In situ electrochemical-X-ray Photoelectron Spectroscopy: Rubidium metal deposition from an ionic liquid in competition with solvent breakdown

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1. Introduction

Rubidium is one of the Group I alkali metals, which are characteristically strong reducing agents. The formal potential ($E^0_f$) of the Rb/Rb$^+$ couple in aqueous solution is $-2.94$ V (vs. SHE) [1], while the $E^0_f$ for Rb/Rb$^+$ in the ionic liquid $\text{[C}_4\text{mPyrr][NTf}_2\text{]}$ has recently been measured as $-3.37$ V (vs. $\text{Fc/Fc}^+$) [2]. This property makes Rb a potential candidate for use in solid batteries [3] as well as energy storage devices [4]. Rubidium cannot be electrodeposited from aqueous solution or many organic solvents as their potential windows are not wide enough.

Room temperature ionic liquids (RTILs or ILs), which are typically comprised entirely of ions, are promising media for the deposition of active metals such as Rubidium [2,5]. Their intrinsic ionic conductivity, chemical stability as well as wide electrochemical windows makes the electrodeposition of many active metals possible [6]. Moreover, another important property of ILs is that they possess near zero vapour pressure. The combination of these properties has facilitated novel spectroelectrochemical techniques under high vacuum conditions, including in situ electrochemical -X-ray spectroscopy. A number of publications are available regarding the use of in situ electrochemical-XPS measurements in conjunction with ILs, probing the oxidation of Cu to Cu$^+$ [7], reduction of Fe(III) to Fe(II) [8], the intercalation of $\text{[C}_2\text{mim][BF}_4\text{]}$ into HOPG [9], and the XPS induced charging [10] and electrochemical shift in binding energy [11] of ionic liquids. The diverse range of other (non-electrochemical) studies relating to combined IL-XPS studies has recently been reviewed [12].

We have reported the electrodeposition of Group I alkali metals from the ionic liquid N-butyl-N-methylpyrrolidinium bis(trifluoromethylsulfonyl)imide ($\text{[C}_4\text{mpyr][NTf}_2\text{]}$) on Pt and Ni electrodes [2,13–15]. The fundamental kinetic and thermodynamic properties have been determined by means of simulation [2,13–15]. In addition, recently we have reported the in situ electrochemical-XPS measurements to monitor the electrodeposition of potassium in the ionic liquid of $\text{[C}_4\text{mpyr][NTf}_2\text{]}$ using in situ electrochemical-XPS measurements [16]. Unlike potassium, rubidium electrodeposition is close to the reductive breakdown of $\text{[C}_4\text{mpyr][NTf}_2\text{]}$. In this Letter, we report the use of in situ electrochemical-XPS to explore the breakdown of the solvent in competition with the electrodeposition of rubidium.

2. Experimental

N-butyl-N-methylpyrrolidinium bis(trifluoromethylsulfonyl) imide, $\text{[C}_4\text{mpyr][NTf}_2\text{]}$, was prepared using standard literature methods [17]. The Rb$\text{[NTf}_2\text{]}$ salt was prepared by the reaction of aqueous solutions of rubidium hydroxide with a 5% molar excess of H$\text{[NTf}_2\text{]}$, followed by repeated dissolution in water then drying under vacuum, until pH neutral.

XPS measurements were performed using a VG ESCALAB MkII spectrometer equipped with a monochromatic Al K$\alpha$ X-ray source (photon energy of 1486.6 eV). Survey scans and detailed scans were recorded with a constant analyser pass energy of 100 and 20 eV, respectively. Prior to measurement, the cell was put under high vacuum conditions, including properties has facilitated novel spectroelectrochemical techniques possessing near zero vapour pressure. The combination of these reduction of Fe(III) to Fe(II) [8], the intercalation of $\text{[C}_2\text{mim][BF}_4\text{]}$ into HOPG [9], and the XPS induced charging [10] and electrochemical shift in binding energy [11] of ionic liquids. The diverse range of other (non-electrochemical) studies relating to combined IL-XPS studies has recently been reviewed [12].

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vacuum in a desiccator overnight to remove dissolved water and gases. In order to prevent ionic liquid loss during degassing, a specially designed lid was used. The cell was then rapidly transferred to the XPS entry chamber and evacuated for a further 2 h before being moved into the sample chamber.

All electrochemical measurements were carried out using a computer-controlled PGSTAT-12 Autolab potentiostat (Eco-Chemie, Netherlands).

3. Results and discussion

3.1. Experimental set-up

The in situ electrochemical-XPS cell (Figure 1a) and holder (Figure 1b) used in this study were fabricated in-house and are modifications of a previously reported electrochemical setup [16]. Briefly, the cell holder was a previously described mobile cell holder [16] that had been fixed permanently onto the end of an extendable and retractable manipulator arm which was inserted into the XPS chamber through a high vacuum flange. The sample-holding cell consisted of two parts, namely two hollow cylinders of PEEK with the bottom of one sealed by a modified copper XPS stub, which were manufactured and joined as previously detailed elsewhere [16]. An arm was placed on the side of the cell in order to allow movement of the cell with a standard manipulator arm. The cell was lowered from above onto two pogo spring pins emerging from the holder which entered tapered holes in the cell and made electrical contact with the working and reference electrodes, respectively, via copper foil. Much of the counter electrode passed through a hole in the holder before coming to rest on a copper o-ring set in the holder. Three shielded wires ran from the holder to the potentiostat via an electrical feed-through in the XPS housing. Once the cell was secured on top of the holder, the standard XPS holder was retracted and the entire assembly extended until the sample was in line with the X-ray source.

3.2. XPS measurement of the ionic liquid

The XPS survey scan of 0.1 M Rb[NTf2] in [C4mpyrr][NTf2] recorded in the XPS-electrochemistry cell prior to any electrochemical experiments is depicted in ‘0 h’ spectrum in Figure 2. Very weak Rb signals were observed, although this is easily explained by the relatively dilute nature of the solution (in terms of atomic % values). Signals were observed corresponding to C, N, O, F and S. Analysis of these signals were similar to those expected based upon the stoichiometric ratio for the pure ionic liquid (deviation less than 5%), using the widely available and frequently used standard atomic sensitivity factors by Wagner et al. [18]. Minor differences between measured and known atomic ratios during XPS measurements of ILs have been reported before, and have been attributed to system-dependant deviations which require the development of system-specific atomic sensitivity factors using ‘ultrapure’ ILs [12,19]. In this work the sensitivity factors of Wagner et al. [18] were found to provide a sufficient degree of accuracy. No impurities were detected in the [C4mpyrr][NTf2], either by XPS or cyclic voltammetry.

Weak signals were also observed corresponding to the Ni mesh electrode (Ni 2p3/2 at 855 eV). This relatively weak signal (compared to the quantity of Ni present) was due to the take-off angle of 75° employed on the curved Ni wires of the mesh, e.g. if the sample was rotated to give a take-off angle of 90° a significantly stronger Ni peak was observed, although measurements could not be performed at this angle when the cell contained a liquid sample.

3.3. In situ electrodeposition-XPS measurements

Galvanostatic electrolysis was performed by passing a constant current at a Ni mesh electrode in the electrochemistry-XPS cell

![Figure 1. In situ electrochemical-XPS cell (a) and associated holder inside the XPS chamber (b).](image)

![Figure 2. XPS survey scans (pass energy 100 eV, 5 scans) recorded during electrolysis at $-5 \times 10^{-4}$ A at a Ni mesh electrode floating on a [C4mpyrr][NTf2] containing 0.1 M Rb[NTf2]. The scan were recorded after 0, 1 and 6 h of electrolysis.](image)
containing 0.1 M Rb[NTf2] in [C4mpyr][NTf2].\textsuperscript{1} The progress of the electrolysis was monitored periodically by XPS, using both wide survey scans as well as detailed scans in the Rb 3d region.

Figure 2 displays the survey scans recorded before and during electrolysis at a fixed current of $-5 \times 10^{-4}$ A. It can be clearly observed that after 1 h of electrolysis a significant Rb 3d signal was present, due to accumulation of Rb by its electrodeposition at the Ni-IL-vacuum three-phase boundary. The signal increased when the electrolysis was extended to 6 h, indicating increasing quantities of Rb metal. In addition to the growth of the Rb features, it was also observed that the stoichiometric ratio of the constituent IL elements (C, N, O, F and S) gradually changed with the atomic percentage of C increasing from ca. 44% to ca. 69% after 1 h electrolysis, indicating significant carbonisation of the ionic liquid was occurring in conjunction to Rb electrodeposition. After 6 h the N features were also observed to merge to form one single feature, rather than the two features expected for the different N present in the anion and cation\textsuperscript{[12]}. Weingarth have previously monitored the reductive decomposition of [C2mim][BF4] at a Pt electrode by XPS, where as an increasingly negative potential was applied a minor N feature (shifted by 2.5 eV relative to the imidazolium N) was observed and was attributed to a decomposition product of the cation\textsuperscript{[11]}. A further experiment was performed by decreasing the current by a factor of 50, to $-1 \times 10^{-5}$ A. Figure 3a shows detailed scans recorded in the Rb 3d region during electrolysis. From the figure it can clearly be seen that a Rb signal was observed after 1 h of electrolysis, and that the Rb signal increased as the electrolysis time was extended. The quantity of Rb detected was found to increase in an approximately linear manner with time (Figure 3b), and after 26 h a total of 0.94 C was passed, corresponding to approximately 0.8 mg of Rb metal deposited (assuming 100% col-

mucic efficiency).

After 26 h the electrolysis was ceased and all connections running from the potentiostat to the XPS unplugged. The system was allowed to remain like that for 1 h before another XPS measurement recorded. There were no significant differences before and after the system was allowed to rest for 1 h, indicating that the Rb electrodeposited was stable. After this the cell was reconnect-

ed, and the Rb deposit oxidised at an applied potential of 0 V vs. Pt wire quasi-reference for 30 min. Figure 4 displays the detailed XPS scans for Rb 3d taken (a) after 26 h of electrodeposition and (b) after the subsequent application of 0 V for 30 min. The de-
crease in the size of the Rb peak corresponds to the oxidation of Rb to Rb[NTf2], some of which diffused away on the timescale of the oxidation.

Detailed analysis of the composition of the IL at the Ni-IL-vacuum interface was performed by examining the IL signals from a range of survey scans (Figure 5). The corresponding atomic % of each IL element obtained from the detailed scans as a function of electrolysis time has been displayed in Figure 6, as well as solid lines representing the expected (stoichiometric) values for the IL based upon. Minor discrepancies between measured and expected elemental compositions at short times are associated with non-optimised atomic sensitivity factors, as described by Kolbeck et al.\textsuperscript{[20]}. The IL composition was observed to stay essentially constant within the first 3 h of electrolysis. However, from 5 h onwards deviation consistent with the carbonisation of the ionic liquid was observed, likely due to the exhaustion of Rb\textsuperscript{+} near the electrode surface after extended electrolysis. The C signal was observed in increase from ca. 44\% to ca. 58\% over 22 h, while the N signal was observed to remain constant, S and O decreased slightly and the F signal decreased significantly. This could be consistent with the reduction of the pyrrolidinium cation at the Ni electrode (likely through cleavage of an N–C bond to form methylpyrrolidine and a butyl radical or ring opening to a dibutylmethylen radical, based upon quantum chemical calculations\textsuperscript{[21]}. followed by subsequent reduction and/or polymerisation of the reduced tertiary amine), and concurrent loss of the [NTf2]- anion at the counter electrode. Alternatively, findings by other researchers have pointed towards the possibility of electrochemical reduction of the [NTf2]- anion\textsuperscript{[22–24]}, with the major gaseous product having been identified as trifluoromethane\textsuperscript{[23]}. The reductive loss of tri-

fluoromethane appears to agree with the XPS monitored

\textsuperscript{1} The potentiostatic electrolysis of K from [C4mpyr][NTf2] with concurrent XPS measurement has been previously reported, with the onset of K electrodeposition from [C4mpyr][NTf2] being clearly resolved from the solvent breakdown features\textsuperscript{[22]} in the case of Rb, potentiostatic electrolysis could not be achieved in [C4mpyr][NTf2] as the difficulties introduced by the similar potentials for Rb nucleation and [C4mpyr][NTf2] reduction are compounded by the limitations of quasi-reference electrodes and the volatility of the ferrocene/ferrocenium reference couple\textsuperscript{[25]}.
degradation of the [C4mpyr][NTf2], namely the rapid loss of F in comparison with the other elements.

In order to show the effect of different currents in the electrodeposition of rubidium and the decomposition of the IL, the change in atomic percentage of Rb and C during the electrolysis is compared (Figure 7a and b). At relatively high current (Figure 7a), the trends show both deposition and decomposition are prevalent. At lower current (Figure 7b) almost constant C is observed although Rb is significantly deposited. Thus the lower current promotes deposition over decomposition.

4. Conclusions

The electrodeposition of rubidium has been performed by in situ electrodeposition-XPS employing a novel cell design. The in situ electrochemical-XPS technique allows monitoring of the progress of Rb electrodeposition as well as the competing decomposition of the ionic liquid during the electrodeposition. Passing a high cathodic current for the electrodeposition resulted in rapid decomposition of the ionic liquid in addition to Rb electrodeposition. On the other hand, lowering the current for electrodeposition slows down the decomposition during the electrodeposition process.

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References