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ORIGINAL PAPER

Lithium-metal potential in Li^+ containing ionic liquids

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Abstract Impedance spectroscopy studies of the interface between lithium and ionic liquid (IL) showed the formation of a film (solid electrolyte interface, SEI), protecting metal from its further dissolution. Consequently, the potential of metallic lithium immersed in an electrolyte containing Li^+ cations may be described as a $Li|SEI|Li^+$ system, rather than simply Li/Li^+. The potential of lithium-metal in a series of ionic liquids (and in a number of molecular liquids) containing Li^+ cation (0.1 M) was measured versus the Ag|(Ag^+ 0.01 M, cryptand 222 0.1 M, in acetonitrile) reference. The lithium-metal potential ($E(Li|SEI|Li^+)$) was ca. −2.633 ± 0.017 V in ILs based on the $[N(CF_3SO_2)_2^-]$ anion, while −2.848 ± 0.043 V in ILs containing $[BF_4^-]$ anion (the difference is ca. 200 mV). In the case of ILs based on the triflate anion ($[CF_3SO_3^-]$), the cation of ionic liquid also influences the $E(Li|SEI|Li^+)$ value: it was ca. −1.987 ± 0.075 V for imidazolium based cations and much lower (−2.855 V) for the pyrrolidinium based cation. In ionic liquid based on the imidazolium cation and hexafluorophosphate anion ($[PF_6^-]$), the $Li/SEI/Li^+$ potential was −2.245 V. The $Li|SEI|Li^+$ potential measured in cyclic carbonates was −2.780 ± 0.069 V while in dimethylsulfoxide showed the lowest value of ca. −3.285 V. The measured potentials were also expressed versus the formal potential of the ferrocene/ferrocinium redox couple, obtained from cyclic voltammetry.

Keywords Ionic liquid · Lithium-ion · Lithium-metal potential · Lithium reference

Abbreviations

IL	Ionic liquid
RTIL	Room temperature ionic liquid
AN	Acetonitrile
SEI	Solid electrolyte interface
DMSO	Dimethylsulfoxide
TMS	Tetramethylene sulfone (sulfolane)
PC	Propylene carbonate
γ-BL	γ-Butyrolactone
EC	Ethylene carbonate
DEC	Diethyl carbonate
DMC	Dimethyl carbonate
$[EtMeIm^+]$	1-Ethyl-3-methylimidazolium cation
$[BuMeIm^+]$	1-Butyl-3-methylimidazolium cation
$[BuMePy^+]$	*N*-Butyl-4-methylpyridinium cation
$[OctPy^+]$	*N*-Octylpyridinium cation
$[MeOct_3N^+]$	*N*-Methyl-*N,N,N* trioctylammonium cation
$[Et_4N^+]$	Tetraethylammonium cation
$[Bu_4N^+]$	Tetrabutylammonium cation
$[BuMePyrrol^+]$	*N*-Butyl-*N*-metylpyrrolidinium cation
$[MePrPip^+]$	*N*-Methyl-*N*-propylpiperidinium cation
$[Et_2MeS^+]$	Diethylmethylsulfonium cation
$[Et_3S^+]$	Triethylsulfonium cation
$[BF_4^-]$	Tetrafluoroborate anion
$[PF_6^-]$	Hexafluorophosphate anion
$[NTf_2^-]$; $[N(CF_3SO_2)_2^-]$	Bis(trifluoromethanesulfonyl)imide anion
$[OTf^-]$; $[CF_3SO_3^-]$	Triflate anion
$Fc|Fc^+$	Ferrocene/ferrocinium(I) redox couple
Cryptand 222	4,7,13,16,21,24-Hexaoxa-1,10-diazabicyclo[8.8.8]hexacosane

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1 Introduction

In lithium-ion batteries, the lithium ion migrates during charging and discharging between the electrodes, and hence, the lithium-ion conducting electrolyte is an important element of the device, strongly influencing its properties [1, 2]. Usually, a lithium salt (for example $LiPF_6$ or $LiN(CF_3SO_2)_2$) dissolved in a mixture of organic solvents, such as cyclic carbonates, serves as the electrolyte [1, 2]. Polymer electrolytes, formed by dissolution of a lithium salt in a polymer network, or in the form of the polymer network swollen in a solution of the lithium salt in an organic solvent (gel-type polymer electrolyte) may also be used as a lithium-ion conductor [3]. Polymer electrolytes may be prepared in the form of thin foils, and therefore, they serve as separators. The non-volatility of solvent-free polymer electrolytes is important from the point of view of safety. However, such a solvent-free polymer electrolyte suffers from low specific conductivity. During the last decade, room temperature ionic liquids (RTIL), being salts of low temperature melting points, have been studied extensively [4, 5]. They may be used as solvents for many processes, as well as electrolytes in electrochemical devices [5]. Ionic liquids, due to strong Coulombic interactions between ions, are characterized by negligible vapor pressure which makes them inflammable. In addition, they often show a broad electrochemical stability window, necessary for the application in lithium-ion batteries with high-energy cathodes. While RTILs based on quaternary ammonium cations cannot be directly applied in any known type of primary or secondary batteries, it is possible to dissolve in them solid lithium salts, with the formation of a new room temperature ionic liquid, consisting of two cations. During the last few years there has been increasing interest in ionic liquids as electrolytes for lithium or lithium-ion batteries [6–44]. When the lithium-ion anode and cathode work together with a solvent-free ionic liquid, instead of a classical salt solution in molecular solvents, it is necessary to find a medium-free scale to compare potential data obtained in non-aqueous solutions with those found for ionic liquids. Since electrode potentials of individual half-cells can only be measured in a complete electrochemical cell, the question of a suitable reference system (an electrode or a redox couple) has become very important. Typically, in laboratory tests of electrodes for lithium or Li-ion batteries, a lithium-metal counter electrode is used. The mass and hence the capacity of lithium is much higher in comparison to the tested electrode. Consequently, even after a strong gradual degradation of the lithium electrode during cell cycling, its capacity is still much higher than that characteristic for the tested one. The lithium-metal counter electrode also serves as a commonly accepted reference electrode. It is usually assumed that the lithium-metal reference electrode reflects potential of the $Li|Li^+$ couple. Moreover, zero of the lithium scale in different solutions is commonly compared. However, due to the solid electrolyte interface (SEI) formation on the lithium surface [45–48], the reference system is rather $Li|SEI|Li^+$ than simply $Li|Li^+$. The general aim of this study was to measure and compare potentials of lithium-metal in different classical electrolytes and solvent-free ionic liquids, together with their electrochemical stability.

2 Experimental

2.1 Materials

Cryptand 222 (4,7,13,16,21,24-hexaoxa-1,10-diazabicyclo [8.8.8]hexacosane, Merck), lithium foil (0.75 mm thick, Aldrich), silver perchlorate ($AgClO_4$, Merck), lithium triflate ($LiCF_3SO_3$, LiOTf, Merck), lithium perchlorate ($LiClO_4$, Merck), lithium tetrafluoroborate ($LiBF_4$, Merck), lithium hexafluorophosphate ($LiPF_6$, Aldrich), lithium bis(trifluoromethanesulfonyl)imide ($LiN(CF_3SO_2)_2$, $LiNTf_2$, Merck), tetraethylammonium perchlorate (Et_4NClO_4, Fluka), tetraethylammonium tetrafluoroborate ($[Et_4N^+][BF_4^-]$, Aldrich), tetrabutylammonium bis(trifluoromethanesulfonyl)imide ($[Bu_4N^+][NTf_2^-]$, Fluka), *N*-methyl-*N*,*N*,*N*-trioctylammonium bis(trifluoromethanesulfonyl)imide ($[MeOct_3N^+][NTf_2^-]$, Fluka), 1-ethyl-3-methylimidazolium bis(trifluoromethanesulfonyl)imide ($[EtMeIm^+][NTf_2^-]$, Iolitec), *N*-butyl-*N*-methylpyrrolidinium bis(trifluoromethanesulfonyl)imide ($[BuMePyrrol^+][NTf_2^-]$, Iolitec), diethylmethylsulfonium bis(trifluoromethanesulfonyl)imide ($[Et_2MeS^+][NTf_2^-]$, Iolitec), triethylsulfonium bis(trifluoromethanesulfonyl) imide ($[Et_3S^+][NTf_2^-]$, Iolitec), *N*-methyl-*N*-propylpiperidinium bis(trifluoromethanesulfonyl)imide ($[MePrPip^+]$ $[NTf_2^-]$, synthesis), *N*-butyl-*N*-methylpyrrolidinium triflate ($[BuMePyrrol^+][OTf^-]$, Merck), 1-ethyl-3-methylimidazolium triflate ($[EtMeIm^+][OTf^-]$, Iolitec), 1-butyl-3-methylimidazolium triflate ($[BuMeIm^+][OTf^-]$, Iolitec), 1-ethyl-3-methylimidazolium tetrafluoroborate ($[EtMeIm^+][BF_4^-]$, Iolitec), 1-butyl-3-methylimidazolium tetrafluoroborate ($[BuMeIm^+][BF_4^-]$, Fluka), *N*-butyl-4-methylpyridinium tetrafluoroborate ($[BuMePy^+][BF_4^-]$, Merck), *N*-octylpyridinium tetrafluoroborate ($[OctPy^+][BF_4^-]$, Iolitec), 1-butyl-3-methylimidazolium hexafluorophosphate ($[BuMeIm^+]$ $[PF_6^-]$, synthesis), *N*-butyl-4-methylpyridinium hexafluorophosphate ($[BuMePy^+][PF_6^-]$, Merck), and ferrocene (Aldrich) were used as purchased.

N-methyl-*N*-propylpiperidinium bromide ($[MePrPip^+]$ $[Br^-]$) was obtained from *N*-methylpiperidine (Aldrich) and bromopropane (Aldrich), then dissolved in 2-propanol (P.O.Ch., Poland) and after an addition of tetrahydrofurane (P.O.Ch., Poland) white crystals of $[MePrPip^+][Br^-]$ were precipitated. *N*-methyl-*N*-propylpiperidinium bis(trifluoromethanesulfonyl)imide ($[MePrPip^+][NTf_2^-]$) was obtained from $[MePrPip^+][Br^-]$ by metathesis with $LiNTf_2$ in aqueous medium. The ionic liquid was dried by evaporation in vacuum at 50 °C for 10 h and kept over A3 molecular sieves. 1-butyl-3-methylimidazolium hexafluorophosphate ($[BuMeIm^+][PF_6^-]$) was obtained by mixing 1-methylimidazole (Fluka) with chlorobutane (freshly distilled, Fluka); the mixture was then refluxed at 70 °C for 3 days. The resulting viscous solution, after cooling to room temperature, was washed with five portions of ethyl acetate (Fluka). The remaining ethyl acetate was evaporated from the solid $[BuMeIm^+][Cl^-]$ at 50 °C at reduced pressure. Aqueous solution of hexafluorophosphoric acid (Fluka) was added dropwise to a solution of $[BuMeIm^+][Cl^-]$ in water and the mixture was stirred for 1 day at room temperature. The lower phase was separated from the aqueous phase in a separating funnel and washed 10 times with water. The ionic liquid $[BuMeIm^+][PF_6^-]$ was dried by evaporation in a vacuum at 60 °C for 10 h.

Ethylene carbonate (EC, Aldrich), diethyl carbonate (DEC, Aldrich), dimethyl carbonate (DMC, Aldrich), and γ-butyrolactone (γ-BL, Aldrich) were used as received. Acetonitrile (AN, Aldrich), propylene carbonate (PC, Aldrich), and dimethylsulfoxide (DMSO, Aldrich) were distilled. Sulfolane (TMS, Merck) was treated with a mixture of crushed ice, solid potassium permanganate, and sulfuric acid, in order to oxidise reducing impurities; after filtration, the solution was treated with sodium pyrosulfite and sulfolane was extracted with three portions of dichloromethane. The extract was dried with sodium sulfate and dichloromethane was distilled off; the remaining sulfolane was dried over phosphorus pentaoxide and distilled off under reduced pressure. Water content in ionic liquids, analyzed with a standard Karl-Fisher titrant (HYDRANAL® Composite 1), was below 0.1%.

2.2 Measurements

Cyclic voltammetric curves were recorded with the µAutolab electrochemical system (EcoChemie, the Netherlands) using a conventional three electrode arrangement. The working glassy carbon (Mineral Poland) or Au electrodes had a surface of 0.0700 and 0.0177 cm^2, respectively. The Ag|(Ag^+, 222, AN) reference electrode was prepared by immersing the Ag wire into a solution of $AgClO_4$ (0.01 M) and cryptand 222 (0.1 M) in acetonitrile. The tube containing the Ag^+ and 222 solution in AN was separated from the tested ionic liquid by a glass frit placed at the tube ending (the tube obtained from a conventional calomel electrode producer, Euro-Sensor, Poland). Preparation of the 'crypate' electrode is very easy and its potential is stable with time. A platinum foil (0.5 cm × 1 cm) served as a counter electrode. The scan rate was 10 mV/s.

The potentials of the lihium-metal was measured in different media against the Ag|(Ag^+, 222, AN) reference. The cell was assembled from a lithium foil (Aldrich 0.75 mm thick) separated from the reference electrode ending with a glass micro-fiber separator (thickness 0.3 mm, GF/A, Whatman), filled with the electrolyte, and placed in an adapted 0.5″ Swagelok® connecting tube. The potential was measured with a pH-meter (5170 Elwro, Poland, input resistance $>10^{13}$ Ω,) with an accuracy of ±0.001 V. Impedance plots of symmetrical two electrode Li|electrolyte|Li cells were taken with the use of a 9121 frequency response analyzer (Atlas–Sollich, Poland).

3 Results and discussion

3.1 Lithium passivation

Metallic lithium is one of the most reactive metals, unstable in contact with non-aqueous electrolytes which may be used in Li-ion batteries. In contact with 'classical' electrolytes, a passive layer (SEI) is formed protecting metal from its further degradation. The composition of the passivation layers formed in different media is not well known, and hence the potential of such a reference (lithium-metal + passivation layer) is not strictly defined. However, it is assumed that generally the SEI consists of two layers: (1) inorganic (lithium compounds such as LiF, Li_2CO_3, etc.,) and (2) organic-polymer layer formed between the liquid electrolyte phase and the solid inorganic layer [45–48]. The nature of the Li^+ conducting SEI as well as that of the electrolyte (ionic liquid) may influence the potential of the $Li/SEI/Li^+$ system. In this study, passivation of lithium-metal was observed with impedance spectroscopy. Figure 1 shows the evolution of impedance of the $Li|[Li^+][BuMeIm^+][OTf^-]$ interface. Just after the $Li|[Li^+][BuMeIm^+][OTf^-]|Li$ cell assembling, impedance is at the level of 10^2 Ω (Fig. 1a) to increase during 24 h to the level of 10^4 Ω and then it remains stable for the next few days (Fig. 1b). This indicates the formation of a resistive passivation film which protects lithium-metal from its further decomposition. A different behavior was observed in the case of ionic liquids based on the sulfonium cation and imide anion. Figure 2a shows that the passivation of lithium-metal in $[Et_3S^+][NTf_2^-]$ occurs with the formation of a less resistive film; impedance of the $Li|[Li^+][Et_3S^+][NTf_2^-]|Li$ cell increases after 1 week to the level of 100 Ω; the passivation film does not protect the lithium foil. Moreover, galvanostatic charging of the symmetrical $Li|[Li^+][Et_3S^+][NTf_2^-]|Li$ cell does not stop further evolution of impedance (Fig. 2b). In contrast to the

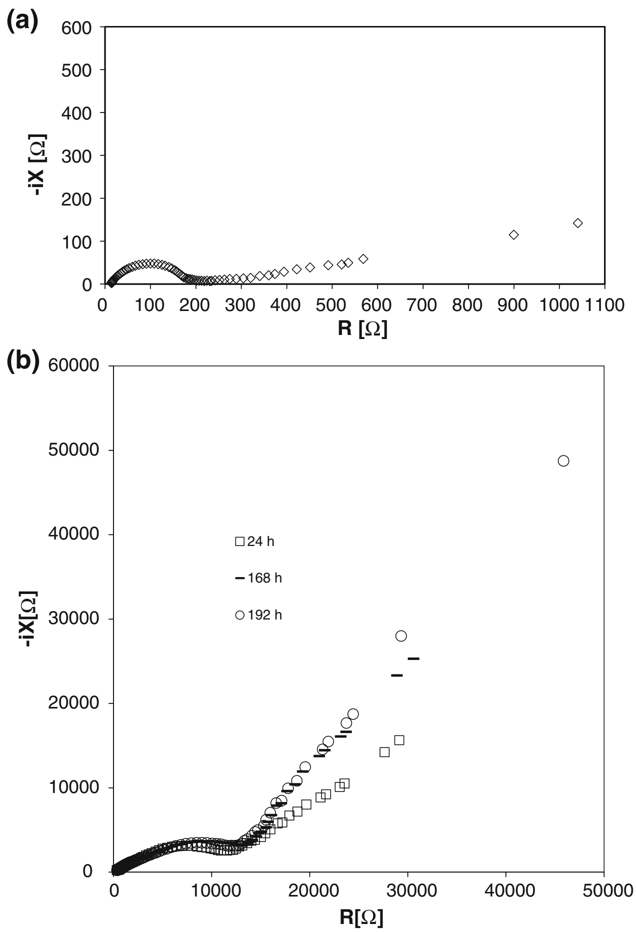

Fig. 1 Impedance plot for the symmetrical Li|0.1 M LiOTf in $[\mathrm{BuMeIm}^+][\mathrm{OTf}^-]$|Li cell (**a**) fresh cell just after its assembling and (**b**) as a function of time

latter system, galvanostatic charging of the $\mathrm{Li}|[\mathrm{Li}^+][\mathrm{EtMeIm}^+][\mathrm{NTf}_2^-]|\mathrm{Li}$ cell results in the formation of a resistive coating. In this case, the chemically formed passivation film is more resistive in comparison to that formed electrochemically. The electrochemical coating leads to impedance at the level of 10^3 Ω (Fig. 3). If lithium-metal is contacted with $[\mathrm{EtMeIm}^+][\mathrm{NTf}_2^-]$ under open circuit conditions, passivation leads to the evolution of impedance to the level of 10^4 Ω (Fig. 4). Impedance and ohmic resistance in Figs. 1, 2, 3, and 4 were expressed in Ω unit and not in specific resistance/impedance unit (Ω cm) as the thickness of the resistive passivation layer is not constant. Formation of a coating on lithium-metal was detected (with the use of impedance spectroscopy) in the case of all ionic liquids tested in this study. On the other hand, the protective coating may be prepared at the lithium-metal surface before its immersion in the electrolyte solution. For example, a lithium electrode coated with the $\mathrm{Li_2CO_3}$ + PVdF film was efficiently protected from a possible reaction with $\mathrm{LiPF_6}$ in EC + DEC electrolyte [49]. All this suggests that when metallic lithium is contacted with different electrolytes, including solvent-free ionic liquids, different types of corrosion products are formed at its surface. The resulting system may be represented by $\mathrm{Li|SEI|Li^+}$ (or Li|passivation film|$\mathrm{Li^+}$), rather than $\mathrm{Li|Li^+}$.

3.2 $\mathrm{Li|SEI|Li^+}$ couple potential

Potentials of lithium-metal (the $\mathrm{Li|SEI|Li^+}$ couple), expressed versus the Ag|($\mathrm{Ag^+}$222, AN) reference, measured in ionic liquids and classical solutions, are listed in Tables 1 and 2, respectively. Measurements were taken for a number of typical ionic liquids reported in literature as potential electrolytes for lithium or lithium-ion batteries. Ionic liquids were based on four types of quaternary ammonium cyclic cations: imidazolium $[\mathrm{R_1R_2Im^+}]$, pyrrolidinium $[\mathrm{R_1R_2Pyrrol^+}]$, pyridinium $[\mathrm{RPy^+}]$, and piperidinium $[\mathrm{R_1R_2Pip^+}]$; they were as well based on tetraalkylammonium cation $[\mathrm{R_1R_2R_3R_4N^+}]$ and sulfonium $[\mathrm{R_1R_2R_3S^+}]$. The most frequently employed anions are bis(trifluoromethanesulfonyl)imide $[\mathrm{NTf_2^-}]$, triflate $[\mathrm{OTf^-}]$, and tetrafluoroborate $[\mathrm{BF_4^-}]$. The LiX solid salt, being a source of the lithium cation, was dissolved in a liquid salt $[\mathrm{A^+}][\mathrm{X^-}]$ (ionic liquid), which resulted in a new ionic liquid: $[\mathrm{Li^+}]_m[\mathrm{A^+}]_n[\mathrm{X^-}]_z$. The concentration of $\mathrm{Li^+}$ in all systems was 0.1 M. Data in Table 1 suggest that the lithium-metal potential depends mainly on the $\mathrm{X^-}$ anion. The $E(\mathrm{Li|SEI|Li^+})$ value is ca. −2.633 ± 0.017 V in ILs based on the $[\mathrm{NTf_2^-}]$ anion, while it is −2.848 ± 0.043 V in ILs containing the $[\mathrm{BF_4^-}]$ anion (the difference is ca. 200 mV). In the case of ionic liquids based on the triflate anion, the $\mathrm{A^+}$ cation may also influence the $E(\mathrm{Li|SEI|Li^+})$ value: it is ca. −1.987 ± 0.075 V for imidazolium cations and much lower (−2.855 V) for the pyrrolidinium cation. In ionic liquid based on the imidazolium cation and hexafluorophosphate anion, the lithium potential is −2.245 V. The difference between the lowest (−2.892 V) and the highest (−1.912 V) potential is almost 1 V (0.980 V). Potential of lithium-metal versus the same cryptate reference was also measured in $\mathrm{Li^+}$ solutions in a number of molecular solvents (Table 2), such as propylene carbonate (PC), diethyl carbonate (DEC), dimethyl carbonate (DMC), and γ-butyrolactone (γ-BL). Cyclic carbonates are used as molecular solvents for the preparation of lithium electrolytes, as they are able to form SEI on the graphite anode without any additives. For comparison, lithium-metal potentials in $\mathrm{Li^+}$ solutions in molecular solvents which are not used in lithium-ion batteries, such as dimethylsulfoxide (DMSO), sulfolane (TMS), and acetonitrile (AN), are also included in Table 2. Cyclic carbonates may be applied as mixtures (EC + PC, EC + DMC, or EC + DEC) as well as additives to ionic liquids to form SEI on the anode. Hence, some solutions containing both ionic liquid and the lithium

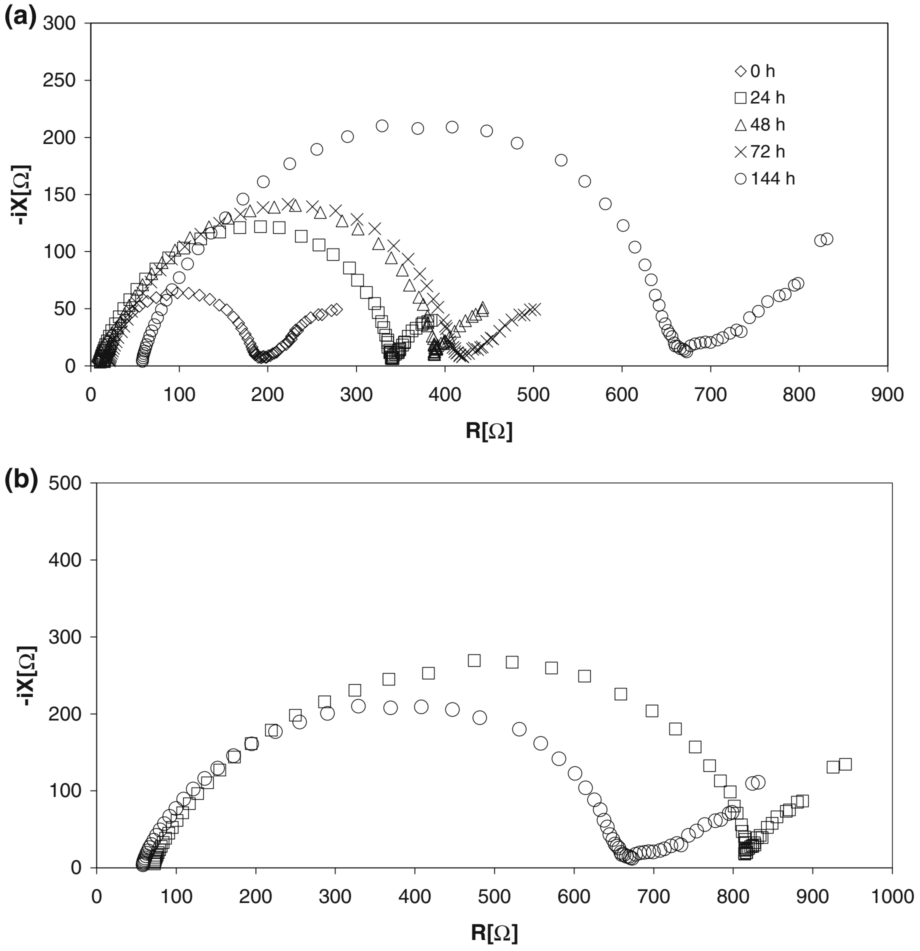

Fig. 2 Impedance plot for the symmetrical Li|0.1 M $LiNTf_2$ in $[Et_3S^+][NTf_2^-]$|Li cell **a** as a function of time and **b** (*open circle*) 144 h after its assembling (*open square*) after galvanostatic (1 mA) charging/discharging process

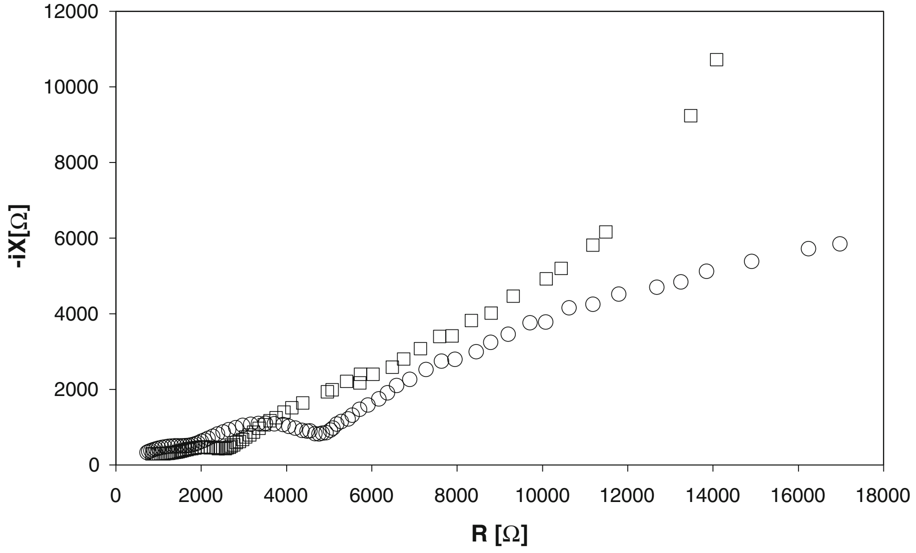

Fig. 3 Impedance plot for the symmetrical Li|0.1 M $LiNTf_2$ in $[EtMeIm^+][NTf_2^-]$|Li (*open circle*) 144 h after its assembling (*open square*) after galvanostatic (1 mA) charging/discharging process

salt in cyclic carbonates have also been included in the table. It can be seen from Table 2 that the lithium-metal potential in cyclic carbonates is -2.780 ± 0.069 V. The $E(Li/SEI/Li^+)$ in DMSO shows the lowest value of ca. -3.285 V. The difference between $E(Li/SEI/Li^+$ in $[EtMeIm^+][OTf^-])$ and $E(Li/Li^+$ in DMSO) is ca. 1.4 V. Generally, potentials of the anode or cathode of lithium-ion cell are expressed versus the potential of lithium-metal in a given solvent, assumed to be zero, independently of the electrolyte. However, it can be seen from Tables 1 and 2

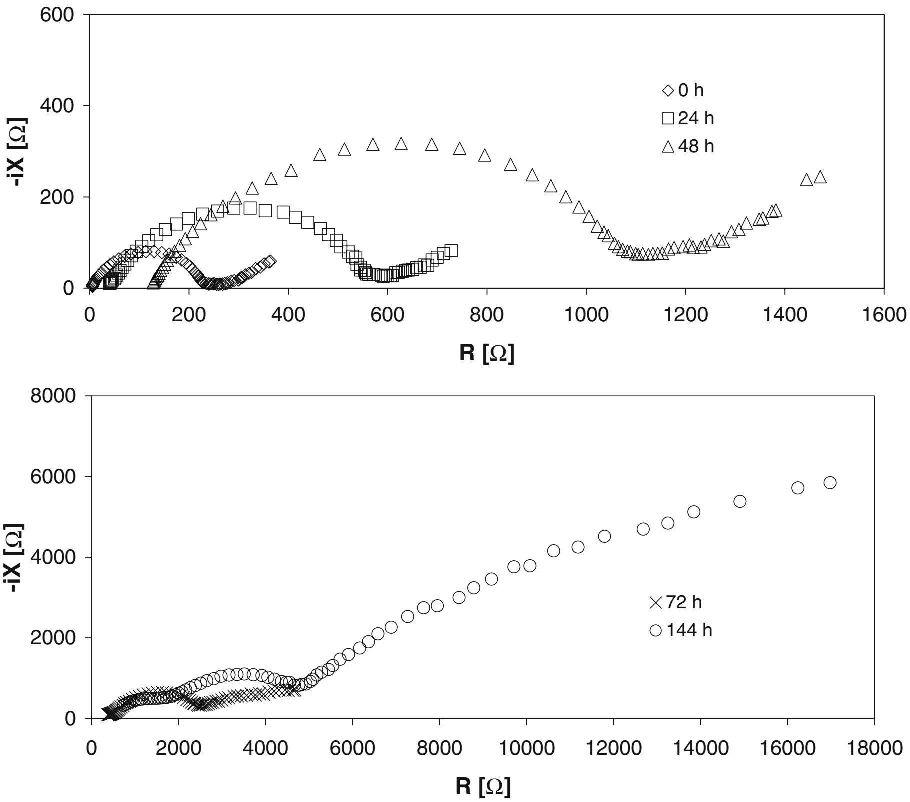

Fig. 4 Impedance plot for the symmetrical Li|0.1 M $LiNTf_2$ in $[EtMeIm^+][NTf_2^-]$|Li cell, kept under open circuit conditions, as a function of time

that the potential changes strongly when lithium-metal is transferred from one medium to another, and hence, lithium foil contacted with the electrolyte cannot be used as an internal universal reference, characterized by a constant potential.

The difference between the lowest and the highest lithium potential in ionic liquids (almost 1 V) is not unexpected, as the transfer of the Li^+ cation from $[A^+][X^-]$ to $[B^+][Z^-]$ ionic liquid, is associated with changes in Li^+ coordination/salvation by the ionic liquid anion:

$$LiX_n^{1-n} + m\,Z^- \rightarrow LiZ_m^{1-n} + nX^-$$

The transfer of the lithium cation from molecular solvent S into ionic liquid $[A^+][X^-]$, is associated with replacement of solvent molecules S from the solvation shell by solvating anions X^-:

$$Li^+S_n + m\,X^- \rightarrow LiX_m^{1-n} + nS$$

In general, properties of an ion (or its chemical potential) in a molecular solvent are determined mainly by ion–solvent and ion–ion interactions, while in ionic liquid mainly by ion–ion interactions. Molar Gibbs energy of the ion transfer from one medium to another, $\Delta_t G$, gives a comparison of the salvation (chemical potential) of the ion in both media. Molar Gibbs energies of individual ion transfer between several pure and mixed molecular solvents have been extensively studied and reviewed [58, 59]. In addition, molar Gibbs energies of Ag^+, Cu^{2+}, Zn^{2+}, and Cd^{2+} transfer from dimethylsulfoxide (DMSO), a reference molecular liquid, to a number of ionic liquids (IL), $\Delta_t G$(DMSO → IL), were obtained from $M|M^{n+}$ electrode potentials [60]. Ionic liquids consisted of various tetraalkylammonium cations and Cl^-, Br^-, BF_4^-, PF_6^-, or $N(CF_3SO_2)_2^-$ anions. The measured $M|M^{n+}$ (0.01 M, IL) potentials depended both on the tetraalkylammonium cation as well as on the anion. The transfer of cations from DMSO to ionic liquids brings about positive or negative changes of the $M|M^{n+}$ potentials. The most important factor influencing the potential was the anionic component of the ionic liquid, which solvates the cation.

3.3 Electrochemical stability of ionic liquids

Tables 1 and 2 also contain cathodic and anodic stability limits of electrolytes (ionic liquids and solutions in molecular solvents) obtained from cyclic voltammetry at GC electrodes and expressed versus the Ag/(Ag^+, 222, AN) reference. Lithium-ion batteries may work at potential differences at the level of 4 V, and hence, the potential electrolyte should be stable within such a range. Inspection of Table 1 shows that apart from two ionic liquids containing the Li^+ cation (both based on the pyridinium cation) this demand is fulfilled. In some cases, the stability is as high as 5 V or even 5.8 V (ionic liquid electrolyte based

Table 1 Potential of lithium-metal (E(Li|SEI|Li$^+$) and electrochemical stability windows (on glassy carbon) of lithium salts dissolved in ionic liquids

Ionic liquid	LiX 0.1 M	E (Li|SEI|Li$^+$) [V]	Stability limit [V]		
			Cathodic	Anodic	ΔE
[MePrPip$^+$][NTf$_2^-$]	LiNTf$_2$	−2.616	−3.0	2.8	5.8
[EtMeIm$^+$][NTf$_2^-$]	LiNTf$_2$	−2.642	−2.4	2.5	4.9
[BuMePyrrol$^+$][NTf$_2^-$]	LiNTf$_2$	−2.627	−2.3	2.8	5.1
[Et$_3$S$^+$][NTf$_2^-$]	LiNTf$_2$	−2.634	−2.2	3.1	5.3
[Et$_2$MeS$^+$][NTf$_2^-$]	LiNTf$_2$	−2.641	−2.2	3.1	5.3
[MeOct$_3$N$^+$][NTf$_2^-$]	LiNTf$_2$	−2.650	−2.0	2.5	4.5
[BuMePyrrol$^+$][OTf$^-$]	LiOTf	−2.855	−2.3	3.0	5.3
[EtMeIm$^+$][OTf$^-$]	LiOTf	−1.912	−1.7	2.3	4.0
[BuMeIm$^+$][OTf$^-$]	LiOTf	−2.062	−2.0	2.4	4.4
[BuMePy$^+$][BF$_4^-$]	LiBF$_4$	−2.863	−1.2	2.5	3.7
[EtMeIm$^+$][BF$_4^-$]	LiBF$_4$	−2.892	−2.0	2.1	4.1
[BuMeIm$^+$][BF$_4^-$]	LiBF$_4$	−2.805	−1.9	2.3	4.2
[OctPy$^+$][BF$_4^-$]	LiBF$_4$	−2.825	−1.0	2.5	3.5
[BuMeIm$^+$][PF$_6^-$]	LiPF$_6$	−2.245	−2.2	2.7	4.9

Potentials expressed versus the Ag|(Ag$^+$, 222 in AN) reference. Scan rate: 10 mV s^{-1}. Room temperature

Table 2 Potential of lithium-metal (E(Li|SEI|Li$^+$) and electrochemical stability (on glassy carbon) of lithium salts dissolved in molecular liquids or molecular liquids + ionic liquids

Solvent	LiX (0.1 M)	E(Li|SEI|Li$^+$) [V]	Stability limit [V]		
			Cathodic	Anodic	ΔE
PC	LiNTf$_2$	−2.845	−2.2	2.8	5.0
PC	LiPF$_6$	−2.849	−2.1	2.2	4.3
γ-BL	LiNTf$_2$	−2.897	−2.4	2.3	4.7
DMC	LiNTf$_2$	−2.712	−2.0	2.1	4.1
DEC	LiNTf$_2$	−2.732	−2.2	2.3	4.5
PC + EC	LiNTf$_2$	−2.827	−2.5	2.0	4.5
DMC + EC	LiNTf$_2$	−2.811	−2.7	2.1	4.9
DEC + EC	LiNTf$_2$	−2.808	−2.6	2.2	4.8
DMSO	LiNTf$_2$	−3.285	−3.0	1.5	4.5
AN	LiNTf$_2$	−2.820	−2.3	3.0	5.3
TMS	LiNTf$_2$	−2.805	−2.5	2.3	4.8
[Et$_4$N$^+$][BF$_4^-$] + PC (3:1 by weight)	LiBF$_4$	−2.945	−2.6	2.8	5.4
[Bu$_4$N$^+$][NTf$_2^-$] + PC (2:1 by weight)	LiNTf$_2$	−2.742	−2.1	2.9	5.0
[BuMePyrrol$^+$][PF$_6^-$] + PC (2:1 by weight)	LiPF$_6$	−2.639	−1.8	3.4	5.2

Potentials expressed versus the Ag|(Ag$^+$, 222 in AN) reference. Scan rate: 10 mV s^{-1}. Room temperature

on the piperidiunium cation). Classical Li$^+$ solutions in cyclic carbonates (Table 2) also show a good stability range, higher than 4 V. Cathodic reduction of the electrolyte should proceed at more negative potentials in comparison to the reduction potential of the Li|SEI|Li$^+$ system in a given electrolyte. Data collected in Table 1 show that the E(Li|SEI|Li$^+$ 0.1 M) value is lower than the potential of the cathodic stability limit only in the case of the ionic liquid based on the piperidinium cation. This may have been expected, as the solvent free [Li$^+$]$_m$[A$^+$]$_n$[X$^-$]$_z$ electrolytes are known to be incompatible with the lithium or carbon–lithium anodes. For the comparison, electrochemical stability was also measured in systems without the lithium cation and the data are collected in Table 3. The comparison of stability windows in systems containing Li$^+$ with those free of the Li$^+$ cation shows that the presence of lithium ion may reduce the stability of the system.

Table 3 Electrochemical stability windows of ionic liquids and molecular liquids on glassy carbon

Solvent	Salt	Stability limit [V]		
		Cathodic	Anodic	ΔE
–	[MePrPip$^+$][NTf$_2^-$]	−3.0	3.2	6.2
–	[EtMeIm$^+$][NTf$_2^-$]	−2.2	2.8	6.0
–	[BuMePyrrol$^+$][NTf$_2^-$]	−2.0	3.2	5.2
–	[Et$_3$S$^+$][NTf$_2^-$]	−2.0	3.1	5.1
–	[Et$_2$MeS$^+$][NTf$_2^-$]	−2.0	3.1	5.1
–	[MeOct$_3$N$^+$][NTf$_2^-$]	−2.0	2.5	4.5
–	[BuMePyrrol$^+$][OTf$^-$]	−3.0	3.0	6.0
–	[EtMeIm$^+$][OTf$^-$]	−2.1	2.5	4.6
–	[BuMeIm$^+$][OTf$^-$]	−2.0	2.7	4.7
–	[BuMePy$^+$][BF$_4^-$]	−1.2	2.8	4.0
–	[EtMeIm$^+$][BF$_4^-$]	−2.0	2.7	4.7
–	[BuMeIm$^+$][BF$_4^-$]	−2.0	2.6	4.6
–	[OctPy$^+$][BF$_4^-$]	−1.1	2.5	3.6
–	[BuMeIm$^+$][PF$_6^-$]	−2.5	2.7	5.2
PC	[BuMePyrrol$^+$][PF$_6^-$] (2.4 M)	−2.8	3.5	6.3
PC	[Bu$_4$N$^+$][NTf$_2^-$] (1.3 M)	−2.9	3.0	5.9
PC	[Et$_4$N$^+$][BF$_4^-$] (1 M)	−2.9	3.2	6.1
DMSO	[Et$_4$N$^+$][BF$_4^-$] (1 M)	−2.9	1.6	4.5
AN	[Et$_4$N$^+$][BF$_4^-$] (1 M)	−2.7	3.6	6.3
TMS	[Et$_4$N$^+$][BF$_4^-$] (1 M)	−2.9	3.3	6.2
γ-BL	[Et$_4$N$^+$][BF$_4^-$] (1 M)	−2.8	3.5	6.3
PC + EC	[Et$_4$N$^+$][BF$_4^-$] (1 M)	−2.9	3.3	6.2
DMC + EC	[Et$_4$N$^+$][BF$_4^-$] (1 M)	−2.9	3.4	6.3
DEC + EC	[Et$_4$N$^+$][BF$_4^-$] (1 M)	−3.0	3.5	6.5

Potentials expressed versus the Ag|(Ag$^+$, 222 in AN) reference. Scan rate: 10mVs^{-1}. Room temperature

3.4 Potential scales in Li$^+$ containing electrolytes

Generally, experimental methods used to establish medium-independent potential scales employ both the reference redox couple and reference electrode concepts. The reference redox couple approximation is based on the idea that large species, both in their oxidized and reduced forms, have a low charge density and hence, should be solvated similarly in different solvents. The first solvent independent electrode was proposed in 1947 by Pleskov [50]. He suggested the redox couples Rb/Rb$^+$ and Rb(Hg)/Rb$^+$, respectively, as 'pilot ions' for comparison of potential data in water, methanol, ethanol, liquid ammonia, hydrazine, formic acid, and acetonitrile. Koepp et al. [51] studied a number of organo-metallic complexes and recommended the ferrocene/ferrocenium ion (Fc/Fc$^+$) and cobaltocene/cobaltocenium (Co/Co$^+$) redox systems for the comparison of standard potentials in different media. Later on, a number of other redox couples have been proposed. IUPAC has therefore recommended the Fc|Fc$^+$ redox system as a reference for non-aqueous and mixed solvents [52]. The reference electrode frequently used in non-aqueous media is that based on the Ag|Ag$^+$ couple. It has been shown [53, 54] that while the potential of the Ag|Ag$^+$ couple strongly depends on the aprotic solvent, the potential of the Ag|(Ag$^+$ + cryptand) system is comparable in various aprotic media, such as acetonitrile, dimetylacetamide, *N*-methylpyrrolidinone, dimethylsulfoxide, or propylene carbonate. The silver cation is encapsulated by the cryptand molecule and hence the formed cryptate is a cation of a large radius and low charge density. The cryptate reference electrode has been used in this study (Tables 1, 2, 3). It has been found recently that the Fc|Fc$^+$ couple maybe used as a reference in a number of ionic liquids [55, 56]. In order to compare both the potential scales, redox potentials of the Fc|Fc$^+$ couple (the most popular redox couple in ILs [57]) was measured against the Ag|(Ag$^+$, 222, AN) reference electrode (an example of the CV curve shown in Fig. 5) and the results are shown in Table 4.

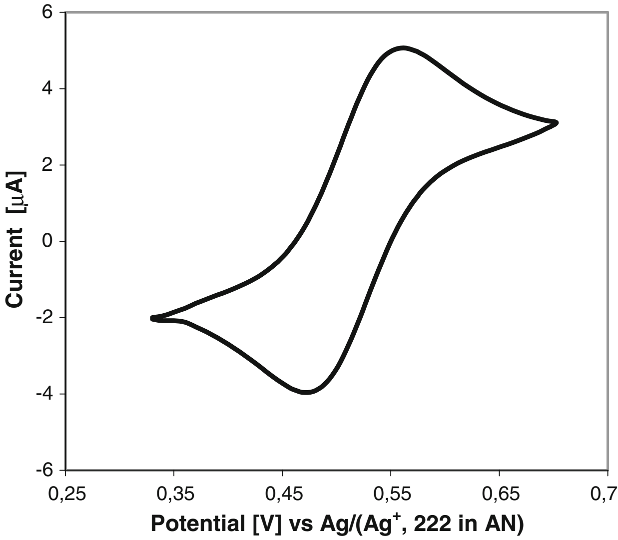

Fig. 5 Ferrocene cyclic voltammetry in [BuMePyrrol$^+$][PF$_6^-$] + PC (2:1 by weight) on Au electrode, sweep rate 100 mVs^{-1}

The $E_{1/2}$(Fc|Fc$^+$) value expressed against the Ag|(Ag$^+$, 222 in AN) reference has an approximately constant value of 0.521 ± 0.026 V (except [MeOct$_3$N$^+$][NTf$_2^-$]), which indicates that both assumptions (the 'cryptate' and Fc|Fc$^+$) lead to similar results. Note that the potential of individual electrodes, as well as the reduction potential of redox couples, estimated with the use of any method, including that applied here, can be neither proved nor disproved. They do not have a strict thermodynamic meaning, however, they provide useful information on differences in the chemical potential of ions in different media. Data collected in Tables 1, 2, 3, and 4 facilitate conversion of the measured lithium-metal (Li|SEI|Li$^+$) potentials to the Fc|Fc$^+$ scale.

Table 4 Potential ($E_{1/2}$) of the Fc|Fc$^+$ oxidation/reduction measured versus the Ag|(Ag$^+$, 222 in AN) reference as well as calculated lithium-metal potentials (Li|SEI|Li$^+$ 0.1 M) expressed versus the $E_{1/2}$(Fc|Fc$^+$), in ionic liquids and molecular liquids (supporting electrolyte: Et$_4$NClO$_4$ 0.1 M)

Medium	Potential [V]	
	$E_{1/2}(\mathrm{Fc}\vert\mathrm{Fc}^+)$ vs. $E(\mathrm{Ag}\vert\mathrm{Ag}^+222)$	$E(\mathrm{Li}\vert\mathrm{SEI}\vert\mathrm{Li}^+)$ vs. $E_{1/2}(\mathrm{Fc}\vert\mathrm{Fc}^+)$
[MePrPip$^+$][NTf$_2^-$]	0.541	−3.157
[EtMeIm$^+$][NTf$_2^-$]	0.502	−3.144
[BuMePyrrol$^+$][NTf$_2^-$]	0.536	−3.163
[Et$_3$S$^+$][NTf$_2^-$]	0.518	−3.152
[Et$_2$MeS$^+$][NTf$_2^-$]	0.508	−3.149
[MeOct$_3$N$^+$][NTf$_2^-$]	0.620	−3.270
[BuMePyrrol$^+$][OTf$^-$]	0.506	−3.361
[EtMeIm$^+$][OTf$^-$]	0.495	−2.407
[BuMeIm$^+$][OTf$^-$]	0.510	−2.572
[BuMePy$^+$][BF$_4^-$]	0.495	−3.358
[EtMeIm$^+$][BF$_4^-$]	0.476	−3.368
[BuMeIm$^+$][BF$_4^-$]	0.496	−3.301
[OctPy$^+$][BF$_4^-$]	0.546	−3.371
[BuMeIm$^+$][PF$_6^-$]	0.505	−2.750
PC	0.536	−3.381
γ-BL	0.525	−3.422
PC + EC	0.506	−3.333
DMC + EC	0.520	−3.331
DEC + EC	0.530	−3.338
DMSO	0.495	−3.780
AN	0.545	−3.365
TMS	0.526	−3.331

4 Conclusions

1. The potential of metallic lithium (E(Li|SEI|Li$^+$ 0.1 M) in ionic liquids (expressed vs. the Ag| (Ag$^+$222, AN) reference) is ca. −2.633 ± 0.017 V in ILs based on the [NTf$_2^-$] anion, while it is −2.848 ± 0.043 V in ILs containing the [BF$_4^-$] anion (the difference is ca. 200 mV). In the case of ionic liquids based on the triflate anion, the cation also influences the E(Li|SEI|Li$^+$) value: it is ca. 1.987 ± 0.075 V for imidazolium cations and much lower (−2.855 V) for the pyrrolidinium cation. In ionic liquid based on the imidazolium cation and hexafluorophosphate anion, the Li|SEI|Li$^+$ potential is −2.245 V.
2. The difference between the lowest (−2.892 V) and the highest (−1.912 V) lithium potential measured in ionic liquids is almost 1 V (0.980 V).
3. The Li|SEI|Li$^+$ (0.1 M) potential measured in cyclic carbonates is −2.780 ± 0.069 V.
4. The E(Li|SEI|Li$^+$) in DMSO shows the lowest value of ca. −3.285 V.
5. The difference between E(Li|SEI|Li$^+$ in [EtMeIm$^+$] [OTf$^-$]) and E(Li|SEI|Li$^+$ in DMSO) is as high as ca. 1.4 V.
6. Generally, potentials of the anode or cathode of lithium-ion cell are expressed versus the potential of lithium-metal (the Li|SEI|Li$^+$ couple) in a given solvent and are assumed to be zero, irrespective of the medium. However, this potential changes strongly when lithium-metal is transferred from one medium to another, and hence, the lithium foil contacted with the electrolyte cannot be used as an internal universal reference, characterized by a constant potential.

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