



Unexpected decomposition of the bis (trifluoromethylsulfonyl) amide anion during electrochemical copper oxidation in an ionic liquid

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ABSTRACT

In this letter we report on the decomposition of the bis (trifluoromethylsulfonyl) amide (TFSA) anion under quite mild electrochemical conditions. The results show clearly that the TFSA anion can easily be decomposed during anodic oxidation of copper in the ionic liquid 1-butyl-1-methylpyrrolidinium bis (trifluoromethylsulfonyl) amide [BMP] TFSA at 70 °C leading to the formation of CuF₂. At room temperature, however, no significant decomposition was obtained. Therefore, one has to be very careful in applying ionic liquids based on TFSA anions under anodic conditions at elevated temperature as the TFSA anion might decompose, depending on the anode material.

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1. Introduction

In recent years, air and water stable ionic liquids have proved to be promising solvents for a wide variety of applications including electrodeposition, batteries, catalysis, separations and organic synthesis [1–3]. Ionic liquids based on the bis(trifluoromethylsulfonyl)amide anion (TFSA) are often recommended as potential solvents for many electrochemical applications: the hydrophobic nature of the TFSA anion makes such ionic liquids easy to dry, furthermore low melting points of the resulting ionic liquid are obtained. Delocalization of the negative charge along the –S–N–S– core of the TFSA anion reduces the strength of cation–anion interactions leading to low melting ionic liquids. We employed TFSA ionic liquids for electrodeposition of metals and semiconductors; see for example [4–6]. Moreover, the TFSA ionic liquids were investigated for use in Li-batteries [7,8].

The electrochemical stability of ionic liquids is a key factor in their successful applications in various electrochemical processes. Unfortunately, little is known on the cathodic and anodic decomposition reactions of both cations and anions of ionic liquids. Witkamp et al. [9] investigated the cathodic decomposition of two ionic liquids, [BMP] TFSA and [BMIm]BF₄, by quantum chemical calculations and NMR. They found that there are several pathways for decomposition of the cations at a potential below their stability limit.

To the best of our knowledge there are no systematic studies available on the anodic decomposition of TFSA ionic liquids, but the decomposition of the TFSA anion under cathodic conditions was reported [10,11]. MacFarlane et al. [10] showed that the TFSA anion is subject to an irreversible cathodic breakdown prior to the massive reduction of the [EMIm] cation in the ionic liquid [EMIm] TFSA. In their opinion the reduction of the TFSA weakens one of the N–S bonds leading to its cleavage to a new anion, SO₂CF₃[–], and a reactive radical, [•]NSO₂CF₃, which can undergo further reduction to NSO₂[–], CF₃SO₂[–] and CF₃. In contrast, Passerini and co-workers [12,13] reported that the TFSA anion is cathodically stable if the ionic liquid is extremely pure and dry, and the reductive decomposition of TFSA can only occur in the presence of water and/or other impurities. Furthermore, they showed that the decomposition mechanism taking place in the presence of water traces seems to be different than the one suggested by MacFarlane et al. [10]. They suggested that the products of water reduction (OH[–] or H₂) are responsible for the TFSA reduction [13]. It is out of the scope of this letter to decide what exactly is the reason for the cathodic instability of the TFSA. At a minimum it is clear that this anion is electrochemically less stable than often assumed.

In this letter we show as a further example that the TFSA anion can easily be decomposed at slightly elevated temperatures during anodic oxidation of copper in the ionic liquid [BMP] TFSA leading to the formation of CuF₂.

2. Experimental

The ionic liquid [BMP]TFSA was obtained from Io.Li.Tec. (Ionic liquids Technologies) in the highest available quality (the ionic liquid does not contain inorganic impurities apart from less than 100 ppm

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bromide as the supplier guaranteed). The liquid was dried under vacuum for 12 h at a temperature of 100 °C, to water content below 3 ppm. All electrochemical measurements were performed in an argon filled glove box (O_2 and $H_2O < 2$ ppm) using a VersaStat™ II Potentiostat/Galvanostat. Copper wires (Aldrich, 99.999%) were used as quasi-reference and counter electrodes, and copper sheets (Alfa, 99.999%) were used as working electrodes. A two compartment electrochemical cell was used for the anodic oxidation of copper, Fig. 1. The counter electrode was separated and connected through an ionic liquid salt bridge. With this setup we avoid the contamination of the electrolyte in the working electrode counterpart by decomposition products from the counter electrode reactions.

A high resolution field emission scanning electron microscope (Carl Zeiss DSM 982 Gemini) was utilized to investigate the surface morphology of the electrolysis product. The X-ray diffractogram of the electrolysis product was acquired by a Siemens D-5000 diffractometer with CoK_{α} radiation.

3. Results and discussions

Before we start a discussion we should mention that our original aim was to anodically dissolve copper in the ionic liquid [BMP]TFSA in order to introduce copper ions into the liquid. Due to the limited solubility of copper salts in the ionic liquid [BMP]TFSA we showed in a former paper [6] that the best way to introduce copper cations into the ionic liquid is the anodic dissolution of pure copper metal. Furthermore, the anodic dissolution of metals at elevated temperatures is usually kinetically favoured leading to a faster reaction. We have investigated the cyclic voltammetry behaviour of copper in the ionic liquid [BMP]TFSA at two different temperatures, 25 and 70 °C (Fig. 2). The rapid increase in the anodic current at a potential of +0.6 V, at 25 °C, and at a potential of +0.5 V, at 70 °C, is attributable to the anodic dissolution of copper. The recorded reduction peak is correlated to redeposition of dissolved copper. Consequently, Cu cations can be anodically introduced into the ionic liquid and the extent of Cu dissolution increases as the temperature increases, as one would expect.

An anodic current density of $90 \mu A cm^{-2}$ (the corresponding potential was about 1 V vs. Cu reference electrode) was applied on the copper electrode in the employed ionic liquid for 1 day at 25 °C in order to anodically dissolve copper. Throughout the duration of the experiment no significant change in the solution was observed apart from a slight alteration in its colour to pale yellow due to the anodic dissolution of copper. There is no hint for a side reaction and as shown in [6] the oxidation state of the copper species introduced into the ionic

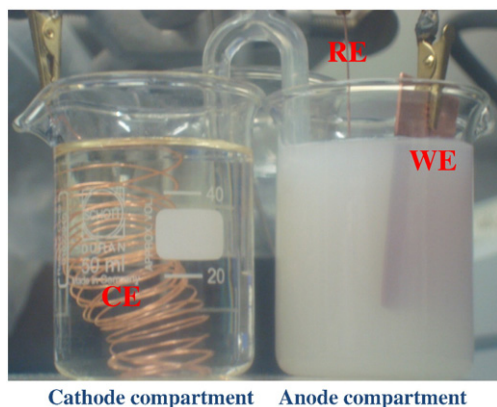


Fig. 1. An optical photo of the electrochemical cell used for the anodic dissolution of copper in the ionic liquid [BMP]TFSA at 70 °C and under applied current density of $90 \mu A cm^{-2}$. The photo clearly shows the formation of a white suspension during the anodic dissolution of copper which is due to CuF_2 formation.

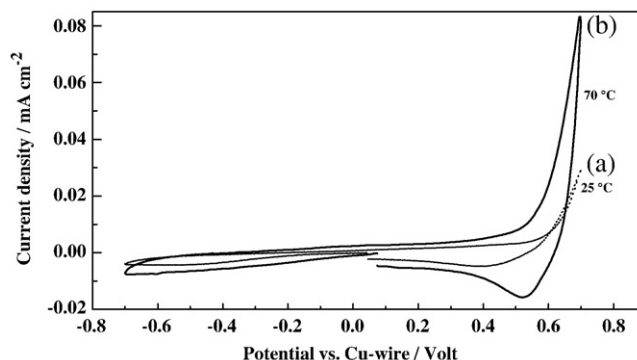


Fig. 2. Voltammetric behaviour of copper electrode in the ionic liquid [BMP]TFSA at 25 and 70 °C. Scan rate 10 mV/s.

liquid [BMP]TFSA after anodic dissolution of copper, is 1, thus Cu^+ ions are the electrolysis product.

Quite surprisingly, after applying a current density of $90 \mu A cm^{-2}$ at 70 °C (the corresponding potential is only about 0.2 V vs. Cu quasi-ref.) the ionic liquid became turbid after about 2 h of electrolysis and the turbidity became more intense with time until a white suspension was obtained after about 6 h, see Fig. 1. After about 12 h electrolysis a white precipitate was obtained on the bottom of the electrochemical cell. Subsequently, the ionic liquid containing the electrolysis product was centrifuged to reclaim the precipitate. The white precipitate was then washed several times with isopropanol to remove the residual ionic liquid.

The electrolysis product was investigated by SEM and XRD to explore its morphology and composition, respectively. The SEM micrograph of Fig. 3a shows the surface morphology of the obtained

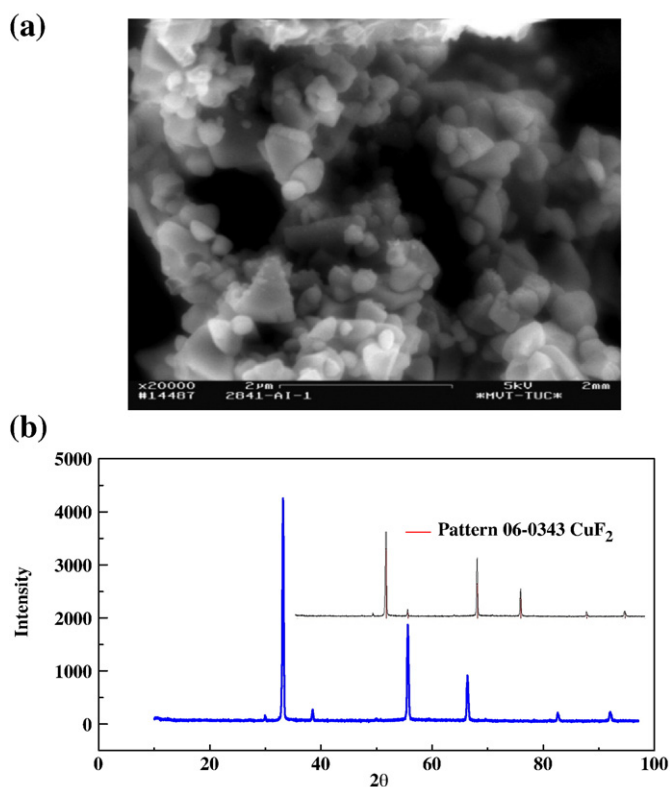


Fig. 3. (a) SEM micrograph of the white powder obtained after anodic dissolution of copper in [BMP]TFSA at 70 °C under applied current density of $90 \mu A cm^{-2}$ for 24 h. (b) XRD pattern of the obtained powder.

powder: it contains fine crystallites with an average size of about 200 nm. The XRD pattern of the obtained powder is shown in Fig. 3b. Surprisingly, all the diffraction peaks recorded for the obtained powder can be perfectly indexed to the data available in the JPCD (06-0343) diffraction file, thus indicating that pure CuF_2 is the yield of the anodic dissolution of copper in [BMP]TFSA at 70 °C, which is a clear evidence for the decomposition of TFSA anions, the only F^- source. It should be mentioned that anodic oxidation of copper in the ionic liquid [EMIm]TFSA, at the same experimental conditions, leads also to the formation of CuF_2 . However, the mechanism of the TFSA decomposition and the formation of CuF_2 is not clear. At the first glance one might expect that the TFSA anion is subject to a direct oxidative decomposition occurring simultaneously with anodic dissolution of Cu to Cu^{2+} leading to F^- which reacts with copper cations to form CuF_2 . However, the charge/mass balance is typical for $\text{Cu} \rightarrow \text{Cu}^+$. Thus, it is excluded that there is at the same time an oxidation of Cu to Cu^{2+} and TFSA oxidation liberating F^- . If the TFSA anion was anodically decomposed at the copper electrode it would also be decomposed at other electrodes (not only copper) which is not the case. Silver can easily be oxidized to Ag^+ without a clear hint for AgF formation. Thus, what else can it be?

As a possible explanation for the formation of CuF_2 we suggest that anodically dissolved copper cations might chemically reduce the TFSA at 70 °C, according to the following equation:



Without a detailed spectroscopical analysis we cannot decide on the mechanism, but it has been reported that the cathodic decomposition of TFSA leads to decomposition products like NSO_2 , CF_2 and F^- , as described in [14]. Thus it is plausible that Cu^+ leads to an irreversible reduction of TFSA liberating at the same time F^- which reacts with Cu^{2+} to CuF_2 . The driving force might be the extreme heat of formation of CuF_2 which is -538.9 kJ/mol [15]. It should be kept in mind that in this letter we do not postulate a reaction pathway for the decomposition of the TFSA as it needs further spectroscopic and chemical investigations. However, we just try to understand why CuF_2 is formed. It is reasonable to assume that CuF_2 is formed as a result of chemical decomposition of the TFSA anion by Cu^+ .

There are some more reports in the literature that make our assumption realistic. In [14] MacFarlane et al. have found, using solid-state NMR, that ionic liquids based on TFSA anion react with magnesium alloy surfaces to form a metal fluoride rich surface in addition to other organic components. This has been attributed to the decomposition of the TFSA anion to SO_2CF_2 , CF_2 and F^- species. The fluoride ions react with the alloy surfaces to form metal fluorides. Furthermore, they have reported in [11] that TFSA based ionic liquids react with lithium giving an interface composed mainly of decomposition products of the TFSA anion with a LiF film close to the lithium

surface. In a corrosion study of Inconel, Brass and commercial steel in [BMIm]TFSA Tolstoguzov et al. [16] have found that [BMIm]TFSA is subject to a decomposition upon chemical interaction with the alloy surfaces. They have shown by SIMS and XPS that the decomposition products of the ionic liquid are CF_3 , $\text{C}=\text{N}$ and $-\text{SO}_2-$ groups. All these results support our assumption on the chemical decomposition of TFSA anion by the interaction with copper cations at elevated temperature leading to the formation of CuF_2 . We cannot comment whether the same result would be obtained by dissolving Cu TFSA in [BMP]TFSA. A direct comparison would require an extremely pure and fully dissociated $\text{Cu}(\text{TFSA})$ made in a purely chemical synthesis routine. We might speculate that Cu^+ “in statu nascendi” is quite a reactive species.

4. Conclusions

We have found that the TFSA anion is subject to an unexpected decomposition under quite mild electrochemical conditions during the anodic dissolution of a copper electrode in the ionic liquid [BMP]TFSA at 70 °C, leading to the formation of CuF_2 . Interestingly, at room temperature no such decomposition was obtained. Although the mechanism of this reaction is not clear at all (even raising some questions), one has to be very careful in applying ionic liquids based on TFSA for electrochemical experiments: the TFSA anion might decompose, depending on the electrode material.

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