Journal of Molecular Liquids xxx (2016) xxx–xxx

Contents lists available at ScienceDirect

Journal of Molecular Liquids

journal homepage: www.elsevier.com/locate/molliq

Surface composition of [BMP][Tf_2N] and [PMIm][Tf_2N] in the presence of NbF_5 and TaF_5. A photoelectron spectroscopy study

Anna Dimitrova, Marit Walle, Marcel Himmerlich, Stefan Krischok *

Institut für Physik and Institut für Mikro- und Nanotechnologien MacroNano, Technische Universität Ilmenau, 98683 Ilmenau, Germany

ARTICLE INFO

Article history:
Received 3 March 2016
Received in revised form 18 August 2016
Accepted 19 August 2016
Available online xxxx

Keywords:
Photoelectron spectroscopy
Ionic liquids
[PMIm][Tf_2N]
[BMP][Tf_2N]
Surface composition

ABSTRACT

The vacuum/liquid interface of ionic liquid/metal salt binary mixtures was investigated under ultra-high vacuum conditions using photoelectron spectroscopy. In this study we compare two ionic liquids 1-Butyl-1-methyl-pyrrolidinium-bis(trifluoromethylsulfonyl)-imide, [BMP][Tf_2N] and 1-Propyl-3-methyl-imidazolium-bis(trifluoromethyl-sulfonyl)-imide [PMIm][Tf_2N] – in combination with two fluoride salts – TaF_5 and NbF_5 – at different concentrations. The results show a clearly different behavior for samples, which were in contact with ambient conditions and those being kept in inert conditions. Under inert atmosphere, the experimental results suggest rather equal anion and cation concentration of the IL constituents in the near surface region.
At ambient conditions and high MF_5 (M = Ta, Nb) concentration, a strong deviation from the expected stoichiometry in the near surface region was observed, obviously caused by chemical reactions of the IL/salt system with the atmospheric environment. It is expected, that these reactions have also impact on the quality of electrodeposited metal films from these solutions.

1. Introduction

The electrodeposition of most metals and alloys is traditionally performed from aqueous solutions, which in some cases are based on toxic components (e.g., cyanide) and using processes that have rather low current efficiencies (e.g., chromium). Moreover, there are a number of metals with a Nernst potential below that of water decomposition, which cannot be electroplated from aqueous baths because of their negative deposition potential (e.g. aluminum, magnesium, tantalum and niobium) [1]. One way to overcome this limitation is the use of ionic liquids (ILs), which in recent years have been introduced as new electrolytes in electrochemistry [2], due to their special physical and chemical properties. They possess a liquid state over a wide temperature range, chemical inertness, high heat capacity, negligible vapor pressure at room temperature and large electrochemical window [3,4]. The later feature permits the electrodeposition of refractory metals with negative potential [5,6]. Special attention from this group of metals deserve niobium (Nb) and tantalum (Ta).

The interest in metallic Nb and Ta has significantly increased in recent years due to their high melting point, high temperature stability, irradiation damage resistance and superconductor properties combined with exceptional corrosion resistance which make their layers ideal for use in the chemical and nuclear industries [7–10].

In attempts to overcome the negative potential of Nb and Ta, their electrodeposition was first performed form alkali-fluoride eutectic mixtures [11–14]. The process requires rather high temperatures (around 750 °C), which in case of Ta leads to irreversible conversion in its metastable phase, and in general – a major concern of the plating baths is the high-energy consumption and severe corrosion during deposition.

Only recently cyclic voltammetry experiments demonstrated that electrodeposition of Nb and Ta at moderate temperature is possible from ILs [15–17]. However, there are still limitations to be overcome: only a thin metal layer of Ta (a few hundred nm) can be electrodeposited under controlled moisture and oxygen content; oxides of Nb are deposited next to elemental Nb, and the electrodeposition is a complex multistep reduction process, which still needs to be elucidated.

Thus, the ability to define the best conditions for electrodeposition of metallic layers with high-quality morphology is of great importance, and requires as a first step understanding of molecular interactions within the IL–metal binary mixture and with the environment.

In this study we analyse data from metal-salt/ionic liquids solutions which have been handled under inert conditions extending previous studies [18], where these samples had contact to ambient conditions during sample transfer. The aim is to shed light on the intrinsic properties of the studied IL/metal-salt systems and to possible influence of reactive environmental species thereon. This is particularly important for applications in electrodeposition. We have chosen two air and water stable ILs as model systems: one pyrrolidinium based and one

---

* Corresponding author.
E-mail address: stefan.krischok@tu-ilmenau.de (S. Krischok).

http://dx.doi.org/10.1016/j.molliq.2016.08.075

Please cite this article as: A. Dimitrova, et al., Surface composition of [BMP][Tf_2N] and [PMIm][Tf_2N] in the presence of NbF_5 and TaF_5. A photoelectron spectroscopy study, J. Mol. Liq. (2016), http://dx.doi.org/10.1016/j.molliq.2016.08.075

imidazolium based. The first one was used for the electrodeposition of Nb and Ta [15,17], while the former is chosen because imidazolium based–ILs is the most widely investigated family of ILs for metal electrodeposition [5]. Comparable to the real electrochemical process, TaF_5 and NbF_5 were used as metal precursors in this work [15,17]. In order to elucidate the surface chemical composition of ILs/MF_5 (M = Ta, Nb) systems and the influence of the dissolved metal fluorides, we utilized X-ray Photoelectron Spectroscopy (XPS). Due to the excellent compatibility between the ultra-high vacuum (UHV) conditions and the negligible vapor pressure of the ILs, XPS is a powerful analytical method for the surface characterization of different ILs [19–26].

2. Experimental

1-**B**utyl-1-**m**ethyl-**p**yrrolidinium-bis(**t**ri**f**luoromethylsulfonyl)-imide, [BMP][Tf_2N] and 1-**P**ropyl-3-**m**ethyl-**im**idazolium-bis(**t**ri**f**luoromethyl-sulfonyl)-imide [PMIm][Tf_2N], air- and water-stable ILs were purchased from IoLiTec, GmbH (Germany) in the highest quality available (ultrapure). Prior to use, the liquids were dried under vacuum conditions at 120 °C to water contents below 10 ppm and stored in a closed bottle in an argon-filled glove box with water and oxygen contents below 2 ppm (OMNI-LAB from Vacuum-Atmospheres CO., USA). TaF_5 and NbF_5 (99.99%) were purchased from Alfa Aesar (GmbH & Co KG, Germany) and used without further purification. The moisture of the neat ILs–metal fluorides mixtures was determined by Karl–Fisher titration. In the presence of TaF_5 and NbF_5 – the water content was in the range of 200–600 ppm and 400–1000 ppm, respectively. Prior XPS analysis, the samples were kept in the preparation chamber for initial pumping for several hours (*see the "XPS data collection"-section for details*) in order to assure that the pressure in the analysis chamber was not affected during the measurement.

The IL–metal salt binary mixtures were prepared by dissolving the required amount of metal salts (TaF_5 or NbF_5) separately in both of the mentioned ILs. In this context, one should note that a shortcoming of commercially available NbF_5 and TaF_5 (and other transition metal halides) is that they can contain some oxo-fluoro-metallates from the fabrication process. In addition, the water content of the used ILs might allow some hydrolysis side reactions.

Two different nominal concentrations of 0.5 M and 2 M were used. In order to speed-up the dissolution, the mixtures were heated to 60 °C while stirring. Upon dissolution of 0.5 M metal fluorides – transparent solutions were obtained. Contrary, the 2 M salt concentration resulted in a saturated solution since there was always a portion non-dissolved salt observed at the bottom of the vessel. For sample preparations a few drops from the upper transparent solution was carefully sucked with a glass pipette. Consequently, the given nominal molarity is an upper limit in these cases. For XPS analysis, all samples were prepared by depositing one droplet of the respective IL, with a volume of about 0.01 ml, onto a polycrystalline Au film of about 250 nm thickness, deposited on Si(100) – both separated by a Ti adhesion layer. During sample preparation the droplet was carefully spread as a thin film, covering almost the whole surface area of the Au-substrate. Supposed that the droplet wets the whole sample surface of ~1 cm^2, the resulting film thickness is in the range of ~100 μm.

As TaF_5 and NbF_5 are volatile, air- and moisture-sensitive solids [27], their solutions with [BMP][Tf_2N] or [PMIm][Tf_2N] are no longer stable. In this respect the effect of ambient conditions is crucial for the correct interpretation of the resulting spectra. Therefore, we perform two sets of experiments: after the sample preparation in argon-filled glove box the samples were placed in a home-built transfer-box inside the glove-box. The samples were kept out of moisture/air exposure by using a nitrogen dry-box (Carl Roth GmbH, Germany), which was mounted to the XPS spectrometer for sample insertion so that the samples could be easily removed from the argon-filled transfer-box within the dry-box, and placed into the transfer chamber. This procedure is referred to as inert transfer. For comparison, samples from the same batches were briefly exposed (max. 5 min) to ambient conditions and then placed into the transfer chamber, giving a similar conditions compared to the previous study [18].

To quantify the ratio between the ILs and the metal salts molecules we introduced in our analysis 'number of IL molecules' *per* 'single molecule MF_5'. To calculate it we used the density (ρ) of both ILs: $\rho = 1{,}395\ g/cm^3$ for [BMP][Tf_2N] [28] and $\rho = 1{,}483\ g/cm^3$ for [PMIm][Tf_2N] [29].

2.1. XPS data collection

All XPS spectra were recorded at normal emission using a Specs SAGE spectrometer employing a focused and monochromated AlKα source ($h\nu = 1486.7$ eV), hybrid (magnetic/electrostatic) optics, a hemispherical analyser and a multi-channel plate and delay-line detector as described elsewhere [30].

The information depth (ID) of these experiments may be defined as the depth, within the sample, from which 95% of the measured signal will originate. ID is assumed to vary mainly with cos(Θ), where Θ is the electron emission angle relative to the surface normal. If we assume that the inelastic mean free path (λ) of photoelectrons in organic compounds is of the order of ~3–5 nm at the kinetic energies of 800–1500 eV (the range were all core levels analysed in this study are observed), we can estimate ID for this experimental geometry ($\Theta = 0°$) to be ~12 nm [31,32].

The measurements were performed using analyzer pass energies of 50 eV for survey spectra and 13 eV for high-resolution spectra. The operation conditions lead to a total energy resolution of 0.6 eV (FWHM of Ag $3d_{5/2}$ at pass energy of 13 eV of sputtered Ag reference sample). The absolute error in the acquisition of binding energies is 0.1 eV, as quoted by the instruments manufacturer (SPECS Surface Nano Analysis GmbH, Germany). Charge neutralisation methods were not required (and employed) during the measurement of these samples.

Initial pumping to high vacuum pressure (1×10^{-7} mbar) was carried out in the load lock chamber immediately after sample transportation. Elaborate pumping was performed overnight in order to ensure the complete removal of adsorbed volatiles including permanent gases, water vapor and other volatile impurities. Note, that this procedure might also impact the metal-salt concentration. The samples were then transferred to the analysis vacuum chamber. The pressure in the main chamber remained 1×10^{-8} mbar during XPS measurements of the samples.

2.2. XPS data analysis

For data analysis, the acquired spectra were corrected by a Shirley-type background subtraction and fitted using Gaussian (70%)–Lorentzian (30%) functions using CasaXPS (Version 23.16 Dev52, Casa Software Ltd.). This lineshape has been used consistently in the fitting of the XPS spectra, and has been found to match experimental lineshapes in the neat ionic liquids and in the presence of MF_5 (M = Ta, Nb). All spectra are charge corrected by setting the measured binding energy of the cationic nitrogen photoemission peak ($N1s^{\mathbf{cation}}$) in [BMP][Tf_2N] and [PMIm][Tf_2N] – containing samples to 402.7 eV and 402.1 eV, respectively [33,34]. The maximum binding energy shift used was +0.4 eV.

For detailed analysis of the core level spectra of [BMP][Tf_2N] and [PMIm][Tf_2N] we refer to [21,33,34]. The fitting procedures discussed in these studies are also employed in our study. For the analysis of the C1s emission we take into account the CF_3 related structure at highest binding energy originating from the anion and two peaks at lower binding originating from the cation, which are related to aliphatic carbon (lowest binding energy) and the central part of the cation.

Please cite this article as: A. Dimitrova, et al., Surface composition of [BMP][Tf_2N] and [PMIm][Tf_2N] in the presence of NbF_5 and TaF_5. A photoelectron spectroscopy study, J. Mol. Liq. (2016), http://dx.doi.org/10.1016/j.molliq.2016.08.075