



On the application of ionic liquids for rechargeable Li batteries: High voltage systems

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ABSTRACT

We examined the possible use of the following ionic liquids all having the same anion, bis(trifluoromethylsulfonyl)imide (TFSI) and the following cations: 1-hexyl-3-methyl imidazolium (HMITFSI), 1-(2-methoxyethyl)-3-methyl imidazolium (MEMITFSI), *N*-ethyl-*NN*-dimethyl-2-methoxyethylammonium (EDMETFSI), 1-methyl-1-butylpyrrolidinium (BMPTFSI), and 1-methyl-1-propylpiperidinium (MPPpTFSI) solutions with LiTFSI (the source of Li ions), as electrolyte systems for 5 V, rechargeable battery systems with Li metal anodes and LiMn_{1.5}Ni_{0.5}O₄ spinel cathodes. Standard solution based on alkyl carbonates and LiPF₆ was examined in this respect for comparison. The ionic liquids (ILs) based on derivatives of piperidinium and pyrrolidinium demonstrate a very wide electrochemical window (up to 5.5 V) and they can be compatible with lithium metal anodes. At low potentials in the presence of Li ions in solutions (or on Li metal surfaces), TFSI anions are reduced to insoluble Li compounds which passivate Li, noble metal and graphite electrodes in the Li salt/IL solutions. The mechanism, kinetics and effectiveness of electrodes' passivation in these systems depend on the nature of both IL and electrode used. It was possible to demonstrate reversible behavior of Li/LiMn_{1.5}Ni_{0.5}O₄ cells (4.8 V) with solutions based on BMPTFSI and MPPpTFSI. Possible parasitic anodic reactions upon charging at the high potentials are much lower in the ILs than in standard solutions.

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1. Introduction

Rechargeable Li ion batteries are pushed recently for more and more demanding applications. After more than a decade since their commercialization, being used mostly for powering portable electronic, electro-optic and communication devices (e.g. cellular phones) Li ion batteries are considered as main electrical storage devices for electric vehicles due to their high energy density. Many hundreds of R&D groups throughout the world work on improving electrode materials and electrolyte systems for this battery technology, in order to maximize both energy and power density of Li batteries. Highly challenging is development of high voltage cells. Over the years several high voltage cathode materials were developed, most of which are based on Li[MnM]₂O₄ spinel compounds (M = Cu, Cr, Ni which are transition metal possessing high red-ox potentials), which red-ox potentials may approach 5 V vs. Li/Li⁺ [1–3]. In recent years we see extensive work on high

capacity, layered Li[MnNiCo]O₂ compounds which relevant red-ox potential can reach 4.6 V vs. Li/Li⁺ [4–6]. We already showed that standard electrolyte solutions for Li ion batteries, based on alkyl carbonate solvents and LiPF₆ can be oxidized on noble metal electrodes below 4 V vs. Li/Li⁺. However, it is accepted that practically, the anodic limit of these standard electrolyte solutions is around 4.5 V vs. Li/Li⁺. We demonstrated that LiMn_{1.5}Ni_{0.5}O₄ electrodes which red-ox potential is around 4.8 V (vs. Li/Li⁺) can work well even at elevated temperatures in some compositions of standard solutions (e.g. EC-EMC 1:2/1.5 M LiPF₆) [7]. In any event, the use of standard electrolyte solutions, specially with high capacity/high potential cathodes may be very problematic in term of safety. We already showed that LiPF₆ and alkyl carbonate solvents are in fact red-ox couples that undergo exothermal, pressure developing dangerous reactions at elevated temperatures in the absence of any other battery components [8]. Other groups demonstrated dangerous possibilities of thermal run-away upon high temperature reactions between delithiated cathode materials and standard electrolyte solutions, in which oxygen evolution is involved [9,10]. Room temperature ionic liquids (ILs) as a new kind of electrolyte materials may improve considerably the electrochemical and thermal stability of Li battery systems possessing high capacity/high

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voltage cathode materials. Many of them demonstrate wide electrochemical windows (>5 V), most of them are much less flammable and volatile than all standard polar-aprotic electrolyte solutions [11]. Consequently, many IL families have been widely tested as solvents in lithium batteries [12–20]. Thus it is interesting to check the possibility of the application of ILs for high potential Li ion batteries and in particular their behavior with high voltage cathode materials. We already showed the compatibility of solutions based on imidazolium tetrafluoroborate ionic liquids for systems comprising $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ 5 V cathodes [21]. However, it was impossible to operate 5 V lithium batteries with this electrolyte system due to the cathodic instability of the electrolyte used so far namely, 1 M LiBF_4 in ethyl-methylimidazolium tetrafluoroborate (EMIBF₄). In the present work we demonstrate a stable reversible cycling of 5 V $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4/\text{Li}$ batteries with the use of ILs with TFSI anions as the electrolyte solvents in combination with the Li salt $\text{Li}(\text{SO}_2\text{CF}_3)_2$ (LiTFSI) which are known to work well with Li electrodes and enable their reversible cycling [17].

2. Experimental

The 1-hexyl-3-methyl imidazolium bis(trifluoromethylsulfonyl)imide (HMITFSI), 1-(2-methoxyethyl)-3-methyl imidazolium bis(trifluoromethylsulfonyl) imide (MEMITFSI), *N*-ethyl-*NN*-dimethyl-2-methoxyethylammonium bis(trifluoromethylsulfonyl)imide (EDMETFSI), 1-methyl-1-butylpyrrolidinium bis(trifluoromethylsulfonyl)imide (BMPTFSI) (Merck KGaA, Germany), and 1-methyl-1-propylpiperidinium bis(trifluoromethylsulfonyl)imide (MPPpTFSI) (Toyo Gosei Co. Ltd., Japan) were used for the IL electrolyte solution preparation (Fig. 1).

The water content in the ILs was determined by Karl Fischer titration. MPPpTFSI ($>99\%$) contained as less than 7 ppm of water, HMITFSI—11 ppm. The remaining three ILs were dried in vacuum at 80°C for 10 h, and water content after drying comprised 12 ppm for MEMITFSI, 20 ppm for EDMETFSI and 17 ppm for BMPTFSI. Lithium

bis(trifluoromethylsulfonyl)imide (LiTFSI) (99.95%) was obtained from Aldrich. 0.5 M LiTFSI/IL solutions were used for the electrochemical measurements.

The electrochemical windows of the TFSI-based ionic liquids were determined with two working electrodes: glassy carbon and Pt. A glassy carbon working electrode (surface area 0.2 cm^2) was pressed into a Teflon cylinder and freshly polished before each anodic and cathodic sweep. The identical glassy carbon was used as a counter electrode. A reference electrode consisting of lithium film was pressed onto the stainless net, immersed in a glass tube with a porous Vycor tip (Bioanalytical Systems Inc.), and filled with a 1 M solution of LiTFSI salt in propylene carbonate. We used a T-type cell for the measurement of an electrochemical window on a glassy carbon working electrode. A Pt working electrode comprised a wire sealed into a glass tube (working surface area 0.168 cm^2) and was cleaned before each cathodic and anodic sweep. We used the Autolab System from Eco Chemie (Netherlands) for our voltammetric studies. The electrochemical stability was determined both for the neat ionic liquids and for their 0.5 M LiTFSI solutions.

$\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ powder was obtained from LG Chem. Composite electrodes comprised 90 wt% of $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$, 5 wt% of carbon black (SuperP, Superior graphite, USA) and 5 wt% of PVdF (Aldrich). The cathode sheets were fabricated by spreading a slurry (suspension of $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ powder and carbon black in a PVdF/*N*-methylpyrrolidone solution) on an aluminum foil current collectors with a doctor blade device. Typically, the electrodes contained 2 ± 0.5 mg of active mass. Two electrode cells comprising $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ composite electrodes, glassy paper separators (Whatman), ILs-based electrolyte and Li foil negative electrodes were assembled in a glove-box filled with pure argon and sealed in 2032 coin-cells (NRC, Canada). Galvanostatic cycling of $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4/\text{Li}$ cells was carried out using a Maccor Inc. model 2000 multi-channel battery tester.

Cyclic voltammetry of the composite spinel $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ electrodes was performed in T-cells. Li foils were used as reference and counter electrodes. The working and the counter electrodes in the cells were separated with glassy paper and were pressed to each

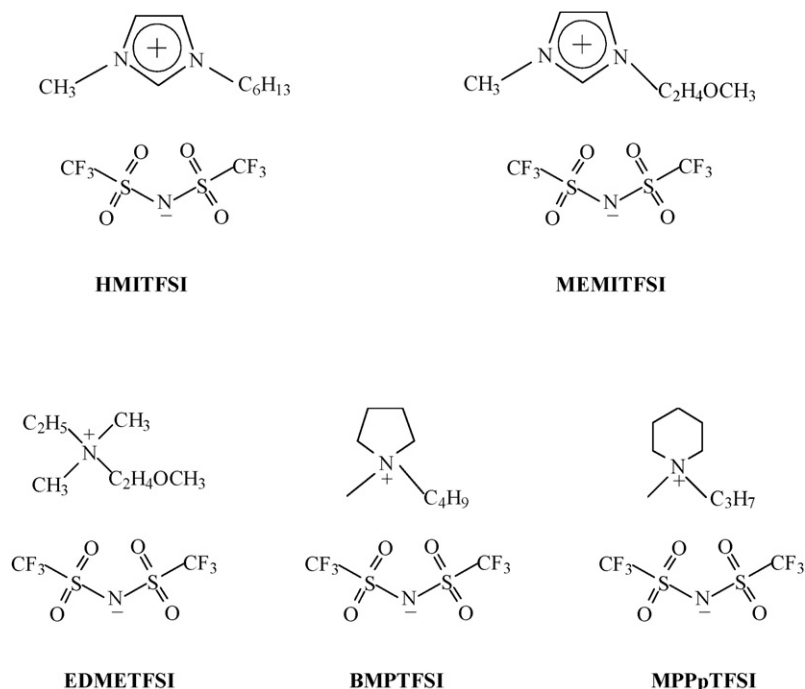


Fig. 1. Structure formulae of the ILs used in this work.

other with stainless steel current collectors inserted into the Teflon cylinders. The R.E. was dipped into the electrolyte from the upper open cylinder of the T cell.

3. Results and discussion

The results of the electrochemical window measurements of neat ILs and IL-based electrolyte solutions, containing 0.5 M LiTFSI are shown in Fig. 2. The measurements were performed on glassy carbon and Pt electrodes. All the neat ILs have approximately an equal anodic stability, measured on a glassy carbon and Pt electrodes. The anodic stability of the five TFSI-based ILs is somewhat

higher on a Pt electrode than that measured with glassy carbon working electrodes and remains nearly unchanged after the addition of the Li salt. This suggests that the anodic stability of these molten salts is determined by the oxidation of TFSI-anions.

It is remarkable, that quite different results were obtained for these two working electrodes regarding the cathodic stability limits of the IL electrolytes. The addition of a lithium salt leaves the cathodic limit of the ILs on a glassy carbon electrode unaffected with only slight extension of the cathodic stability region for MPPpTFSI and BMPTFSI. On Pt electrode a drastic broadening of about 1 V of the cathodic stability limits is observed for all Li-salts containing IL solutions. It suggests that protective Li⁺-containing films are formed on a Pt metal surface due to the reduction of TFSI

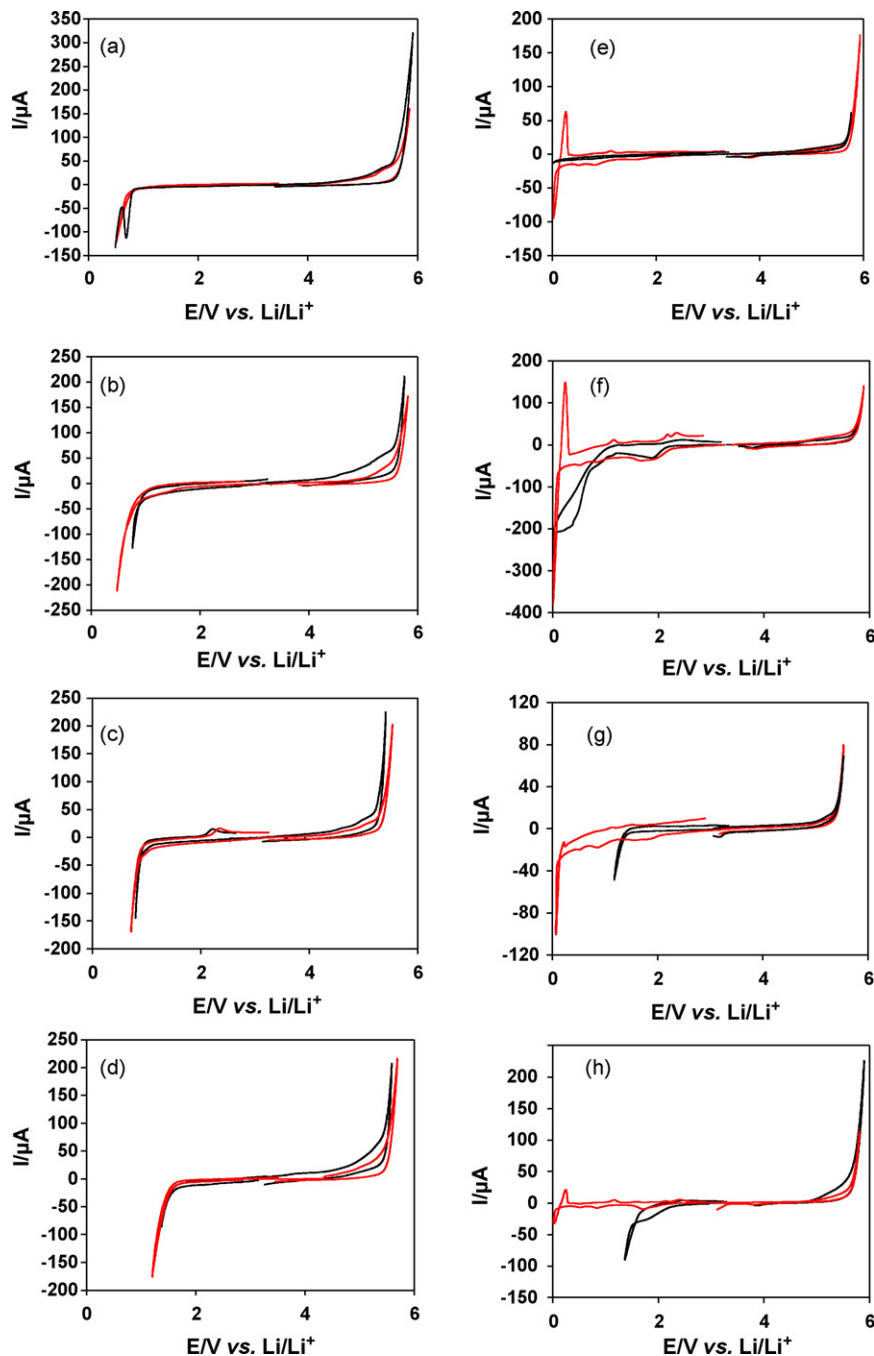


Fig. 2. CV curves of glassy carbon electrodes (a–d) and Pt electrodes (e–h) in four neat ILs (black curves) and the same ILs containing 0.5 M LiTFSI (red curves), 25 °C, scan rate 20 mV s⁻¹. (a and e) MPPpTFSI; (b and f) BMPTFSI; (c and g) HMITFSI; (d and h) EDMETFSI.

anions in the presence of Li ions. The role of Li ions in the formation of surface films on different electrodes in IL was already discussed in the literature previously [17,22–25]. The presence of Li salts in the IL electrolytes extends their cathodic limit. It is important to note that the cathodic behavior of many important polar-aprotic solutions depends very strongly on the nature of the cation [26]. The thermodynamics of the possible reduction processes that polar-aprotic solvents can undergo depends on the identity of the cations present in solutions. When Li ions are present, polar-aprotic solvents such as ethers, esters and alkyl carbonates are reduced to insoluble organic Li salts (Li-alkoxides, Li-carboxylates and Li-alkyl carbonates respectively) [27]. Salt anions such as MX_x ($M = B, P, Cl, As$; $X = F, O$) are also reduced to insoluble Li salts (inorganic) such as LiX , Li_yMX_z , etc. [28,29]. These insoluble Li salts, reduction products of the solution species, precipitate on the electrodes surfaces (Li, carbon, noble metals) thus forming surface films that behave according to the SEI model: the surface films blocks electron transport but behave as solid electrolyte interphase for Li ion transport between the solution and the electrode [30]. Hence, the electrochemical behavior of ethers, esters or alkyl carbonates with tetra-alkyl-ammonium salts with non-active electrodes (carbon, Pt, Au) is completely different than that of the same solvents with Li salts. In the former case there are no passivation phenomena at low potentials while in the latter case surface films and passivation phenomena are developed when the electrodes are polarized below 1.5 V (Li/Li^+) [26,27]. TFSI can be reduced in the presence of Li ions to a variety of surface species including LiF , Li_xSO_y , $Li_2NSO_2CF_3$, Li_xCF_y , etc. [31], all of which can be considered as insoluble Li compounds that can precipitate on the electrode's surface, thus forming passivating surface films. Hence, the behavior of the IL systems studies herein due to the presence of LiTFSI salt can be well understood. As one can see from the data in Fig. 2, the passivation processes due to the presence of Li ions in solutions and probably the formation of Li^+ -containing surface films formation are highly dependent on the nature of the electrode. Carbon and platinum are inert for most relevant polar-aprotic electrolyte solutions within a wide electrochemical window. Hence, the difference in the passivation behavior of these electrodes in the ILs-based systems demonstrated in Fig. 2 is somewhat surprising. This difference may be explained by the fact that platinum undergoes under-potential deposition (UPD) of lithium at potentials higher by 0.7 V from that of bulk Li deposition. This phenomenon relates to depositions of one or two mono-layers of lithium on the noble metal and is connected to the difference between the work function of Li and Pt [32]. Hence, platinum may become much more reactive towards the electrolyte solutions below 0.7 V vs. Li/Li^+ than carbon. This should induce more intensive surface reactions of solution species (mostly TFSI ions) with the Li layers thus deposited on Pt and a resulting efficient precipitation of passivating agents (insoluble Li compounds) on the platinum surface. Due to the high reactivity of Li metal and the variety of possible insoluble Li compounds that can be produced by TFSI anions reduction, it is not surprising that Li electrodes are relatively easily passivated in the TFSI-based ILs when containing Li ions. Indeed, stable cycling of $LiCoO_2/Li$ cells, could be demonstrated even with ILs of relatively low cathodic stability of their cations [12,15,16,33–35], attributable to the passivation of lithium metal electrodes in TFSI-based systems (see data on Li cycling efficiency in ILs in [17]). It should be noted that in the absence of Li salts graphite electrodes cannot be passivated in ILs and may intercalate irreversibly the IL cations [36]. In the presence of Li TFSI in ILs-based electrolytes graphite electrodes can reach effective passivation that enables their reversible intercalation with lithium. Such passivation can be enhanced by the use of reactive additives such as vinylene carbonate (VC).

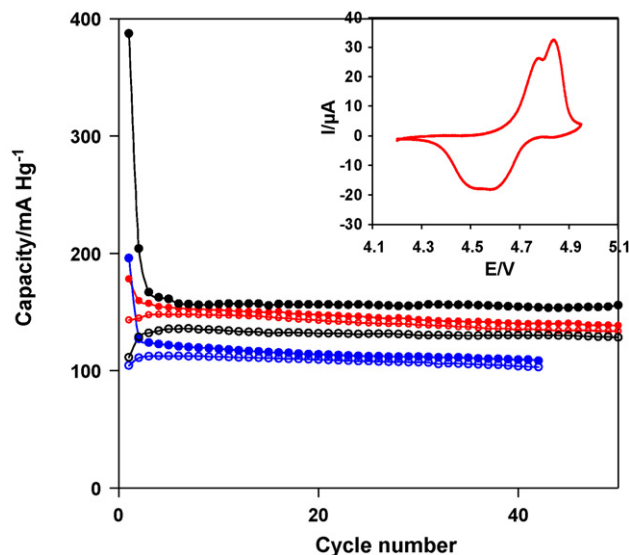


Fig. 3. Curves of charge and discharge capacity vs. cycle number, obtained upon galvanostatic cycling ($C/16$ h rates) of $LiNi_{0.5}Mn_{1.5}O_4$ electrodes vs. Li metal anodes in IL electrolyte solutions which cathodic stability is high and in standard electrolyte solution for comparison 30 °C. Electrolyte solutions composition: 0.5 M LiTFSI in BMPTFSI, blue curves; 0.5 M LiTFSI in MPPpTFSI, red curves; 1.5 M $LiPF_6$ in EC/EMC 1:2, black curves. Insert: typical steady state CV of $LiNi_{0.5}Mn_{1.5}O_4$ electrodes in MPPpTFSI/LiTFSI, 20 $\mu V s^{-1}$, 20 °C.

The extent of passivation of graphite electrodes in ILs/Li salt solutions and its effectiveness depends to a great extent on the type of graphite particle used, their morphology and existence of surface groups on the edge plans [36–39]. Thus, it can be said that in terms of ease and effectiveness of passivation in Li^+ ions containing TFSI-based ILs graphite electrodes demonstrate intermediate behavior between lithium metal or Pt and glassy carbon. This is because Li and Pt possess reducing Li atoms on the surface (due to Li UPD starting around 0.7 V vs. Li/Li^+ in the latter case), while glassy carbon not. (Thereby, graphite which intercalates with lithium at potentials below 0.3 V vs. Li/Li^+ can be considered as an intermediate in this respect.)

The charge & discharge capacity of $LiNi_{0.5}Mn_{1.5}O_4/Li$ cells with the two most electrochemically stable ILs—BMPTFSI and MPPpTFSI, as a function of cycle number (galvanostatic cycling, capacity calculated per the cathode's active mass) is shown in Fig. 3. For comparison, the data obtained in identical experiments with standard electrolyte solutions (optimal ones: 1.5 M $LiPF_6$ in EC/EMC 1:2, as described in Ref. [40]) are presented as well in this figure. One can see that cycling the $LiNi_{0.5}Mn_{1.5}O_4$ electrodes in the standard solution involves irreversible processes: the charge capacity is higher than the discharge capacity. The irreversibility in the charge–discharge behavior of these cells, decreases considerably in the ILs-based electrolyte solutions. Note, however, that cycling was performed with a very low cycling rate of $C/16$, which is not optimal for the standard electrolyte solution because as the charging rates are slower, the weight of possible parasitic anodic reactions (due to the high voltage) in the total anodic charge measured, is higher. It is possible to improve considerably the reversibility of these electrodes in standard solutions by the use of additives (beyond the scope of this paper). Nonetheless, these results demonstrate much lower rates of parasitic side reactions (anodic oxidation of solutions' components on cathode at the high charging potentials) in the case of the BMPTFSI and MPPpTFSI-based electrolytes compared to standard solutions. Thus, in this application (5 V cells) one of the main advantages of room temperature ionic liquids—their wide electrochemical window and high anodic stability is well exploited.

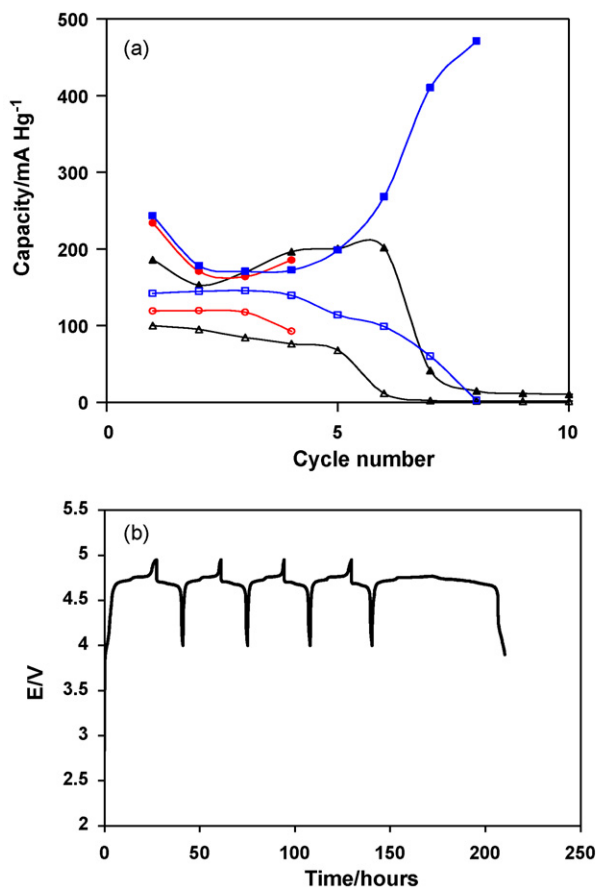


Fig. 4. Curves of charge and discharge capacity vs. cycle number, obtained upon galvanostatic cycling ($C/16$ h rates) of $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ electrodes in IL electrolyte solutions (containing 0.5 M LiTFSI) which cathodic stability is relatively low. HMITFSI, black curves; EDMETFSI, red curves; MEMITFSI, blue curves. (b) Typical voltage profile obtained for the galvanostatic cycling of $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ vs. Li, in the IL electrolyte solution: 0.5 M LiTFSI/EDMETFSI 30 °C.

The results of the galvanostatic cycling (capacity vs. cycle number curves) for the three less cathodically stable IL electrolytes studied herein are shown in Fig. 4a. Very high irreversible capacity in the initial cycles grows drastically in the subsequent cycles, and eventually the cycling ends with continuous charging of the cells within the potential limits, around 5 V. A typical voltage profile, obtained for EDMETFSI, is shown in Fig. 4b. In the case of HMITFSI-based solutions, the voltage profiles reflect pronounced increase in the internal resistance of the cells during cycling. XRD and Raman analysis of the electrodes (see experimental details of such measurements in Refs. [36,39]) after these types of failure did not reveal any changes in their structure due to cycling in solutions. The only explanation of such behavior of the cells in these electrolytes is a development of a shuttle mechanism due to pronounced cathodic reactions in the absence of good enough passivation of the Li electrodes. The reduction products of these less cathodically stable ILs, which are formed on the anode due to an imperfect passivation of the anode surface, migrate to the cathode and undergo oxidation at the high anodic potentials, and vice versa. Accumulation of these products leads to an increasing irreversible capacity from cycle to cycle up to the point in which the anodic current, caused by the parasitic oxidation process, becomes higher enough to prevent the possibility of the cathode charging. This scenario is confirmed by the fact that LiCoO_2/Li cells exhibited a stable reversible cycling both in HMITFSI and in other imidazolium-based IL electrolytes [15,16,34], and in DEMETFSI [33]. Obviously

potential needed for charging LiCoO_2 is low enough NOT to oxidize back the solutions reduction products which are formed on the anode and hence the shuttle cycles seen with the $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4/\text{Li}$ cells with imidazolium-based electrolyte are not relevant to the LiCoO_2/Li cells.

4. Conclusions

“5 V” $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4/\text{Li}$ cells can be cycled with relatively low parasitic processes upon charging, with ionic liquids based on derivatives of pyrrolidinium and piperidinium cations. In this respect, these ILs are much better for 5V, rechargeable Li batteries, than standard electrolyte solutions based on alkyl carbonate solvents LiPF_6 . To the best of our knowledge, we demonstrate herein the first “5 V” rechargeable Li batteries systems in IL-based electrolytes. The nature of the anion, TFSI in the present case is highly important because it determines the anodic stability of these systems. Reduction of TFSI anions in the presence of Li ions in solutions, form a variety of insoluble Li compounds that can precipitate on electrodes surfaces and thus passivate Li, Pt and graphite electrodes. This passivation is indeed effective for Li electrodes in the ILs based on the piperidinium and pyrrolidinium cations. In ILs based on imidazolium derivatives, $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4/\text{Li}$ cells demonstrate shuttle mechanism due to the insufficient passivation of the Li anodes: solution reduction products formed on lithium migrate to the cathode and are oxidized there upon charging at the high anodic potentials. Thereby cycling of $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4/\text{Li}$ cells with these systems is poor, while cycling LiCoO_2/Li cells with them is possible (the lower charging potentials thus needed, are not high enough to oxidize the solution reduction products). It should be emphasized that what is demonstrate in this paper are only trends and directions. There are questions of high rates and low temperature performance. Also, advantages in terms of safety features (compared to standard solutions) have to be demonstrated by appropriate thermal studies (which are in progress).

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