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Anion effect on lithium electrodeposition from *N*-propyl-*N*-methylpyrrolidinium bis(fluorosulfonyl)imide ionic liquid electrolytes

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ABSTRACT

The electrodeposition of lithium metal from room temperature ionic liquid (RTIL) electrolytes consisting of *N*-propyl-*N*-methylpyrrolidinium bis(fluorosulfonyl)imide (Pyr_{13}[FSI]) with LiFSI, LiTFSI, $LiBF_4$, $LiPF_6$ or $LiAsF_6$ salts onto Pt and Li electrodes was undertaken to identify mechanistic details. Cyclic voltammetry at both Pt and Li electrodes is complicated by the chemical reaction between fresh/electrodeposited Li metal and electrolyte to form a solid-electrolyte interphase (SEI). As such, all electrolyte systems depict quasi-reversible cycling, owing to the concomitant chemical breakdown of the electrolyte and deposition of a passivation product onto the electrode surface. The rate at which the SEI forms can be observed through cyclic voltammetric scan rate studies. Chronoamperometry data supports the cyclic voltammetry studies and indicates that an instantaneous nucleation and growth type mechanism is taking place at all potentials as determined through modelling the current-time transients utilising the Hills-Scharifker theory. We show herein that these RTIL based electrolytes can be cycled effectively in an order of stability of salt inclusion as follows: $LiBF_4 > LiFSI > LiAsF_6 > LiTFSI > LiPF_6$.

1. Introduction

With the world focus on the reduction of CO_2 emissions through development of more benign transportation technologies, the role of batteries to enable zero emission vehicles is becoming crucial. It has already been shown that the current generation of lithium or nickel batteries are at the limits of power and energy they can supply [1]. Clearly a step-change technology is required to power transportation according to consumer demand. Lithium metal batteries have long been touted as the preferred lithium battery technology to realise this highly challenging goal. Even though this technology in principle can provide a practical energy density similar to petroleum [2] this has not yet been accomplished. Numerous technical challenges still exist, including the key issues around dendrite formation and subsequent short circuiting, stability of electrolytes, robustness of the solid electrolyte interphase (SEI) formed from electrolyte breakdown on the lithium surface and critically the ability for safe and repetitive cycling. [3], Developing next generation lithium metal battery technologies, such as Li-S and Li-Air (O_2) is entirely dependent on the long term stability and reliability of the Li metal anode. Previous research conducted for lithium metal batteries using carbonate based electrolyte systems show that these solvents are not suitable for lithium metal batteries [4,5]. Since lithium metal battery technology has been notoriously set back by problems such as dendrite formation and subsequent short circuiting during cycling of lithium metal anodes, it is hypothesised that using room temperature ionic liquids, RTILs, may overcome this issue [6,7]. The tailorable properties of ionic liquids such as conductivity, viscosity and electrochemical (EC) window and stability, through appropriate choices of anion and cation is what makes these solvents ideal for this application. Furthermore, it has been documented that RTILs typically demonstrate instantaneous nucleation and growth mechanisms for electrodeposited metals [8–13], which is ideal for dendrite suppression.

Studies have been conducted using several RTILs which include, imidazolium cation based RTILs using the bis(trifluoromethanesulfonyl)imide $TFSI^-$, tetrafluoroborate BF_4^-, and hexafluorophosphate PF_6^- anions [14], quaternary ammonium cations paired with $TFSI^-$ anions[15] as well as several studies using RTILs based on the pyrrolidinium cation paired with the $TFSI^-$ anion as well as the

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analogous bis(pentafluoroethanesulfonyl)imide PFSI$^-$ and bis(fluorosulfonyl)imide anions FSI$^-$ [16–20].

Recent studies have demonstrated that the *N*-propyl-*N*-methylpyrrolidinium bis(fluorosulfonyl)imide (Pyr_{13}[FSI]) ionic liquid is the most suitable electrolyte for lithium plating and stripping [21]. These studies showed that the pyrrolidinium cation based RTIL provides the best cathodic stability compared to a range of other cations [21]. The work also provided insight into the benefits of utilising the FSI$^-$ anion to facilitate highly reversible electrodeposition and stripping facilitated by stable SEI formation on a lithium surface. Indeed, a recent study by our group demonstrated commercially acceptable battery cycling utilizing lithium metal anodes with lithium iron phosphate cathodes [22,23]. Li electrodeposition and subsequent morphological changes of lithium foil surfaces, during cell cycling has also been investigated at a variety of different current densities [24].

In another study lithium electrodeposition and stripping was investigated at nickel and platinum electrodes from a Pyr_{13}[FSI] and LiFSI electrolyte [8]. A cyclic voltammetric (CV) study showed that platinum electrodes provided the most stable electrodeposition/stripping results, displaying high coulombic efficiency in comparison to the nickel electrode. That study highlighted that cycling behaviour is highly dependent upon the choice of electrode material which led to two diverse SEI formation pathways. Chronoamperometry (CA) data showed that the deposition mechanism conformed to an instantaneous nucleation and growth type mechanism when analysed using Scharifker and Hills theory [25].

Following on from these studies, we herein report an investigation into the electrochemical properties and behaviour of five salt/RTIL mixtures at a platinum electrode as well as a lithium metal substrate to determine which particular salt/RTIL mixture will provide the best coulombic efficiency, stability and cyclability lifetime using the techniques of cyclic voltammetry and chronoamperometry. These techniques are also used to gain an understanding of the processes which occur at the electrode during cycling, and to ascertain why there may be a salt dependence on cycling performance. Salts used are lithium bis(fluorosulfonyl)imide (LiFSI), lithium hexafluoroarsenate ($LiAsF_6$), LiTFSI, $LiPF_6$ and $LiBF_4$.

2. Experimental

2.1. Reagents and Materials

Lithium metal foils (China Energy Lithium, 0.33 mm, 99%) foils were cleansed of surface contaminants using a nylon brush under n-hexane (Merck). The RTIL Pyr_{13}[FSI] (Dai-Ichi Kogyo Seigaku, >99%) was dried using Schlenk line techniques at 100 °C for 12 h prior to handling and storage within an Ar atmosphere (<5 ppm H_2O, <1 ppm O_2) Karl Fischer titration of the RTIL dried using this method indicated less than 10 ppm moisture content. Lithium salts were dried according to literature reports [6]. Electrolyte mixtures containing 0.5 mol kg^{-1} of a lithium salt in the Pyr_{13}[FSI] were stored and used within the Ar atmosphere after drying for 24 h *in vacuo*. The lithium salts were purchased commercially; LiFSI (Dai-Ichi Kogyo Seigaku, >95%), LiTFSI (3 M Fluorad, >99.5%), $LiBF_4$ (Stella Chemica, >98%), $LiPF_6$ (Sigma, 98%) and $LiAsF_6$ (Sigma-Aldrich, 98%). A density of 1.34 g cm^{-3} was measured for the IL/Li salt solutions and used for calculations where required.

2.2. Electrochemical measurements

Voltammetric experiments were conducted at 20 ± 2 °C with an Autolab (CHI 760C) electrochemical analyser in an electrochemical cell that allowed reproducible positioning of the working, reference, and auxiliary electrodes. A 0.0078 cm^2 platinum electrode (BASi) was used as the working electrode. Prior to electrodeposition on Pt the electrode was polished with an aqueous 0.3 μm alumina slurry (Electron Microscopy Sciences) on a polishing cloth (Microcloth, Buehler), thoroughly rinsed with Milli-Q water, acetone, and then dried with a flow of nitrogen gas. The reference electrode was Ag/Ag$^+$ (10 mM AgOTf in Pyr_{14}[TFSI]) [32]. In the case of experiments carried out on lithium, a lithium foil masked using Kapton (DuPont) exposing a circular 0.1256 cm^2 was used. A platinum wire (CH Instruments) was used as the counter electrode. All electrochemical experiments were commenced after degassing the electrolyte solutions with Ar for at least 10 m prior to any measurement.

3. Results and Discussion

3.1. Cyclic voltammetry of lithium salts on platinum metal

The electrolyte systems used in this study are: LiFSI/Pyr_{13}[FSI], LiTFSI/Pyr_{13}[FSI], $LiBF_4$/Pyr_{13}[FSI], $LiPF_6$/Pyr_{13}[FSI] and $LiAsF_6$/Pyr_{13}[FSI], were all at a salt concentration of 0.5 mol kg^{-1}. It is hypothesised that similarities/differences exist between the highly fluorinated LiTFSI and the analogous but less viscous LiFSI salt, both of which are imides that differ in replacement of both the TFSI pendent CF_3^- functional groups by F$^-$ to form the FSI$^-$ anion. These salts are then compared to the second lithium salt group comprising of tetrahedral $LiBF_4$ and the octahedral salts $LiPF_6$ and $LiAsF_6$. Thus, the effect of the structural composition of the Li salt anions on cycling properties can be ascertained.

Fig. 1a shows typical cyclic voltammograms recorded at a platinum electrode in neat Pyr_{13}[FSI] starting at 0.0 V vs. Ag|Ag$^+$ (-0.39 V vs. Fc/Fc$^+$). The electrochemical window for the FSI based IL at a lithium electrode is consistent with previous studies [8,26]. Two scans were measured, one in which the potential was scanned positively, and another negatively in order to understand if any scan direction dependent processes were occurring. As expected a peak at *ca.* −0.5 V is present in the scan which was initially ramped positively using a Pt electrode. This peak has been reported[26] to be an oxidation product of the IL as it is absent from the negatively ramped scan. The electrochemical window is *ca.* 6.0 V exhibiting a reductive limit (defined as a threefold increase from baseline current) nearing −4.0 V which is consistent with work published previously [26,27]. Also shown in Fig. 1a are typical cyclic voltammograms observed using a lithium electrode in the absence of Li$^+$ salts in the region of −3.0 V to −4.7 V. As expected, in the absence of Li$^+$ no reduction processes are observed.

The redox behaviour of the Li$^{+/0}$ couple at a platinum electrode was observed using cyclic voltammetry in a LiFSI/Pyr_{13}[FSI] electrolyte over a potential region from −2.0 V, where no processes occur at a polished platinum electrode, to a lower limit of −4.25 V, Fig. 1b. The Li electrodeposition process, E_p^{red}, is observed at −3.71 V and the stripping process, E_p^{ox}, at −3.22 V at a scan rate of 10 mV s^{-1}. The peak-peak separation (ΔE_p^{ox-red}) of 483 mV is far greater than the expected 70 mV for a reversible process. The combination of IR_u effects and concomitant chemical SEI formation on the surface of the freshly deposited Li metal accounts for the large differences observed for all the systems investigated. The shoulder observed more positive than E_p^{ox} resolves into a distinct peak (-3.24 V) at a scan rate of 2 mV s^{-1}. An additional oxidative process at *ca.* −2.85 V can also be observed and is attributed to lithium stripping from a lithium-platinum metal alloy also formed during the deposition process [8].