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Investigating the Electrode Kinetics of the Li/Li$^+$ Couple in a Wide Range of Room Temperature Ionic Liquids at 298 K

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Cyclic voltammetry experiments are carried out using a 0.1 M Li$^+$ solution in 12 different room temperature ionic liquids (RTILs), [C$_4$mpyrr][NTf$_2$], [C$_4$dmim][NTf$_2$], [N$_{2,1,1,3}$][NTf$_2$], [N$_{6,2,2,2}$][NTf$_2$], [C$_4$mim][OTf], [C$_4$mpyrr][N(CN)$_2$], [C$_2$mim][NTf$_2$], [P$_{14,6,6,6}$][FAP], [C$_4$py][NTf$_2$], [C$_4$mim][PF$_6$], [C$_4$mim][NTf$_2$], and [N$_{1,8,8,8}$][OTf], on a Ni microelectrode to investigate the deposition and stripping of lithium from the electrode surface. [C$_4$mpyrr][N(CN)$_2$], [C$_2$mim][NTf$_2$], [P$_{14,6,6,6}$][FAP], [C$_4$py][NTf$_2$], [C$_4$mim][PF$_6$], [C$_4$mim][NTf$_2$], and [N$_{1,8,8,8}$][OTf] did not have a wide enough potential window to observe the deposition and stripping of bulk lithium. In the experimental data recorded for [C$_4$mpyrr][NTf$_2$], [C$_4$dmim][NTf$_2$], [N$_{2,1,1,3}$][NTf$_2$], [N$_{6,2,2,2}$][NTf$_2$], and [C$_4$mim][OTf], a single stripping peak for bulk lithium is seen, and kinetic data for the Li/Li$^+$ couple are extracted by comparison with computational simulations. The electrochemical rate constant, k^0, is found to have values ranging from $(1.3 \cdot 10^{-6}$ to $1.2 \cdot 10^{-5})$ cm·s^{-1}. Diffusion coefficients for the Li$^+$ ion in these five RTILs are also reported.

Introduction

Research into the deposition and dissolution of lithium has attracted considerable interest over the last three decades.[1] This is because theoretically lithium has a high energy capacity (3860 mA·h·g^{-1}) which makes lithium a potential metal to be applied in battery and fuel cell technology. The current issue in performing this research is the need to find suitable electrolytes which possess electrochemical stability as well as low reactivity to lithium.[2] Room temperature ionic liquids (RTILs), often mentioned as molten organic salts at 298 K, are typically comprised of a bulk unsymmetric cation and an inorganic anion and exist in a liquid state at around 298 K. RTILs possess a number of physical properties including wide electrochemical windows, high electrical conductivity, high chemical and thermal stability, and favorable solvating properties which make them suitable for use in energy storage applications.[3−5] For safety reasons, low volatility and low combustibility make RTILs potentially more suitable as electrolytes for such applications than organic solvents.[6] Aqueous solutions cannot be used as the potential window is not wide enough and the deposited lithium would react with the water. The high viscosity of RTILs compared to traditional solvents (1 to 2 orders of magnitude) contributes significantly to the differences observed in the voltammetry. The structure of the ionic liquid determines its physical properties such as conductivity, potential window, and viscosity. Once a suitable electrolyte has been found, the deposition/dissolution of lithium can be performed, and the thermodynamics and kinetics of the process can be studied. Providing information about the electrochemical parameters of the Li/Li$^+$ couple in different ionic liquids is important especially when considering potential applications in battery technology.

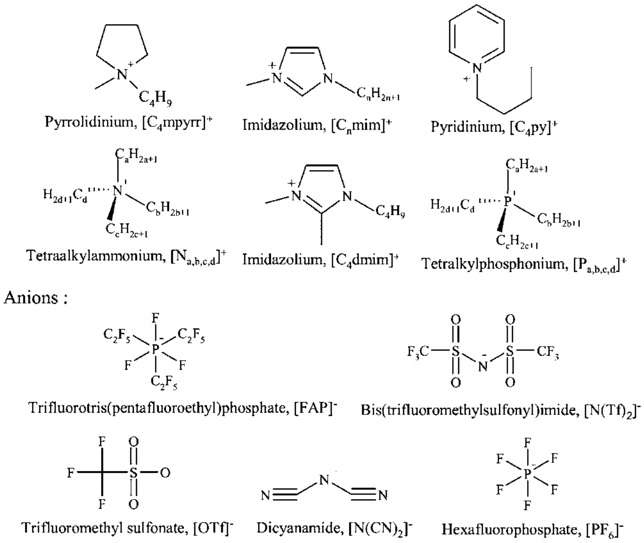

Figure 1. Structure of the cations and anions of the room temperature ionic liquids used in this study.

The aim of this paper is to study the Li/Li$^+$ couple in a range of RTILs to establish which have potential windows wide enough to observe the bulk deposition and stripping of lithium. These experiments are conducted using a nickel microelectrode as platinum and gold are known to show complicated voltammetry due to the formation of alloys with lithium. For RTILs that have a wide enough potential window, electrochemical parameters will be extracted using a mathematical model previously developed to study such deposition/dissolution systems.

Experimental Details

The structure and abbreviations of the cations and anions comprising the RTILs used in this study are shown in Figure 1. [C$_4$mim][OTf], [C$_4$mim][PF$_6$], and [P$_{14,6,6,6}$][FAP] were kindly donated by Merck KGaA, while all other ionic liquids used were obtained from QUILL, Belfast, having been prepared using

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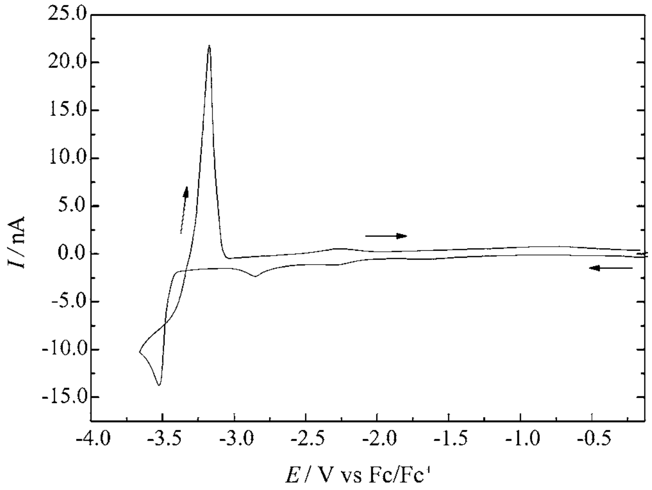

Figure 2. Cyclic voltammogram recorded for a 0.1 M $LiAsF_6$ in $[C_4dmim][NTf_2]$ solution on a 50 μm diameter Ni electrode. Scan rate = 10 $mV \cdot s^{-1}$.

standard literature procedures.[7] The structure of the cations and anions comprising the RTILs used in this study are shown in Figure 1. Lithium hexafluoroarsenate ($LiAsF_6$, Aldrich, 98 %) and ferrocene ($Fe(C_2H_5)_2$, Fc, Aldrich, 98 %) were used as received, without further purification.

Electrochemical measurements were conducted using a conventional two-electrode arrangement in a T-cell[8,9] purged under vacuum for 6 h prior to and during the experiments. A nickel microelectrode (50 μm diameter, fabricated in house, polished using (1.0, 0.3, and 0.05) μm alumina slurries (Buehler, Illinois) on a microcloth polishing pad (Buehler, Illinois) and further cleaned in an ultrasonic bath) was used as a working electrode, and a silver wire (Advent Research Materials Ltd., UK, 99.99 %) served as a quasi-reference electrode. Cyclic voltammetry was carried out using a computer-controlled μ-Autolab potentiostat (Eco-Chemie, Netherlands). For each experiment, a section of a disposable micropipet tip (Eppendorf, Germany) was placed on the top of the working electrode, into which 20 μL of the RTIL of interest containing 0.1 M $LiAsF_6$ and 10 mM ferrocene (Fc) was inserted. All potentials in this paper are quoted versus the Fc/Fc^+ reference couple in the RTIL being studied, and all experiments reported were carried out at 298 K in a temperature-controlled box which also functioned as a Faraday cage.

Results and Discussion

Figure 2 shows an example of the voltammetry recorded on a clean electrode on the first cycle when the potential window of the RTIL is wide enough. This cyclic voltammetry was recorded by sweeping the potential from (−0.2 to −3.65) V versus Fc/Fc^+ and back with a 0.1 M $LiAsF_6$ solution in the RTIL $[C_4dmim][NTf_2]$ at a scan rate of 10 $mV \cdot s^{-1}$. The small peaks observed on the forward scan between (−2 and −3) V were due to the underpotential deposition (UPD) of lithium, whereas the current recorded below −3.4 V is due to bulk lithium deposition. On the reverse scan, a sharp stripping peak for bulk lithium is observed at ca. −3.2 V, and the small peaks above this are due to the stripping of the UPD layers.

The potential window of a clean Ni electrode in a blank RTIL solution is smaller than that when lithium ions are present. This is due to the underpotential deposition of a lithium monolayer onto the nickel surface which changes the character of the working electrode. It is therefore not possible to judge whether the potential window of an ionic liquid is wide enough to study bulk lithium deposition without running a full cyclic voltammogram with lithium ions present.

Twelve different ionic liquids were used as supporting electrolytes to perform lithium electrochemistry, and a summary of the results is provided in Table 1. Five different ionic liquids (Table 1a−e) were found to be stable enough to reach the potential of the bulk Li/Li^+ process and showed voltammetry with the same characteristics as shown in Figure 2; however, the magnitude of the current recorded and amount of lithium deposited and stripped varied. Seven other ionic liquids (Table 1f−l) seem to be too unsuitable to support lithium electrochemistry as they tend to breakdown before reaching the deposition and dissolution process of bulk lithium. Therefore no observable bulk stripping signals can be seen in the voltammetry. It is noticed however that the underpotential deposition signals can still be observed in $[C_4mpyrr][N(CN)_2]$, $[C_2mim][NTf_2]$, $[C_4mim][NTf_2]$, and $[N_{1,8,8,8}][OTf]$. The ionic liquids $[C_4mim][PF_6]$ and $[P_{14,6,6,6}][FAP]$ seem to react with $LiAsF_6$ as suggested by the observation of a color change of the solutions to blue and green, respectively.

For the ionic liquids that are stable enough to observe bulk lithium deposition and stripping, the kinetics and thermodynamics of the Li/Li^+ can be studied by comparing the experimental data to simulation generated using a mathematical model and its associated computer program previously developed.[10,11] In this model, the simple one-electron transfer for the deposition and stripping of lithium is considered. The diffusion of Li^+ in the solution is assumed to follow Fick's second law of diffusion and is incorporated within the mathematical model. The electrode surface boundary condition is based on the bulk deposition and stripping of lithium on the electrode surface where the surface coverage of lithium, Γ_{Li}, present on the surface

Table 1. Experimental Observations and Parameters Extracted by Simulation for the Li/Li^+ Couple in a Range of Room Temperature Ionic Liquids (RTILs) at 298 K

no.	RTIL	viscosity η/(mPa·s) (T = 298 K)	bulk lithium stripping observed?	diffusion coefficient[a] $10^8 D/(cm^2 \cdot s^{-1})$	rate constant[a] $10^5 k^0/(cm \cdot s^{-1})$	formal potential[a] E_f^0/(V) vs Fc/Fc^+	transfer coefficient[a] α
a	$[C_4mpyrr][NTf_2]$	89[14]	yes	4.5 ± 0.1	1.20 ± 0.05	−3.26 ± 0.01	0.63 ± 0.01
b	$[C_4dmim][NTf_2]$	105[14]	yes	5.0 ± 0.1	5.50 ± 0.05	−3.13 ± 0.01	0.50 ± 0.01
c	$[N_{2,1,1,3}][NTf_2]$	–	yes	2.8 ± 0.1	1.00 ± 0.05	−3.24 ± 0.01	0.50 ± 0.01
d	$[N_{6,2,2,2}][NTf_2]$	167[15]	yes	1.9 ± 0.1	5.00 ± 0.05	−3.17 ± 0.01	0.50 ± 0.01
e	$[C_4mim][OTf]$	90[16]	yes	3.1 ± 0.1	1.30 ± 0.05	−3.39 ± 0.01	0.70 ± 0.01
f	$[C_4mpyrr][N(CN)_2]$	–	no - UPD[b] only	–	–	–	–
g	$[C_2mim][NTf_2]$	34[16]	no - UPD[b] only	–	–	–	–
h	$[P_{14,6,6,6}][FAP]$	464[17,18]	no	–	–	–	–
i	$[C_4py][NTf_2]$	60[19]	no	–	–	–	–
j	$[C_4mim][PF_6]$	371[20]	no	–	–	–	–
k	$[C_4mim][NTf_2]$	52[16]	no - UPD[b] only	–	–	–	–
l	$[N_{1,8,8,8}][OTf]$	–	no - UPD[b] only	–	–	–	–

[a] All electrochemical parameters (D, k^0, E_f^0, and α) are obtained by means of fitting experimental results with the theoretical model. These values are given with their corresponding uncertainties. [b] UPD stands for underpotential deposition.

does not have an effect on the rate of deposition or stripping and is given by eq 1

$$\frac{\partial \Gamma_{\mathrm{Li}}}{\partial t} = D \cdot \frac{\partial [\mathrm{Li}^+]}{\partial z} = k_a \cdot [\mathrm{Li}^+]_{z=0} - k_d \qquad (1)$$

where D is the diffusion coefficient and k_a and k_d are the Butler−Volmer rate constants for the addition and dissolution of lithium from the surface, respectively. As the stripping process must stop when all lithium has been removed from the surface and the surface coverage is therefore not permitted to go below zero, an addition condition is needed within the model: when $(\partial \Gamma_{\mathrm{Li}}/\partial t) > k_a \cdot [\mathrm{Li}^+]_{z=0} - k_d$, k_d is set so that $k_d \cdot \partial t = -\partial \Gamma_{\mathrm{Li}} + k_a \cdot [\mathrm{Li}^+]_{z=0} \cdot \partial t$. In some cases, it is necessary to baseline correct the experimental data before simulation can take place.

Table 1a−e presents the electrochemical parameters for Li/Li^+ couple at room temperature in five different ionic liquids extracted from the experimental data using the mathematical model described above. $[\mathrm{C_4mpyrr}][\mathrm{NTf_2}]$, $[\mathrm{C_4dmim}][\mathrm{NTf_2}]$, $[\mathrm{N_{2,1,1,3}}][\mathrm{NTf_2}]$, $[\mathrm{N_{6,2,2,2}}][\mathrm{NTf_2}]$, and $[\mathrm{C_4mim}][\mathrm{OTf}]$ all show good electrochemical responses for Li/Li^+, and the kinetics are all within a narrow range. The combination of the $[\mathrm{NTf_2}]^-$ anion with the butylmethylpyrrolidinium cation ($[\mathrm{C_4mpyrr}]^+$) provides both a relatively fast rate constant and diffusion coefficient for the Li/Li^+ couple compared to other ionic liquids. Other $[\mathrm{NTf_2}]^-$ salt families that indicate good performance to support lithium electrochemistry are quaternary ammonium ($[\mathrm{N_{2,1,1,3}}]^+$ and $[\mathrm{N_{6,2,2,2}}]^+$) and immidazolium ($[\mathrm{C_4dmim}]^+$). These types of ionic liquid have been used to study the lithium system due to their stability upon application of extreme cathodic potentials.[12] The differences in the diffusion coefficients may result from the differences in the viscosities (η), which have an impact on the transport property of lithium ions to the electrode surface. However, the diffusion coefficient for Li^+ did not scale with η^{-1} as would be expected from Stokes−Einstein behavior.[13] $[\mathrm{C_4mim}][\mathrm{OTf}]$ shows a slightly slower rate constant and a higher transfer coefficient than any of the $[\mathrm{NTf_2}]^-$ salts indicating that changing the anion of the ionic liquid can make a difference to the voltammetry. However, the electrochemical rate constant, k^0, does not vary over a significant range, and the slight difference between the various RTILs probably reflects the slightly altered solvation of the Li^+.

Conclusions

The Li/Li^+ couple has been investigated in a range of RTILs. A number of these RTILs ($[\mathrm{C_4mpyrr}][\mathrm{N(CN)_2}]$, $[\mathrm{C_2mim}][\mathrm{NTf_2}]$, $[\mathrm{P_{14,6,6,6}}][\mathrm{FAP}]$, $[\mathrm{C_4py}][\mathrm{NTf_2}]$, $[\mathrm{C_4mim}][\mathrm{PF_6}]$, $[\mathrm{C_4mim}][\mathrm{NTf_2}]$, and $[\mathrm{N_{1,8,8,8}}][\mathrm{OTf}]$) were found to break down before the onset of the deposition and stripping of bulk Li and were therefore not investigated further. For the RTILs that have potential windows wide enough to observe the bulk deposition and stripping of lithium ($[\mathrm{C_4mpyrr}][\mathrm{NTf_2}]$, $[\mathrm{C_4dmim}][\mathrm{NTf_2}]$, $[\mathrm{N_{2,1,1,3}}][\mathrm{NTf_2}]$, $[\mathrm{N_{6,2,2,2}}][\mathrm{NTf_2}]$, and $[\mathrm{C_4mim}][\mathrm{OTf}]$), mathematical modeling and numerical simulation have been used to extract kinetic data for the Li/Li^+ couple. The rate constant, k^0, for the Li/Li^+ couple did not vary significantly when the $[\mathrm{NTf_2}]^-$ anion was used with a range of cations to form the ionic liquid; however, a slight changing was observed in the voltammetry when the anion was changed to $[\mathrm{OTf}]^-$. The slight differences in the rate constant and transfer coefficient probably reflect the different solvation of the Li^+ ions in the different RTILs. Formal potentials for the Li/Li^+ couple are also reported.

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