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About charging and referencing of core level data obtained from X-ray photoelectron spectroscopy analysis of the ionic liquid/ultrahigh vacuum interface

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The ionic liquid [EMIM][TFSI] was investigated by X-ray Photoelectron Spectroscopy (XPS) on different substrates, ranging from metallic to semiconductor type materials. Parallel angle-resolved XPS was performed utilising a wide-angle lens hemispherical analyser with an acceptance angle of 60°. ARXPS data show no preferential orientation/accumulation of certain species at the ionic liquid/ultra-high vacuum interface. Charging caused by the electron emission process and electron flood gun experiments was recorded. The data indicate that the binding energies of the spectra depend on the properties of the substrate material, specifically on the substrate/ionic liquid interface. Observations are discussed by means of electric double layer and other processes that may effect on the potential of the ionic liquid.

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1. Introduction

In X-ray photoelectron spectroscopy (XPS) – originally known as Electron Spectroscopy for Chemical Analysis (ESCA) – charging becomes an issue if insulating samples are investigated as the continuous removal of electrons from the surface results in the build-up of a positive charge in the sample, thus changing the surface potential and leading to a decrease of kinetic energy of the ejected electrons. As a consequence apparent binding energy shifts towards higher values are observed in the XP spectra, as already described by Siegbahn et al. in 1967 [1].

In case of uniform surface charging, as often observed if achromatic X-ray sources are used, the energy shift is often referenced by means of a known core level BE, such as adventitious carbon, internal carbon or by gold decoration. Non-uniform charging also referred to as differential or partial charging is often observed if monochromatic X-ray sources are used with and without combination of bombarding the surface with electrons of low energy for charge compensation using a flood gun. Differential charging is a challenge and can lead to misinterpretation of spectral features if for instance assigned to chemical differences of the elements present at the surface (see [2] and references therein). However, differential sample charging can also be an opportunity as these phenomena are a result of the chemical nature of the surface. Some of these opportunities were published in a special issue of JESRP in 2010 [2]. The investigations of charging phenomena presented in [2] range from, for instance, dynamics of charging [3], time dependent band bending at the SiO_2/Si interface [4], or neutralization kinetics in charged polymer–metal nanocomposite materials [5] to effects of the electrical double layer at the mineral-aqueous solution interface [6], just to name a few.

Common XPS investigations require ultrahigh vacuum (UHV) conditions ($p < 10^{-8}$ mbar). Therefore XPS is usually restricted to UHV compatible materials and mostly conducted at a solid/UHV interface. However, as most (electro-)chemical reactions and biological processes occur in a solution phase, XPS analysis of the liquid/UHV interface is also of fundamental importance. First experimental setups of that kind were described by H. and K. Siegbahn et al. [7,8] in the 1970s and, later, largely used and further improved by H. Siegbahn et al. [9]. The issue of evaporation of the liquid was overcome by use of differential pumping systems and a moving metal surface (wire or disc) acting as a backing of the liquid sample (see [7–10] and references therein). Angular resolved XPS (ARXPS) was, for instance, used to show accumulation of dissolved ionic species at the liquid/UHV interface. Similar setups were also realized and used by Morgner et al. [11,12]. In these studies, charging was reported to occur and XP spectra were commonly referenced to the C 1s line with respect to vacuum level.

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Instead of a moving metal surface covered by a liquid, a liquid jet can be investigated to study the liquid/UHV interface. Ottoson et al. used this approach to study chemical shifts of biomolecules as a function of pH [13] or the electronic structure of aqueous I_3^- [14], Brown et al. [15] to study surface potential at electrolyte-nanoparticle interface using synchrotron radiation. Nowadays, ambient pressure XPS (APXPS) instruments are commercially available and widely used, not only in synchrotron facilities, but also in combination with laboratory-based X-ray sources [16].

With respect to analysis of a liquid/UHV interface, ionic liquids (IL) are particularly interesting to study, due to their negligible vapor pressure. Thus analytical tools requiring UHV are suitable to investigate ILs without requirement of differential pumping systems. First XPS measurements on IL were performed in 2005 [17]. Several subsequent studies showed that XPS is suitable for quantitative chemical analysis of IL [18–22].

Binding energies, however, were found to vary between different occasions by up to 0.8 eV and continuous changes towards higher BE were recorded for several IL prepared on steel [23]. From these investigations it was suggested that the surface of the IL becomes charged and that the position of the C 1s line of aliphatic chains of eight carbon atoms or more may be used as internal reference for charge correction [23].

Foelske-Schmitz et al. [24] investigated the charging phenomena in more detail, and showed that the interface of IL/support should also be considered if BE are discussed. These authors prepared IL on low surface area aluminium foil and high surface area activated carbon (AC) support and showed improved XPS data with respect to charging for the latter. The lack of charging observed on the AC support was explained by the high double layer capacitance of the AC/IL interface. Same authors developed an in situ electrochemical (EC) XPS cell with three electrode arrangement [25]. Using that cell, charging was followed by recording the open circuit potential (OCP) of a platinum working electrode in comparison to a high surface area AC working electrode with X-ray illumination of the IL electrolyte [26]. The shift of the OCP observed for the platinum electrode was directly related to shifts of core level data originating from the IL electrolyte. In contrast, the OCP remained constant for the high surface area activated carbon working electrode. This observation further confirmed that the electrochemical double layer formed at the support/IL interface has to be considered when irradiating/measuring at the IL/UHV interface.

Herein, we report on parallel ARXPS measurements of the ionic liquid [EMIM][TFSI] on different substrates like Au, Ag, differently pre-treated glassy carbon as well as n-type doped silicon. XPS and flood gun experiments suggest that significant charging caused by the photoemission process does not occur during the XPS measurement. BE values of IL signals from preparation on annealed glassy carbon substrates were constant in course of flood gun experiments. On semiconductor materials a large decrease of BE has been recorded while on the metallic substrates decrease of BE was significantly smaller during flood gun experiments. The findings again confirm that the potential drop within the solid/liquid interface influences on the potential of the liquid with respect to the substrate.

2. Experimental

2.1. Materials

The following substrates have been used as support for the ionic liquid:

Ag and Au films sputter deposited on Si substrates (thickness >3 μm) after Ar ion cleaning. K-type glassy carbon (HTW Werkstoffe, Germany) as received (capacitance: 7 μF/cm^2) and after heat treatment at 450 °C for 20 min in air (capacitance: 18 mF/cm^2) [27]. n-type Silicon after Ar ion cleaning. All Substrates were mounted on the sample holder using metallic clips.

Degassing of the ionic liquid ethyl-methyl-imidazolium-bis[(trifluoromethane)-sulfonyl]imide ([EMIM][TFSI]) (Iolitec, Germany, purity: >99%) was performed in the loadlock chamber at a pressure of roughly 10^{-6} mbar overnight. Preparation of IL droplets (1–2 μL, droplet diameter: 2–3 mm) onto the differently treated substrates was done under ambient conditions using a pipette. Thus, droplet size and thickness were chosen for probing the IL/UHV interface and not the IL/support interface with the X-ray beam. Air exposure time of the liquid and the previously sputter-cleaned substrates was about 5 min during the preparation procedure.

2.2. XPS measurements

XPS analysis was carried out using a SPECS XPS-spectrometer (μ-Focus 350) equipped with a monochromatic Al-Kα source (1486.6 eV at 93 W, beam diameter: 500 μm) and a hemispherical WAL-150 analyser mounted in a 51° angle with respect to the sample surface normal. ARXPS was performed simultaneously using five independent angle channels, covering angles from 27° to 75° with respect to the sample surface normal. Survey spectra and narrow scans were recorded using pass energies of 100 eV and 30 eV with energy resolutions of 1 eV and 0.05 eV and step sizes of 0.5 eV and 0.025 eV, respectively. In order to study the influence of the X-ray induced photoemission on binding energy, the N 1s lines were recorded after 4 h of X-ray irradiation for a second time. Subsequently, a broad spot flood gun (SPECS FG 22) mounted 55° from sample surface normal was used for charging experiments utilising electrons of low energy, i.e. 5 eV, at different intensities (from 5 μA to 20 μA).

CASA-XPS software was used for data analysis. Quantification of the detected elements was carried out from survey scans using transmission corrections as described in [28], Scofield sensitivity factors [29] and Tougaard backgrounds [30]. Accuracy of the quantification was better than ±5% of the determined values. Pseudo-Voigt functions, i.e. Gaussian-Lorentzian (GL30) lines, were used for peak fitting of narrow scans.

3. Results & discussion

3.1. Quantitative analysis and ARXPS

High purity and possible effects from preferential orientation of the IL are crucial to ensure equal conditions for observation of possible substrate effects. Thus, we examined XPS survey spectra with high signal to noise ratio for signals from elements other than C, O, F, S or N. No evidence of contaminations (>0.1 at.%) could be found at the IL/UHV interface on any of the samples. This is exemplarily shown for the [EMIM][TFSI] deposited on the Ag and n-type Si supports by means of survey scans taken from data recorded at a mean angle of 51° in Fig. 1a. Quantification for all investigated samples shows no significant deviations from the expected stoichiometry, thus confirming cleanliness of the IL (Table 1).

Deconvolution of the C 1s signal of the [EMIM][TFSI] on Argon ion cleaned Si is shown in Fig. 1b. The ΔBE values, FWHM as well as ratios of components assigned to different carbon species are in good agreement with values published in literature [31]. Changing the surface sensitivity has also no detectable effect on the C 1s line shape which is shown for the C 1s spectra recorded from the [EMIM][TFSI] deposited on the n-type silicon (Fig. 1b, top). The C 1s lines recorded at 27° ± 6° (red curve) and at 75° ± 6° (blue curve) are

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