Comparison of usual electrode materials in a n,n-trimethylbutylammnium bis (trifluoromethanesulfonyl) imide ionic liquid

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COMPARISON OF USUAL ELECTRODE MATERIALS IN A N,N-TRIMETHYLBUTYLAMMNIUM BIS(TRIFLUOROMETHANESULFONYL)IMIDE IONIC LIQUID

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Ionic liquids (ILs) have been studied for two decades as electrolytes for various electrochemical experiments and more specifically for separation and electrodeposition of metals or semiconductors [1]. Among the numerous anions synthesized to design ILs, the bis(trifluoromethanesulfonyl)imide (NTf_2^-) anion is commonly used for its electrochemical stability and hydrophobicity. In particular, the combination of short-chained quaternary ammonium cations and the NTf_2^- anion gives hydrophobic ILs that have large electrochemical windows (5,0 to 6,0 V) and reasonably low viscosities (20 - 150 mPa.s) [2]. Thus, this family of ILs has become a very common one for electrochemical studies. However, fundamental understanding on the phenomena occurring at the electrode/electrolyte interface in these ILs is still needed in order to select the right electrode material for a given application.

The use of electrochemical techniques requires electrodes that are inert in the working potential range. Thus, the present work focusses on a study and comparison of the behavior of three common electrode materials (glassy carbon, platinum and gold) in N-Trimethyl-N-butylammonium bis(trifluoromethanesulfonyl)imide ($[N_{4111}][NTf_2]$). These three materials are commonly considered as totally inert on the electrochemical window of $[N_{4111}][NTf_2]$ (-3,0 to +2,7 V vs Fc^+/Fc [3]), with current densities in the mA range. However, when trying to observe and interpret signals in the uA range, extensive study of phenomena occurring at the electrode/IL interface has to be completed [4,5]. Thanks to transient electrochemistry, and by studying the influences of water concentration and acidity in the IL, we could get a better understanding of the different phenomena occurring at the electrode/electrolyte interface. The relative role of the anion was also investigated.

Platinum and gold are very good candidates for studies at negative potentials but are subject to interfacial reactions at positive potentials. As can be seen on figure 1, the activity of protons is observed on platinum and gold, although the mechanisms are different. These reactions have to be taken into account in electrochemical studies on IL, since these electrolytes always contain at least a trace amount of water (≥ 20 ppm). Moreover, in the case of platinum, the activity of protons is combined with adsorption and reaction of the NTf_2^- anion on the electrode surface. Glassy carbon is completely inert but induces a significant capacitive current likely to hide subtle signals.

We can see two major benefits to this study: First of all, it gives new elements to understand and possibly master the interfacial phenomena observed during electrochemical studies in ILs. This is, to our opinion, a key issue towards meaningful results and interpretation in the field of analytical electrochemistry in ILs. Moreover, platinum and gold being classified as strategic raw materials, we expect that this study will also contribute to the development of electrochemical-based processes to recycle these elements and all the others whose supply is made critical by depletion of natural resources and geopolitical issues.

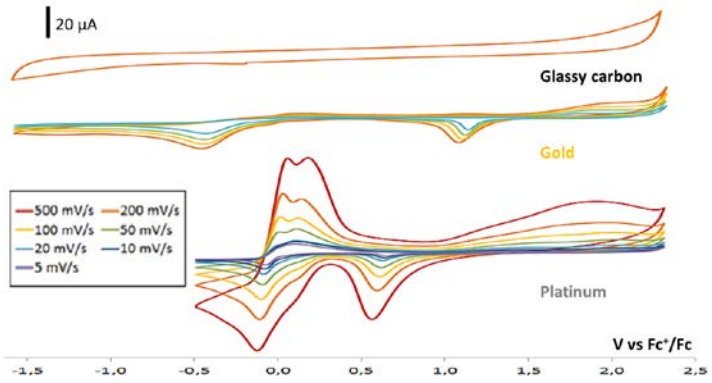

Figure 1 – Voltammograms of 25 mM $HNTf_2$ in $[N_{4111}][NTf_2]$ on glassy carbon, gold and platinum disc electrodes (A = 3,14 mm²) at 40°c and different scan rates under natural convection regime and inert atmosphere, $[H_2O]_{IL}$ ≈ 8 mM (100 ppm)

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