text{MoO}_2/\text{LiMn}_2\text{O}_4$  cells,  $\text{Li}_4\text{Ti}_5\text{O}_{12}/\text{LiMn}_2\text{O}_4$  cells*

## Introduction

Traditional molten salts are non-aqueous ionic solvents that are liquid at high temperature (for example,  $\text{LiCl}$  mp 610 °C). Ionic liquids is the term applied recently to low temperature molten salts or room temperature molten salts that are liquid at temperatures below 100 °C. High temperature molten salts are also ionic liquids although they are molten only at high temperature. Ionic liquids have been known since the 19<sup>th</sup> century.<sup>1</sup> However, it is accepted that their faster development and basic research involving ionic liquids started in 1948 when Hurley and Weir developed  $\text{AlCl}_3$  based ionic liquids for electroplating.<sup>2</sup> These early research efforts were centered around haloaluminate ionic liquids and related to electrochemistry.<sup>3</sup> They have been employed as solvents for electrochemical investigations of a wide range of inorganic, organic, and organometallic solutes. Further, these ionic liquids demonstrated to be useful electrolytes for electrowinning and electrodisolution of metals, for the modification of electrodes by electropolymerization, electrosynthesis, and for batteries.

Ionic liquids possess a characteristic structure, usually consisting of large organic cations and inorganic anions. The resulting ionic liquids have low melting points due to weaker coulombic interactions as well as asymmetric cations which are commonly used.<sup>4</sup>

For example, replacing  $\text{Na}^+$  cation in  $\text{NaCl}$  with dialkylimidazolium cation will result in dialkylimidazolium chloride, an ionic liquid with much lower melting point (mp 78 °C for 1-ethyl-3-methylimidazolium chloride) than the original molten salt (mp 800 °C for  $\text{NaCl}$ ).<sup>5</sup>

Generally, ionic liquids show the following properties:

- low melting point (even below 0 °C),
- good conductivity,
- non-flammability,
- non-volatility,
- good thermal stability (> 300 °C),
- good chemical stability and electrochemical stability (electrochemical window > 4V).

The initially developed ionic liquids consisted of 1-(1-butyl)-pyridinium or dialkylimidazolium cations and haloaluminate anions.<sup>3</sup> However, the haloaluminate ionic liquids are moisture sensitive which is a disadvantage and an obstacle for their wider application.

In 1992 Wilkes and Zaworotko synthesized low melting ionic liquids which contained water stable anions.<sup>6</sup> Thus a new class of water stable ionic liquids was born. These ionic liquids contained dialkylimidazolium cation combined with tetrafluoroborate, hexafluorophosphate, nitrate, sulfate, and acetate anions.

Since the synthesis of these water stable ionic liquids numerous new ionic liquids have been developed. In the same time, selection of properties also increased from hydrophilic to hydrophobic, acidic to basic, as well as task specific. Function of the ionic liquid could be designed to direct reaction(s) in the desired direction and toward desired products. Some of the ways for changing the function of the ionic liquid are replacing the substituents on the cation or changing their position with respect to each other, or using different types of cations and anions.

The number of ionic liquids increased significantly in the last 10 years as a consequence of these new options. Their application also expanded from original application in electrochemistry to batteries, capacitors, and solar cells.<sup>7–10</sup> Recently, their application in chemistry exploded and ionic liquids began to be used in catalysis, synthetic reactions, separations, material sciences, liquid phase transfer chemistry, liquid surfactants, and in Green chemistry as a replacement for volatile organic solvents.<sup>1,11</sup>

This paper describes application of imidazolium and pyrazolium tetrafluoroborate ionic liquids as electrolytes in rechargeable lithium-ion batteries. Present rechargeable lithium-ion batteries use intercalation compounds, for both positive and negative electrodes, and a non-aqueous liquid electrolyte.<sup>12</sup> The non-aqueous electrolyte consists of a lithium salt dissolved in an organic solvent(s). In lithium-ion cells intercalated carbon replaced lithium metal used in rechargeable lithium cells. When lithium is used to construct a primary or a secondary cell a passivating film (Solid Electrolyte Interface-SEI) forms on the surface of lithium by reaction with the non-aqueous (organic) electrolyte components. This passivating film prevents or minimizes further reaction of the electrolyte components. However, at high current densities the thickness of the SEI decreases, and direct reaction between lithium and cathode material and electrolyte occurs.<sup>13</sup> This leads to loss of capacity with cycling. The loss of capacity and dendrite formation leading to cell short-circuiting are the main causes for the failure of rechargeable lithium cells.

During initial cell operation of a lithium-ion cell a passivating film forms at the carbon electrode surface caused by the reaction between solvent and lithium in  $\text{Li}_x\text{C}$ . The passivating layer protects the carbon electrode from direct contact with the electrolyte thus preventing further decomposition of the solvent. It allows only the reversible lithium intercalation-deintercalation reaction in subsequent cycles. Low voltage spinels and rutile type metal oxides can also be used as anodes in lithium ion cells.<sup>7,14</sup> However, they intercalate/deintercalate at higher voltage vs. lithium; in addition,

in the case of oxides such as  $\text{Li}_4\text{Ti}_5\text{O}_{12}$ , lithium ion intercalation occurs at a voltage ( $\sim 1.5$  V vs.  $\text{Li}/\text{Li}^+$ ) higher than the reduction voltage of most electrolytes, and therefore a protective layer does not form on the surface of such an anode.

The cell voltage of lithium-ion cells is determined by the difference between the electrochemical potentials of lithium within the two lithium intercalating compounds. Therefore to produce high voltage cells, strongly oxidizing compounds must be used as the positive electrode. The layered compounds  $\text{LiCoO}_2$  and  $\text{LiNiO}_2$ , and  $\text{LiMn}_2\text{O}_4$  spinel, are some of the materials known to intercalate Li reversibly at voltages larger than 3.5 V vs. Li.<sup>15</sup>

Most of the solvents used in lithium-ion cells have an electrochemical window in the range of 4.1–4.3 V. Therefore in these high voltage cells, the oxidation of the electrolyte during charge (overcharge) can occur which leads to cathode degradation.<sup>16</sup> In addition, these solvents are volatile, some are flammable, thus presenting a safety hazard. Further, their operating range is rather narrow (for example,  $-99$  °C to  $32$  °C for methyl formate).<sup>17</sup>

Room temperature molten salts (ionic liquids) due to their high thermal stability, nonvolatility, electrochemical stability, nonflammability do not present a safety hazard. Therefore, they may be used as electrolytes in lithium-ion cells. However, preliminary results with lithium-ion cells constructed with carbon anodes and imidazolium or pyrazolium tetrafluoroborate ionic liquids showed that decomposition of the ionic liquid occurs when the cell is charged. This suggests that a passivating film does not form on carbon when those ionic liquids are used, resulting in continuous reduction of the electrolyte. However, non passivating anodes may be used instead of carbon to produce lithium-ion cells containing ionic liquids that operate at both low and high temperature.<sup>18</sup> The disadvantage of these solvents is in their low conductivity and higher viscosity at low temperatures (close to melting point of ionic liquid) .

Authors have developed pyrazolium based ionic liquids which, in addition to previously mentioned properties, demonstrated very high stability toward lithium.<sup>19,20</sup> The melt remained unchanged even after being in contact with lithium for several months at  $150$  °C. Both imidazolium (1-ethyl-3-methylimidazolium tetrafluoroborate-EMIBF<sub>4</sub>) and pyrazolium(1-ethyl-2-methylpyrazolium tetrafluoroborate-EMPBF<sub>4</sub>) based ionic liquids were used as electrolytes in lithium-ion cells.  $\text{LiMn}_2\text{O}_4$  was used as the cathode.  $\text{LiMn}_2\text{O}_4$  is inexpensive, environmentally benign, and presently has wide application in many batteries so that its toxicity and disposal method are known. Lithium-ion cells were built employing metal oxides ( $\text{MoO}_2$ ,  $\text{Li}_4\text{Ti}_5\text{O}_{12}$ ) for anode material instead of carbon.

## Experimental

### Materials

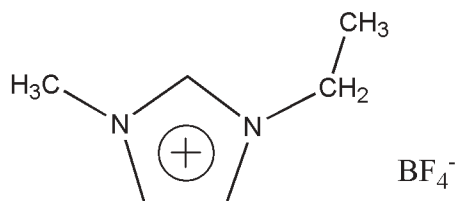
All employed materials were of the highest available purity. Electrolytes were prepared by dissolving lithium salts in ionic liquids. Following ionic liquids were used: 1-ethyl-3-methylimidazolium tetrafluoroborate (EMIBF<sub>4</sub>) and 1-ethyl-2-methyl-pyrazolium tetrafluoroborate (EMPBF<sub>4</sub>). The above mentioned molten salts were synthesized; proce-

dures for preparation are described in the text below.  $\text{LiBF}_4$  (ultra dry),  $\text{LiAsF}_6$ , and  $\text{AgBF}_4$  were obtained from Alfa-Aesar.

Electrode materials: Carbon black Vulcan VXC-72R Cabot, Waltham, Mass. was utilized for preparation of  $\text{LiMn}_2\text{O}_4$ ,  $\text{MoO}_2$ , and  $\text{Li}_4\text{Ti}_5\text{O}_{12}$  electrodes.  $\text{LiMn}_2\text{O}_4$  SP 30 Selectipur EM Industries, Hawthorne, NY was utilized as cathode material. Polyvinylidene Fluoride (PVDF; Kynar 2800-00 Elf Atochem NA, Philadelphia, PA and PVDF, Solvay 20810, Solvay Advanced Polymers, Inc. Houston, TX) were used as binder. Aluminum foil thickness 0.025 mm, Sumitomo Corp. of America, Atlanta, GA, was used as cathode current collector. Celgard 2500 (Hoechst-Celanese) thickness 0.025 mm was used as separator. Copper foil thickness 0.020 mm, Sumitomo Corp. of America, was used as current collector for anode in Li-ion cells.  $\text{MoO}_2$  was obtained from Alfa Aesar.

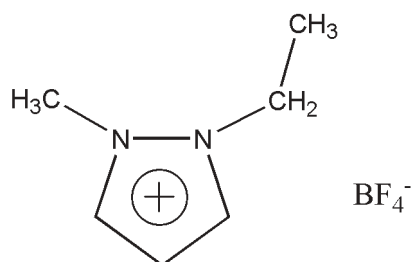
$\text{Li}_4\text{Ti}_5\text{O}_{12}$  was synthesized following modified procedure described in the literature.<sup>21,22</sup>

Synthesis of 1-ethyl-3-methylimidazolium tetrafluoroborate ( $\text{EMIBF}_4$ ):



Method by Fuller et al. was employed to synthesize  $\text{EMIBF}_4$ .<sup>23</sup> This method consists of directly mixing aqueous solutions of equimolar amounts of 1-ethyl-3-methylimidazolium chloride (EMIC) and  $\text{AgBF}_4$ . The end point was determined by potentiometry. The reaction product  $\text{AgCl}$  and the solvent (water) were removed in order to obtain pure  $\text{EMIBF}_4$  which is a liquid at room temperature.

Synthesis of 1-ethyl-2-methylpyrazolium tetrafluoroborate ( $\text{EMPBF}_4$ ):



The  $\text{EMPBF}_4$  was synthesized in two steps. In the first step ethyl iodide was reacted with 1-methylpyrazole to obtain 1-ethyl-2-methylpyrazolium iodide. In the second step the obtained pyrazolium salt was ion exchanged with  $\text{AgBF}_4$  to obtain a white solid  $\text{EMPBF}_4$  (~80 % yield, overall yield 48 %).<sup>20</sup>

### Analytical and test methods

*Melting points* were determined visually and by Differential Scanning Calorimetry (DSC).

Perkin-Elmer 7 Series/Unix DCS 7 was used for Differential Scanning Calorimetry (DSC). Thermal Gravimetric Analysis (TGA) was performed on Perkin-Elmer 7 Series/Unix TGA 7 Thermal Gravimetric Analyzer.

The *isothermal TGA* was performed by sealing approximately 10 mg of sample in an aluminum pan in the dry box to avoid moisture in the sample. The sample was equilibrated at 100 °C for five minutes, then heated to the required temperature at 200 °C  $\text{min}^{-1}$  and held there for two hours. The degradation rates were calculated four minutes after the temperature jump so as to allow the temperature to equilibrate.

*Water content* in the ionic liquids was determined on Denver Instruments Model 260 Karl-Fisher titration apparatus. The conductivity was measured using Oakton, Inc. Model WD 35607-10 and YSI Model 31 conductivity meters. Temperature during conductivity measurements was monitored with a digital thermometer (Traceable Thermometer, Control Company) with a range of -50 °C to +150 °C  $\pm$  1 °C.

The small conductivity cell (Microelectrodes Inc., series MI-900) was employed which had two platinized electrodes and approximate cell constant 3  $\text{cm}^{-1}$ . The cell constant was determined using aqueous KCl standard solutions 0.01, 0.02, 0.04, 0.06, 0.08, and 0.1 molar.

*Sample preparation.* The sample was prepared inside a dry box by weighing the appropriate amounts of components (150 mg). Once mixed and liquefied, the sample was transferred to a pre-dried glass tube of inner diameter 5 mm. The calibrated conductivity cell was placed inside the glass tube so that the electrodes were immersed in the sample. Conductivity measurements at room temperature were performed in a dry box. The cell was moved outside the dry box for temperature dependent studies. Temperatures above ambient were achieved with a heated oil bath. Subambient temperatures were obtained by adjusting a liquid nitrogen acetone bath in a Dewar bottle. Conductivity measurements were initially performed at ambient temperature, then at increasing temperatures, next decreasing to -50 °C (or to sample solidification), and finally back to 50 °C (or ambient temperature). When temperature values stabilized for at least 10 min, the sample conductivity was recorded.

Cyclic voltammetry (CV) measurements were performed on a PAR Model 173 Potentiostat/Galvanostat and a PAR Model 175 Universal Programmer and on EG&G Model 273 Potentiostat/Galvanostat. Cyclic voltammograms were acquired in small volume cells (0.1 mL to 3 mL) obtained from Cypress Systems, Inc., Lawrence, KS modified in house utilizing mini-glassy carbon electrodes (diameter 1 mm), platinum (diameter 1.5 mm) as working electrode, mini-platinum electrode as counter electrode, and silver wire electrode as quasi reference electrode or lithium electrode as reference electrode.

*Test cells.* Test cell consists of a positive electrode 1.22 cm in diameter ( $\text{LiMn}_2\text{O}_4$ ), a 1.22 cm diameter negative electrode ( $\text{MoO}_2\text{Li}_4\text{TiO}_{12}$ ), separator placed between the electrodes (Celgard), and melt used as electrolyte.<sup>24</sup>

Electrodes. Positive electrode (Cathode).  $\text{LiMn}_2\text{O}_4$  cathode was made by mixing  $\text{LiMn}_2\text{O}_4$  and carbon with a solution of polyvinylidene fluoride (PVDF) in acetone to form a slurry which was stirred to obtain a homogeneous composition. The slurry was evenly spread on an aluminum foil and dried in vacuum at  $60\text{ }^\circ\text{C}$  to  $80\text{ }^\circ\text{C}$  for at least 6 h, usually overnight. The coating was performed on an in-house built apparatus using the so called precision knife over plate method. Ratio of  $\text{LiMn}_2\text{O}_4$ :C: PVDF was in the range of 85 % : 5 % : 10 % by mass.

Negative electrode (Anode).  $\text{MoO}_2$  and  $\text{Li}_4\text{TiO}_{12}$  were utilized as the materials for anode in lithium-ion cells. The oxide electrodes were made by using the same procedure as for cathodes. For oxide electrodes the ratio oxide : C : PVDF was 85 % : 5 % : 10 % by mass.

Testing of lithium-ion cells was carried out on MACCOR series 4 000 cyler.

Preparation and determination of properties of the molten salts as well as the construction and operation of cells were carried out in a VAC dry box and a custom made dry box. The combined concentration of oxygen and water in the argon atmosphere inside the dry box was  $< 1\text{ ppm}$ .

## Results

### Melting points

For  $\text{EMIBF}_4$  melting point of  $15\text{ }^\circ\text{C}$  was determined.  $\text{EMPBF}_4$  has a melting point of  $47.5\text{ }^\circ\text{C}$  to  $49\text{ }^\circ\text{C}$ . For 0.8 molal  $\text{LiAsF}_6$  in  $\text{EMPBF}_4$  (0.8 mol  $\text{LiAsF}_6/1\text{ kg EMPBF}_4$ ) the melting point is  $21\text{ }^\circ\text{C}$  to  $26\text{ }^\circ\text{C}$ .

### Thermal stability

Fig. 1 presents results of isothermal stability measurements (isothermal TGA) of  $\text{EMPBF}_4$  melt in nitrogen. The melt contained 40 ppm  $\text{H}_2\text{O}$ . Weight loss of the melt was measured during 120 min at constant temperature of  $200\text{ }^\circ\text{C}$ ,  $250\text{ }^\circ\text{C}$ , and  $300\text{ }^\circ\text{C}$ . It appears that the mass loss increases with increase in temperature; thus at  $200\text{ }^\circ\text{C}$  the mass loss is  $0.00322\text{ } \%\text{ min}^{-1}$  while at  $300\text{ }^\circ\text{C}$  it is  $0.05485\text{ } \%\text{ min}^{-1}$  which corresponds to complete disintegration of the melt in 30 hours. However, isothermal stability measurements of  $\text{EMIBF}_4$  at  $300\text{ }^\circ\text{C}$  showed weight loss of  $0.02596\text{ } \%\text{ min}^{-1}$ .<sup>25</sup> It is clear that the melt  $\text{EMIBF}_4$  is thermally more stable than the  $\text{EMPBF}_4$  melt.

### Conductivity

Conductivity of the following ionic liquid compositions were measured:

1.  $\text{EMPBF}_4$
2. 0.8 molal  $\text{LiBF}_4$  in  $\text{EMPBF}_4$  (0.8 mol  $\text{LiBF}_4/1\text{ kg EMPBF}_4$ )
3. 0.4 molal  $\text{LiAsF}_6$  in  $\text{EMPBF}_4$  (0.4 mol  $\text{LiAsF}_6/1\text{ kg EMPBF}_4$ )
4. 0.8 molal  $\text{LiAsF}_6$  in  $\text{EMPBF}_4$  (0.8 mol  $\text{LiAsF}_6/1\text{ kg EMPBF}_4$ )

Fig. 2 shows conductivity vs. temperature for neat  $\text{EMPBF}_4$  melt, 0.4 molal  $\text{LiAsF}_6$  in  $\text{EMPBF}_4$ , 0.4 molal  $\text{LiAsF}_6$  in  $\text{EMPBF}_4$ , and 0.8 molal  $\text{LiBF}_4$  in  $\text{EMPBF}_4$ .

From Fig. 2 it is clear that conductivity increases with increase in temperature. By adding  $\text{LiBF}_4$  or  $\text{LiAsF}_6$  to the

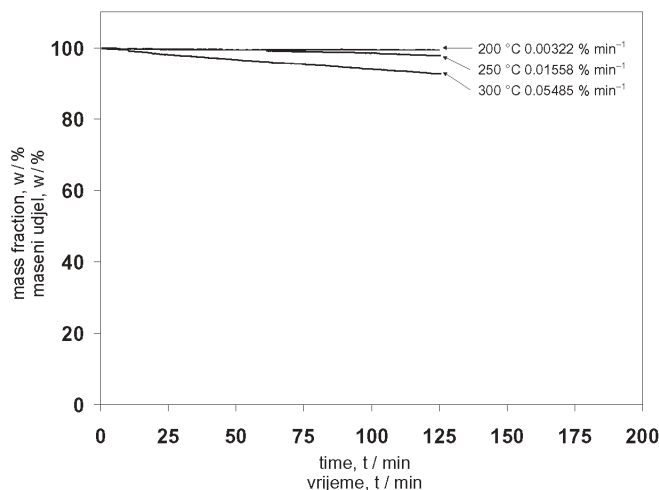


Fig. 1 – Thermal stability of  $\text{EMPBF}_4$  melt at  $200\text{ }^\circ\text{C}$ ,  $250\text{ }^\circ\text{C}$ , and  $300\text{ }^\circ\text{C}$

Slika 1 – Toplinska stabilnost za  $\text{EMPBF}_4$  taljevinu pri  $200\text{ }^\circ\text{C}$ ,  $250\text{ }^\circ\text{C}$  i  $300\text{ }^\circ\text{C}$

$\text{EMPBF}_4$  melt the conductivity of these same compositions also decreased when compared to the conductivity of the neat  $\text{EMPBF}_4$ .

This is unlike the solvents (non-ionic) commonly used in lithium-ion batteries, such as ethylene carbonate (EC) and propylene carbonate (PC), where the dissolution of lithium salts introduce ions into the solution increasing the conductivity. However, the inverse effect observed with the dissolution of lithium salts in ionic liquids is probably due to the highly coordinating nature of the small cation ( $\text{Li}^+$ ) which limits transport properties of ions.

The conductivity of 0.8 molal  $\text{LiBF}_4$  in  $\text{EMPBF}_4$  is higher than the conductivity of 0.4 molal  $\text{LiAsF}_6$  in  $\text{EMPBF}_4$  while conductivity of 0.8 molal  $\text{LiAsF}_6$  in  $\text{EMPBF}_4$  is much lower than those for both of these previously mentioned compositions. Furthermore, 0.8 molal  $\text{LiAsF}_6$  in  $\text{EMPBF}_4$  is liquid well below its melting point (super cooled liquid) thus its conductivity could be measured to  $-10\text{ }^\circ\text{C}$ . For example, the

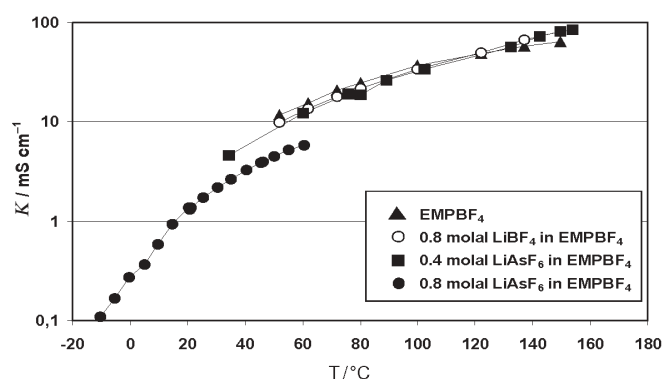


Fig. 2 – Conductivity vs. temperature for  $\text{EMPBF}_4$ , 0.4 molal  $\text{LiAsF}_6$  in  $\text{EMPBF}_4$ , 0.8 molal  $\text{LiAsF}_6$  in  $\text{EMPBF}_4$ , and 0.8 molal  $\text{LiBF}_4$  in  $\text{EMPBF}_4$

Slika 2 – Provodnost u zavisnosti o temperaturi za:  $\text{EMPBF}_4$ , 0,4 molalni  $\text{LiAsF}_6$  u  $\text{EMPBF}_4$ , 0,8 molalni  $\text{LiAsF}_6$  u  $\text{EMPBF}_4$ , i 0,8 molalni  $\text{LiBF}_4$  u  $\text{EMPBF}_4$



conductivity for EMPBF<sub>4</sub> at 52 °C is 11.63 mS cm<sup>-1</sup> and for 0.8 molal LiBF<sub>4</sub> in EMPBF<sub>4</sub> it is 9.96 mS cm<sup>-1</sup> at the same temperature. For 0.8 molal LiAsF<sub>6</sub> in EMPBF<sub>4</sub> at 50.1 °C the conductivity is 4.45 mS cm<sup>-1</sup> while at 25.4 °C it is 1.71 mS cm<sup>-1</sup>.

The conductivity of neat EMIBF<sub>4</sub> vs. temperature was also measured. Results obtained correspond to the data in literature.<sup>26</sup> For example, at 21.5 °C the conductivity was 13.4 mS cm<sup>-1</sup>. For 0.8 molal LiBF<sub>4</sub> in EMIBF<sub>4</sub> conductivity was 11.9 mS cm<sup>-1</sup> at 25 °C.

The conductivity of imidazolium based ionic liquid containing the identical type and concentration of lithium salts is much higher than for pyrazolium based ionic liquid.

However, all these melts show non Arrhenius behavior.<sup>27</sup>

### Electrochemical stability

Electrochemical window of electrolytes was determined by cyclic voltammetry (CV).

Table 1 summarizes results obtained for electrochemical window, oxidation and reduction potentials for EMIBF<sub>4</sub>, 0.7 molal LiBF<sub>4</sub> in EMIBF<sub>4</sub>, EMPBF<sub>4</sub>, and 0.7 molal LiBF<sub>4</sub> in EMPBF<sub>4</sub> at glassy carbon electrode (GCE) and platinum electrodes (PE) at 55 °C.

From Table 1 it appears that the electrochemical window for EMIBF<sub>4</sub>, 0.7 molal LiBF<sub>4</sub> in EMIBF<sub>4</sub>, depends on the electrode material. For example, for EMIBF<sub>4</sub> and 0.7 molal LiBF<sub>4</sub> in EMIBF<sub>4</sub> the window is slightly wider at PE (4.20 V, 4.49 V, respectively) than at GCE (4.16 V, 4.31 V, respectively). The oxidation potential is slightly more positive for

EMIBF<sub>4</sub> at PE 5.10 V vs. Li electrode than at GCE 5.06 V vs. Li electrode. Reduction potential is identical for both electrodes (0.91 V). For 0.7 molal LiBF<sub>4</sub> in EMIBF<sub>4</sub> there is almost no difference in oxidation potential at GCE and PE (5.13 V, 5.11 V, respectively). Reduction potential is less positive at PE than at GCE (0.60 V vs. 0.80 V).

It is clear that the electrochemical window for EMPBF<sub>4</sub>, 0.7 molal LiBF<sub>4</sub> in EMPBF<sub>4</sub> also depends on the electrode material. For example, for EMPBF<sub>4</sub> and 0.7 molal LiBF<sub>4</sub> in EMPBF<sub>4</sub> the window is slightly wider at PE (4.56 V, 4.60 V, respectively) than at GCE (4.38 V, 4.37 V, respectively). The oxidation potential is slightly more positive for EMPBF<sub>4</sub> at GCE 5.47 V vs. Li electrode than at PE 5.29 V vs. Li electrode. Reduction potential is less positive for EMPBF<sub>4</sub> at PE than at GCE (0.71 V vs. 1.08 V). For 0.7 molal LiBF<sub>4</sub> in EMPBF<sub>4</sub> the difference in oxidation and reduction potentials at PE and GCE is small. The electrochemical window calculated for the same electrolytes based on potentials measured vs. Ag quasi reference electrode gives similar values at GCE and PE. However, a shift in oxidation and reduction potentials at GCE compared to PE was observed. It is expected that the EMP<sup>+</sup> cation is adsorbed stronger at the PE than at GCE. Therefore, it can form a passivating layer on the surface of the electrode affecting the reduction potential.

### Lithium-ion cells using metal oxide anode

A number of oxides can be used as anode which intercalate/deintercalate lithium at voltages higher than the intercalation/deintercalation voltage for carbon (for example,

Table 1 – Electrochemical windows, oxidation and reduction potentials for EMIBF<sub>4</sub>, 0.7 molal LiBF<sub>4</sub> in EMIBF<sub>4</sub>, EMPBF<sub>4</sub>, and 0.7 molal LiBF<sub>4</sub> in EMPBF<sub>4</sub> at GCE, PE at 55 °C

Tablica 1 – Razlika potencijala redukcije i oksidacije ionske kapljavine, oksidacijski i redukcijski potencijali za EMIBF<sub>4</sub>, 0,7 molalni LiBF<sub>4</sub> u EMIBF<sub>4</sub>, EMPBF<sub>4</sub>, i 0,7 molalni LiBF<sub>4</sub> u EMPBF<sub>4</sub> na ugljenoj (GCE) i platinskoj elektrodi (PE) kod 55 °C

Melt molality Molalnost taljevine b/mol kg <sup>-1</sup>	Electrode Elektroda	Window* (V) Razlika potencijala red. i oksid.	E <sub>ox</sub> */V	E <sub>red</sub> */V	Window** (V) Razlika potencijala red. i oksid	E <sub>ox</sub> **/V	E <sub>red</sub> **/V
EMIBF <sub>4</sub>	GCE	4.16	5.06	0.9			
	PE	4.20	5.10	0.9			
0.7 molal LiBF <sub>4</sub> in EMIBF <sub>4</sub>	GCE	4.31	5.13	0.81			
	PE	4.49	5.11	0.60			
EMPBF <sub>4</sub>	GCE	4.38	5.47	1.08			
	PE	4.56	5.29	0.71			
0.7 molal LiBF <sub>4</sub> in EMPBF <sub>4</sub>	GCE	4.37	5.33	0.97	4.31	2.68	- 1.63
	PE	4.60	5.43	0.83	4.68	2.88	- 1.80

\* Potential vs. lithium reference electrode (lithium in 0.7 molal LiBF<sub>4</sub> in EMPBF<sub>4</sub> separated by glass frit from main compartment)  
Potencijal prema litijevoj referentnoj elektrodi (litij u 0.7 molalnom LiBF<sub>4</sub> u EMPBF<sub>4</sub> odjeljenoj sa staklenom membranom od glavnog odjeljka članka)

\*\* Potential vs. Ag quasi reference electrode (Ag wire immersed directly in the studied ionic liquid or Ag wire immersed in any of above melts separated by glass frit from the main compartment)  
Potencijal prema srebrnoj kvazireferentnoj elektrodi (srebrna žica umočena izravno u ispitivanu ionsku kapljevina ili srebrna žica umočena u jednu od gore navedenih ionskih kapljevina odjeljena sa staklenom membranom od glavnog odjeljka ćelije)

Sweep rate 50 mV s<sup>-1</sup>. Potential measured at  $j = 1 \text{ mA cm}^{-2}$ .

Brzina promjene potencijala 50 mV s<sup>-1</sup>. Potencijal mjeren kod  $j = 1 \text{ mA cm}^{-2}$ .

$\text{Fe}_2\text{O}_3$ ,  $\text{WO}_2$ ,  $\text{MoO}_2$ ,  $\text{Li}_4\text{Ti}_5\text{O}_{12}$ , and other). Intercalation voltage for  $\text{Fe}_2\text{O}_3$  is from 0.1 V to 0.8 V vs. Li, for  $\text{WO}_2$  from 0.3 V to 1.4 V vs. Li, for  $\text{MoO}_2$  from 0.8 V to 1.4 V vs. Li, for  $\text{Li}_4\text{Ti}_5\text{O}_{12}$   $\sim$ 1.56 V vs. Li.<sup>12</sup> When lithium-ion cell is built employing a high voltage intercalation cathode and lower voltage intercalation anode the cell voltage is lower than for the cells containing carbon anodes.

Test cells were built employing  $\text{LiMn}_2\text{O}_4$  as cathode and  $\text{MoO}_2$  or  $\text{Li}_4\text{Ti}_5\text{O}_{12}$  as an anode.  $\text{MoO}_2/\text{LiMn}_2\text{O}_4$  cell containing 0.8 molal  $\text{LiBF}_4$  in  $\text{EMIBF}_4$  was constructed and submitted to charge/discharge testing in a dry box at room temperature (RT) and 50 °C. Cut off voltage was set at 3.0 V/1.0 V. The OCV of the charged cell was  $\sim$ 2.5 V (Fig. 3).

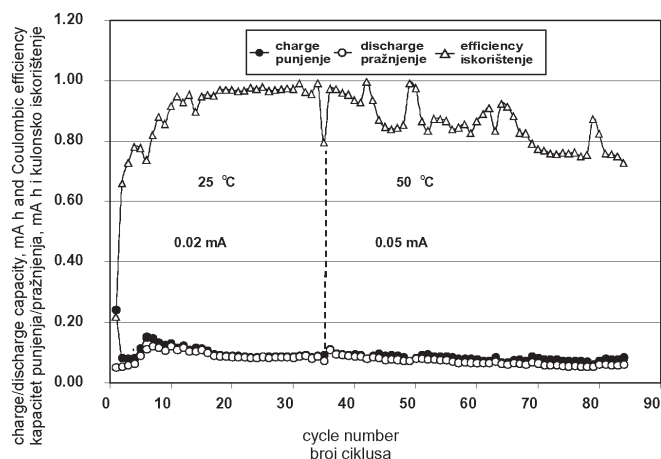


Fig. 3 – Charge/discharge capacity and coulombic efficiency ( $\text{mA h}_{\text{dc}}/\text{mA h}_{\text{ch}}$ ) vs. cycle number for the cell  $\text{MoO}_2/\text{LiMn}_2\text{O}_4$  containing 0.8 molal  $\text{LiBF}_4$  in  $\text{EMIBF}_4$  at 25 °C and 50 °C

Slika 3 – Kapacitet punjenja/praznjenja i kulonsko iskorištenje ( $\text{mA h}_{\text{pr}}/\text{mA h}_{\text{pu}}$ ) u ovisnosti o broju ciklusa kod konstantne struje za članak  $\text{MoO}_2/\text{LiMn}_2\text{O}_4$  koja rabi 0,8 molalni  $\text{LiBF}_4$  u  $\text{EMIBF}_4$  kao elektrolit pri 25 °C i 50 °C

The charging capacity was  $\sim$ 0.12 mA h at RT, which corresponds to  $\sim$ 27 % of theoretical capacity (theoretical capacity of  $\text{MoO}_2$  electrode 99 mA h/g<sup>-1</sup>). This is because intercalation/deintercalation of lithium in  $\text{MoO}_2$  is 50 % efficient. Coulombic efficiency ( $\text{mA h}_{\text{dc}}/\text{mA h}_{\text{ch}}$ ) is lower at the beginning; it started at  $\sim$ 60 %, and then increased to  $\sim$ 97 to 98 %. At 50 °C charging capacity decreased with cycling. Coulombic efficiency also decreased from 94 % to 76 %.

Obtained results indicate that at RT the cell capacity is stable and reversible, however, increase in temperature affected both the charging capacity and coulombic efficiency.

Pyrazolium melt based cells were also assembled and tested.

Fig. 4 gives a typical charge/discharge curve for the cell  $\text{MoO}_2/\text{LiMn}_2\text{O}_4$  containing 0.8 molal  $\text{LiAsF}_6$  in  $\text{EMPF}_4$  at room temperature.

Fig. 5 shows charging and discharging capacity and coulombic efficiency vs. cycle number for that type of cell at RT, 65 °C and 100 °C.

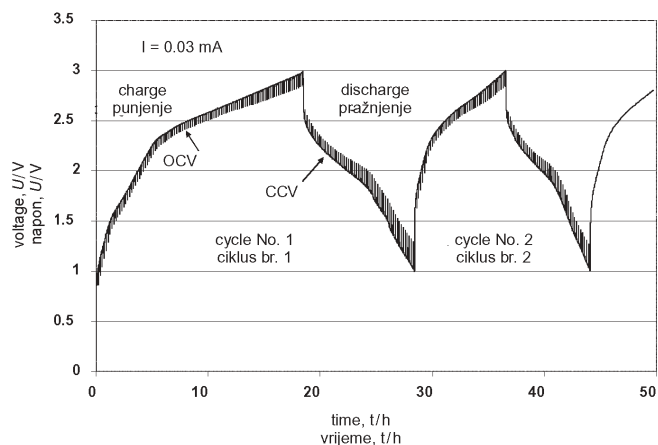


Fig. 4 – Constant current charge/discharge curves for the cell  $\text{MoO}_2/\text{LiMn}_2\text{O}_4$  containing 0.8 molal  $\text{LiAsF}_6$  in  $\text{EMPF}_4$  at room temperature.  $I = 0.03$  mA. OCV-open circuit voltage. CCV-closed circuit voltage.

Slika 4 – Dijagram punjenja/praznjenja pri konstantnoj struji za članak  $\text{MoO}_2/\text{LiMn}_2\text{O}_4$  koja sadrži 0,8 molalni  $\text{LiAsF}_6$  u  $\text{EMPF}_4$  kao elektrolit na sobnoj temperaturi.  $I = 0,03$  mA OCV-napon otvorenog kruga. CCV-napon zatvorenog kruga.

From Fig. 5 it is observed that the charging and discharging capacity is quite stable 0.12 mA h ( $\sim$ 36 % of theoretical capacity). There is no loss in capacity during more than 90 cycles. Coulombic efficiency is also very stable ( $\approx$ 96 %) with some fluctuations due to the change in ambient temperature.

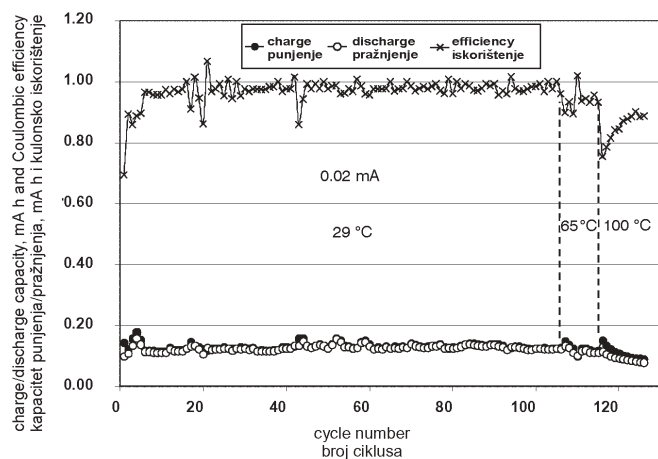


Fig. 5 – Charge/discharge capacity and coulombic efficiency vs. cycle number for the cell  $\text{MoO}_2/\text{LiMn}_2\text{O}_4$  containing 0.8 molal  $\text{LiAsF}_6$  in  $\text{EMPF}_4$  at 29 °C, 65 °C, and 100 °C

Slika 5 – Kapacitet punjenja/praznjenja i kulonsko iskorištenje u ovisnosti o broju ciklusa pri konstantnoj struji za članak  $\text{MoO}_2/\text{LiMn}_2\text{O}_4$  koja sadrži 0,8 molalni  $\text{LiAsF}_6$  u  $\text{EMPF}_4$  kao elektrolit pri 29 °C, 65 °C, i 100 °C

At 65 °C the charging capacity slightly decreased and the coulombic efficiency was  $\sim$ 93 %, however, at 100 °C capacity decreased with cycling while coulombic efficiency first dropped to  $\sim$ 75 % then increased with cycling to  $\sim$ 90 %.

$\text{Li}_4\text{Ti}_5\text{O}_{12}/\text{LiMn}_2\text{O}_4$  cells containing 0.8 molal  $\text{LiBF}_4$  in  $\text{EMIBF}_4$  were built.

Most of the cells were anode limited.

Fig. 6 shows a typical charge/discharge curve for the cell  $\text{Li}_4\text{Ti}_5\text{O}_{12}/\text{LiMn}_2\text{O}_4$  using 0.8 molal  $\text{LiBF}_4$  in  $\text{EMIBF}_4$  as electrolyte at RT.

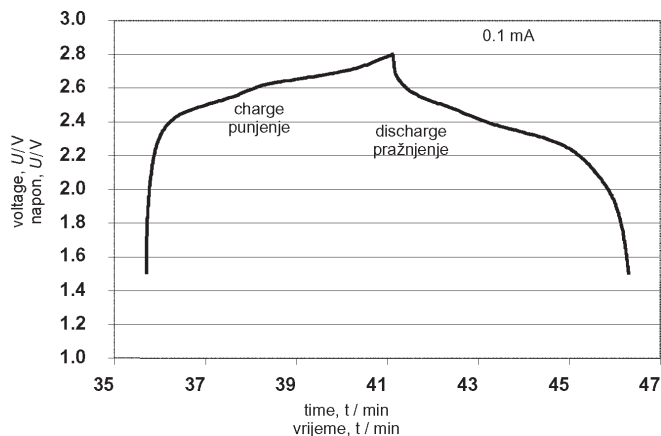


Fig. 6 – Charge/discharge curves for the cell  $\text{Li}_4\text{Ti}_5\text{O}_{12}/\text{LiMn}_2\text{O}_4$  containing 0.8 molal  $\text{LiBF}_4$  in  $\text{EMIBF}_4$  at room temperature

Slika 6 – Krivulje punjenja/pražnjenja pri konstantnoj struji za članak  $\text{Li}_4\text{Ti}_5\text{O}_{12}/\text{LiMn}_2\text{O}_4$  koji sadrži 0,8 molalni  $\text{LiBF}_4$  u  $\text{EMIBF}_4$  kao elektrolit pri sobnoj temperaturi,  $I = 0,1 \text{ mA}$

Fig. 7 gives charge/discharge efficiency and coulombic efficiency depending on cycle number for the cell  $\text{Li}_4\text{Ti}_5\text{O}_{12}/\text{LiMn}_2\text{O}_4$  using 0.8 molal  $\text{LiBF}_4$  in  $\text{EMIBF}_4$  at RT and  $80^\circ\text{C}$ .

From Fig. 6 it appears that the cell operates at high coulombic efficiency and that the charge/discharge curve is quite flat with an open circuit voltage of the charged cell at  $\sim 2.5 \text{ V}$ .

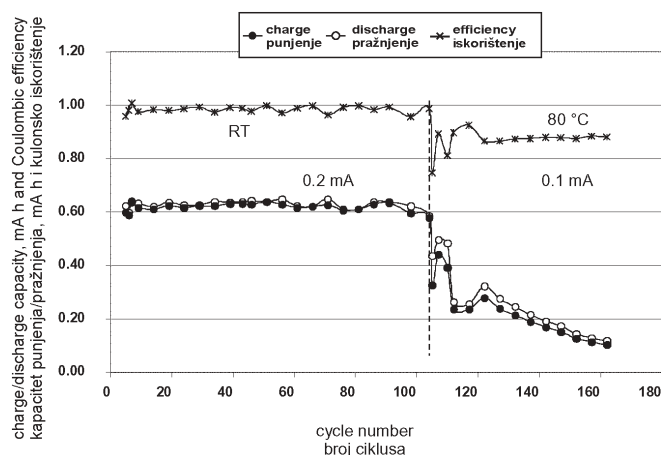


Fig. 7 – Charge/discharge capacity and coulombic efficiency vs. cycle number for the cell  $\text{Li}_4\text{Ti}_5\text{O}_{12}/\text{LiMn}_2\text{O}_4$  containing 0.8 molal  $\text{LiBF}_4$  in  $\text{EMIBF}_4$  at room temperature and  $80^\circ\text{C}$

Slika 7 – Kapacitet punjenja/pražnjenja i kulonsko iskorištenje u ovisnosti o broju ciklusa pri konstantnoj struji za članak  $\text{Li}_4\text{Ti}_5\text{O}_{12}/\text{LiMn}_2\text{O}_4$  koji sadrži 0,8 molalni  $\text{LiBF}_4$  u  $\text{EMIBF}_4$  kao elektrolit pri sobnoj temperaturi i  $80^\circ\text{C}$

From Fig. 7 it is observed that at room temperature the cell operates at 69 % of the theoretical cell capacity (theoretical capacity of  $\text{Li}_4\text{Ti}_5\text{O}_{12}$  electrode  $175 \text{ mA h g}^{-1}$ ) corresponding to  $121 \text{ mA h g}^{-1}$  and with coulombic efficiency 96 %. However, at  $80^\circ\text{C}$  capacity decreased very fast. Coulombic efficiency also decreased to about 88 %. Fig. 8 gives plot for of charge/discharge capacity and coulombic efficiency vs. cycle number for another  $\text{Li}_4\text{Ti}_5\text{O}_{12}/\text{LiMn}_2\text{O}_4$  cell containing 0.8 molal  $\text{LiBF}_4$  in  $\text{EMIBF}_4$  at  $60^\circ\text{C}$  and  $85^\circ\text{C}$ .

From Fig. 8 it is observed that at  $60^\circ\text{C}$  charge/discharge capacity is very slowly decreasing with cycling and coulombic efficiency is close to 90 %. However, at  $85^\circ\text{C}$  charge/discharge capacity decreased very fast and coulombic efficiency dropped to a very low value. Results from Fig. 7 and 8 indicate a very large cell self-discharge at  $80^\circ\text{C}$  and above.

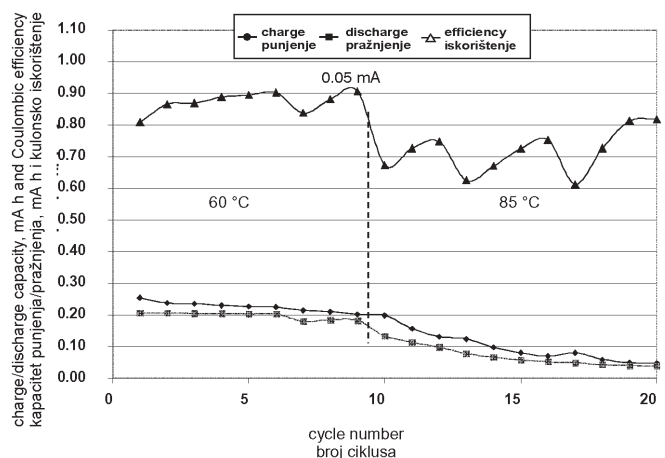


Fig. 8 – Charge/discharge capacity and coulombic efficiency vs. cycle number for the cell  $\text{Li}_4\text{Ti}_5\text{O}_{12}/\text{LiMn}_2\text{O}_4$  containing 0.8 molal  $\text{LiBF}_4$  in  $\text{EMIBF}_4$  at  $60^\circ\text{C}$  and  $85^\circ\text{C}$

Slika 8 – Kapacitet punjenja/pražnjenja i kulonsko iskorištenje u ovisnosti o broju članaka pri konstantnoj struji za članak  $\text{Li}_4\text{Ti}_5\text{O}_{12}/\text{LiMn}_2\text{O}_4$  koji sadrži 0,8 molalni  $\text{LiBF}_4$  u  $\text{EMIBF}_4$  kao elektrolit pri  $60^\circ\text{C}$  i  $85^\circ\text{C}$

Fig. 9 shows charge/discharge capacity and coulombic efficiency vs. cycle number for the cell  $\text{Li}_4\text{Ti}_5\text{O}_{12}/\text{LiMn}_2\text{O}_4$  containing 0.8 molal  $\text{LiBF}_4$  in  $\text{EMPF}_4$  at  $85^\circ\text{C}$  to  $90^\circ\text{C}$ .

From Fig. 9 it is clear that charge/discharge capacity for this cell does not change with cycling at  $85^\circ\text{C}$  to  $90^\circ\text{C}$  and coulombic efficiency is close to 90 %.

Results obtained indicate that  $\text{Li}_4\text{Ti}_5\text{O}_{12}/\text{LiMn}_2\text{O}_4$  cells containing  $\text{EMPF}_4$  electrolyte are not affected by temperature up to  $80^\circ\text{C}$ , however, the same type of cells using  $\text{EMIBF}_4$  electrolyte are less stable and could operate up to  $60^\circ\text{C}$  only.

A decrease in capacity and coulombic efficiency with increase in operating temperature observed for the cells employing  $\text{MoO}_2$  and  $\text{Li}_4\text{Ti}_5\text{O}_{12}$  anodes is probably due to the changes introduced in the cell by the dissolution of  $\text{LiMn}_2\text{O}_4$ . It was shown that in lithium-ion cells containing conventional organic solvents, the  $\text{LiMn}_2\text{O}_4$  cathode dissolves in the electrolyte affecting the cell performance, especially at higher temperature ( $55^\circ\text{C}$ ) when capacity starts

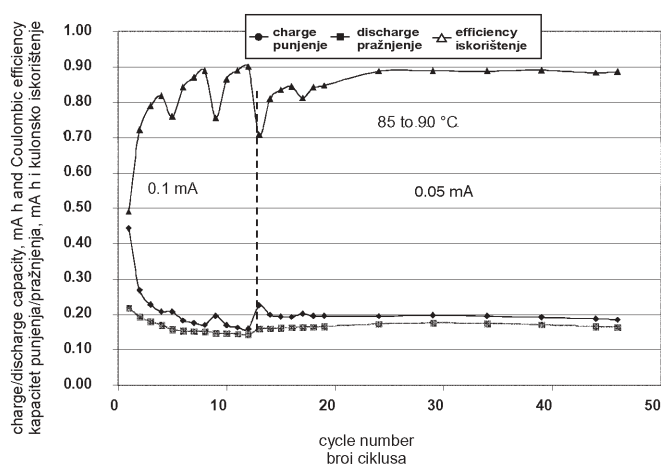


Fig. 9 – Charge/discharge capacity and coulombic efficiency vs. cycle number curves for the cell  $\text{Li}_4\text{Ti}_5\text{O}_{12}/\text{LiMn}_2\text{O}_4$  containing 0.8 molal  $\text{LiBF}_4$  in  $\text{EMPBF}_4$  at 85 °C to 90 °C

Slika 9 – Kapacitet punjenja/pražnjenja i kulonsko iskorištenje u ovisnosti o broju ciklusa pri konstantnoj struji za članak  $\text{Li}_4\text{Ti}_5\text{O}_{12}/\text{LiMn}_2\text{O}_4$  koji sadrži 0,8 molalni  $\text{LiBF}_4$  u  $\text{EMPBF}_4$  kao elektrolit pri 85 °C do 90 °C

fading quite fast with cycling.<sup>28,29</sup> Intercalation voltage for anodes in the above studied cells was much greater than 1.0 V vs. Li (for example, 1.5 V vs. Li for  $\text{Li}_4\text{Ti}_5\text{O}_{12}$ ) while the reduction potential of ionic liquids was  $\sim 1$  V vs. Li (Table 1). Further, thermal stability of ionic liquids should not be affected in the temperature range studied (Fig. 1). It is not clear why the increase in temperature is affecting the cells employing imidazolium tetrafluoroborate more than the ones employing pyrazolium tetrafluoroborate.

Fig. 10 shows discharge capacity as a function of discharging current rate for two cells  $\text{Li}_4\text{Ti}_5\text{O}_{12}/\text{LiMn}_2\text{O}_4$  using 0.8 molal  $\text{LiBF}_4$  in  $\text{EMIBF}_4$ . These two cells differ in composition of the  $\text{Li}_4\text{Ti}_5\text{O}_{12}$  electrode. Cell 1 has anode containing some percentage of  $\text{Li}_4\text{Ti}_5\text{O}_{12}$  nanoparticles while cell 2 has anode prepared using exclusively microsize particles. From the figure it is clear that for the cell 1, the decrease in capac-

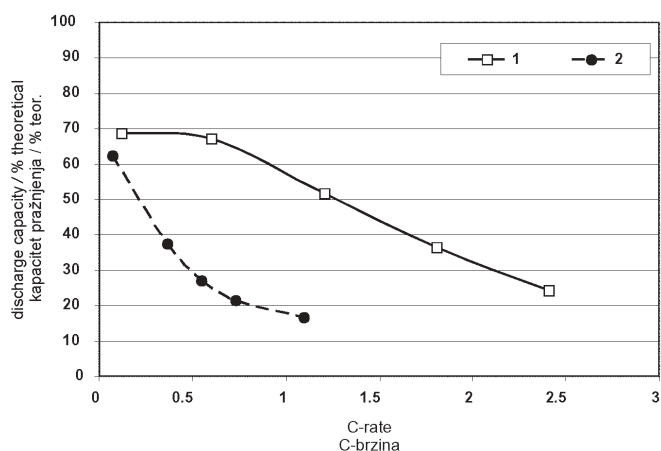


Fig. 10 – Discharge capacity vs. discharge rate for the  $\text{Li}_4\text{Ti}_5\text{O}_{12}/\text{LiMn}_2\text{O}_4$  cells No. 1 and No. 2 at room temperature

Slika 10 – Kapacitet pražnjenja u ovisnosti o brzini pražnjenja za članke  $\text{Li}_4\text{Ti}_5\text{O}_{12}/\text{LiMn}_2\text{O}_4$  br. 1 i br. 2 pri sobnoj temperaturi

ity depending on increase in discharging rate is smaller than for the cell 2. For the cell 1 capacity is unchanged until 0.6 C – rate; then starts to decrease slowly with increase in discharge rate. For example, at 0.6 C the capacity is 122  $\text{mA h g}^{-1}$  while at 1.2C it is 91  $\text{mA h g}^{-1}$ . For the cell 2 capacity decreases significantly with increase in discharging rate. Thus at 0.07 C the discharge capacity is 112  $\text{mA h g}^{-1}$  while at 0.36 C it is 38  $\text{mA h g}^{-1}$ .

These results compare well with the data given in literature for a similar cell. Nakagawa et al. cycled the cells  $\text{Li}_4\text{Ti}_5\text{O}_{12}/\text{LiCoO}_2$  using 1 mol  $\text{L}^{-1}$   $\text{LiBF}_4$  in  $\text{EMIBF}_4$  as electrolyte.<sup>30</sup> Their results showed the discharge capacity of 113  $\text{mA h g}^{-1}$  at 0.4 C; however, at higher rates the capacity decreased significantly (at  $\sim$ C-rate 40  $\text{mA h g}^{-1}$ ). These cells showed good performance up to 50 cycles.

The studied lithium-ion cells demonstrated a number of advantages compared to the standard lithium-ion cells. First, there will be no dendrite formation under any circumstances. Conventional lithium-ion cells form lithium metal and grow dendrites under some conditions (for example, at low temperature). However, in this cell a protective layer does not form on the surface of the anode and there is no solvent reduction during cell operation thus the cell will show long cycle life and it will show minimal or no loss in capacity with cycling. In addition, the cells containing  $\text{EMPBF}_4 + 0.8$  molal  $\text{LiBF}_4$  can be operated safely to 85 °C with minimal loss in capacity. Furthermore, this is a completely safe cell. It will not catch fire or develop pressure even when heated. The electrolyte employed is thermally stable to  $> 300$  °C.

The disadvantages of these cells are lower cell voltage (for  $\text{MoO}_2/0.8$  molal  $\text{LiAsF}_6$  in  $\text{EMPBF}_4/\text{LiMn}_2\text{O}_4$  OCV  $\sim 2.5$  V) compared to conventional lithium-ion cells (3.8 V) and lower capacity, especially, at lower temperature. Capacity can be increased by adequate engineering of electrodes (particle size, porosity, mixing, thickness, etc.) which will allow the full usage of material for the electrochemical reaction. Presently used electrodes were not optimized for this application. They are more suitable for conventional solvents (low viscosity, low salt concentration). In addition, by selecting the anodes with low intercalation voltage (e.g.  $\text{SnO}_2$ ) which will also intercalate more  $\text{Li}^+$  ions, the cells with higher OCV, bigger capacity and energy can also be achieved. Low temperature operation can also be improved by optimizing the electrodes as well as by using mixtures of molten salts ( $\text{EMIBF}_4$  and  $\text{EMPBF}_4$ ) which possess a very low glass transition ( $-80$  °C) and good conductivity at  $-40$  °C.

## Conclusions

The results described in this paper demonstrated that ionic liquids,  $\text{EMIBF}_4$  and  $\text{EMPBF}_4$ , can effectively be used as electrolytes in the lithium ion cells constructed of  $\text{LiMn}_2\text{O}_4$  cathode and metal oxide anodes ( $\text{MoO}_2$ ,  $\text{Li}_4\text{Ti}_5\text{O}_{12}$ ).

Studied ionic liquids ( $\text{EMIBF}_4$  and  $\text{EMPBF}_4$ ) showed low melting point, high thermal stability, good electrochemical stability and high conductivity as expected.

The  $\text{MoO}_2/\text{LiMn}_2\text{O}_4$  cells which contained  $\text{EMPBF}_4$  seem to achieve higher capacity than the cells which employed



EMIBF<sub>4</sub> and they are less affected by an increase in temperature. Thus the cells with 0.8 molal LiBF<sub>4</sub> in EMIBF<sub>4</sub> electrolyte showed high coulombic efficiency (96 %) and stable capacity at room temperature. At 50 °C charging capacity decreased and changed slightly with cycling. Coulombic efficiency also decreased. However, similar cells with 0.8 molal LiAsF<sub>6</sub> in EMPBF<sub>4</sub> delivered higher capacity which remained unchanged for ~90 cycles at 65 °C while at 100 °C the delivered capacity decreased. Coulombic efficiency was affected in similar manner being 96 % at room temperature, 93 % at 65 °C and 90 % at 100 °C.

Li<sub>4</sub>Ti<sub>5</sub>O<sub>12</sub>/LiMn<sub>2</sub>O<sub>4</sub> cells containing EMIBF<sub>4</sub> achieved 69 % of theoretical capacity for about 100 cycles and coulombic efficiency >96 % at room temperature. However, temperature affected the cell operation. The cells employing EMIBF<sub>4</sub> are affected more than the cells using EMPBF<sub>4</sub>. It was observed that the former show stable capacity only up to 60 °C while the latter can operate with no apparent change in capacity up to 85 °C.

The cells employing the studied molten salts as electrolytes show several important advantages compared to the lithium-ion cells (for example, Li<sub>x</sub>C/LiCoO<sub>2</sub>) using conventional organic solvents.

First, these cells are completely safe. They will neither catch fire nor burst under pressure because the electrolyte is not flammable and does not develop pressure even at high temperature. Further, the cells can operate at high temperature not affecting significantly the cell performance except for the loss in capacity due to the self-discharge. Due to these properties the cell design can be simpler. Therefore Li-ion cells from very low capacity and size to very large capacity and size can be constructed.

Deficiency of these cells, at the present time, is lower capacity, especially, at low temperature and lower cell voltage compared to conventional lithium-ion cells. However, both can be improved.

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## SAŽETAK

**Ionske kapljevine kao elektrolit u litij-ion člancima: imidazolij- i pirazolij-tetrafluoroborat u  $\text{LiMn}_2\text{O}_4$ /metalni oksid člancima***J. Čaja, T. Don, J. Dunstan, H. A. Dyar\*, H. Krall\* i V. Katović\**

Opisana je primjena ionskih kapljevine, 1-etil-3-metilimidazolijevog tetrafluoroborata ( $\text{EMIBF}_4$ ) i 1-etil-2-metilpirazolijevog tetrafluoroborata ( $\text{EMPBF}_4$ ) kao elektrolita u litij-ionskim člancima. U litij-ionskim člancima upotrijebljen je  $\text{LiMn}_2\text{O}_4$  kao katoda te metalni oksid ( $\text{MoO}_2$ ,  $\text{Li}_4\text{Ti}_5\text{O}_{12}$ ) kao anoda. Fizikalno-kemijska svojstva kao što su npr. talište, toplinska stabilnost, provodnost i elektrokemijska stabilnost također su određena. Talište za  $\text{EMPBF}_4$  je 47,5 °C do 49 °C i 21 °C do 26 °C za 0,8 molalnu  $\text{LiAsF}_6$  u  $\text{EMPBF}_4$ .  $\text{EMPBF}_4$  je termalno stabilan do 300 °C. Određena je provodnost čistih ionskih kapljevine kao i ionskih kapljevine u kojim su otopljene litijeve soli ( $\text{LiBF}_4$ ,  $\text{LiAsF}_6$ ). Za ove posljednje vodljivost je manja nego za čiste ionske kapljevine. Nadalje, vodljivost se smanjuje s povećanjem koncentracije litijeve soli. Razlika potencijala redukcije i oksidacije ionskih kapljevine bila je >4,3 V za sve mjerene sastave ionskih kapljevine osim za čistu  $\text{EMIBF}_4$ , koja je bila nešto niža (4,2 V). Potencijal za redukciju i oksidaciju mjereno prema litijevoj elektrodi bio je manji za ionske kapljevine koje su sadržavale  $\text{EMIBF}_4$  nego za one koje su sadržavale  $\text{EMPBF}_4$ . Članci su punjeni/praznjeni pri nekoliko različitih temperatura. Opaženo je da povišenje temperature manje utječe na članke u kojima se upotrebljava  $\text{EMPBF}_4$ . Oba tipa članaka,  $\text{MoO}_2/\text{LiMn}_2\text{O}_4$  i  $\text{Li}_4\text{Ti}_5\text{O}_{12}/\text{LiMn}_2\text{O}_4$  pokazala su stabilan kapacitet pri sobnoj temperaturi tijekom cikličkog punjenja/praznjenja i zadržale su stabilnost do 60 °C za članke koji sadrže  $\text{EMIBF}_4$  ionsku kapljevinu. U člancima koji su imali  $\text{EMPBF}_4$  stabilan kapacitet dobio je do 80 °C. Kulonsko iskorištenje pokazalo je slično ponašanje. Dobiveno je iskorištenje od 96 % za oba tipa članaka kod sobne temperature. Kod 80 °C smanjilo se na 90 % za članke koji su upotrijebili  $\text{EMPBF}_4$  ionsku kapljevinu, dok je u člancima u kojima je upotrijebljen  $\text{EMIBF}_4$  dobiveno kulonsko iskorištenje od 90 % kod 60 °C ili ispod te temperature.

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