Electronic Supplementary Information

XPS Investigation of the Vacuum Interface of an Ionic Liquid under Triangular Electrical Excitation for Slow Transients

Merve Taner Camci, a†* Burak Ulgut, a Coskun Kocabas b† † and Sefik Suzer a

a Department of Chemistry, b Department of Physics, Bilkent University, Ankara 06800, Turkey
Present addresses:
†CNRS Institut Charles Sadron, Strasbourg 67034, France.
††School of Materials, The University of Manchester, Manchester M13 9PL, U.K.

Experimental details

The gold electrodes were deposited on 20 µm thick polyethylene membrane (Celgard 2730, Gelon LIB Group) with porosity of 43%. Electrochemistry grade ionic liquid (≥98.5%) DEME-TFSI (N,N-Diethyl-N-methyl-N-(2-methoxyethyl) ammonium bis ( trifluoromethanesulfonyl) imide) was purchased from Sigma-Aldrich (CAS Number: 464927-84-2). 5µl of DEME-TFSI was injected from the bottom part of PEM between the Au-electrodes. Thermo Scientific K-Alpha X-ray Photoelectron Spectrometer with monochromatized AlKα photon energy 1486.68 eV was used for all XPS measurements. Sample holder is connected to either ground for Static XPS analysis or to DS340 Synthesized Function Generator (Stanford Research) for external biasing.

Additional Information on data gathering with the TRW Excitation

Below given in Figure S1 is the actual data, recorded sequentially once in the increasing binding energy and afterwards in decreasing binding energy, respectively, under one cycle of TRW excitation of -5 to +5 V with 1 mHz frequency, for extracting both the position of the two N1s peaks and also their intensity ratio. Each spectrum takes 16 seconds to record, during which, the applied bias varies as much as (16/500) x 10 V = 0.320 V. Note also that, due to the EDL screening of the applied bias, only half of the bias translates to the binding energy change to give 160 meV shift in the positions of the peaks in between the scans. This was thoroughly discussed in our previous paper. Data presented in Figure 3 in
the manuscript is extracted by fitting the entire data for the binding energy positions and also the intensity ratio of the two N1s peaks.

Figure S1. Time-resolved N1s spectral evolutions, recorded sequentially first in the forward and later in the reverse directions while a 5 V TRW excitation is imposed from one of the metal electrodes. This is part of the data presented in Figure 2 of the manuscript.

**Double-checking on the consistency of intensity ratio change of the N1s peaks**

There are two major experimental parameters contributing to the measured intensity ratio of the N1s peaks, which are; (i) calibration of the snap-shot intensity ratio, and (ii) variation in the transmission function of the instrument under external bias. Therefore, in order to mitigate these experimental artifacts, we have also analyzed the Au4f spin-orbit doublet peaks under exactly the same conditions, i.e. during exposure to 5V TRW with 1 mHz frequency, with the emphasis on the experimentally determined Au4f\(_{7/2}\)/Au4f\(_{5/2}\) ratio. The Au4f doublet is separated by 3.67 eV, which also matches that of the N1s peaks. Collected and corrected data are shown in Figure S2.

To increase the precision, the entire data is evaluated by summation of three regions where each region corresponds to one +5V to -5V and reversed -5V to +5V cycles. Intensity ratio of the Au peaks (Au4f\(_{7/2}\)/Au4f\(_{5/2}\)) is found to be mostly independent of change in the peak positions as a result of TRW electrification, except at the extreme points, due mostly to the transmission function of the
spectrometer. However, in contrast the N1s A/ N1s B intensity ratio follows very closely the electrification of the interface.

**Figure S2.** Time-resolved Au4f and N1s spectral regions, recorded in the forward direction while a 5 V TRW excitation is imposed from one of the metal electrodes. Extracted B.E. positions of the Au4f\(\frac{7}{2}\) and N1sA peaks, together with computed intensity ratio are also shown as insets.

The black square-graph is the binding energy change with respect to the applied TRW pulses that follow one cycle from +5V to -5V. Since Au4f XP spectra were acquired from the reference Au-metal the amplitude of the applied potential [10 V = +5V – (-5V)] is directly observable in binding energy shift of 10 eV. However, N1s peak of DEME-TFSI medium has an average change of only 5 eV in its position which corresponds to half of the imposed potential, as was discussed in our previous work in details.\(^1\) The ratio between Au4f\(\frac{7}{2}\)/ Au4f\(\frac{5}{2}\) is expected to be constant since the ratio of these two spin orbit doublet peaks are fixed and the experimental graph is in consistency with the theoretical ration of 1.27.\(^2\)

Although the binding energy position varied by the exposed TRW potential, the ratio between two peaks for Au 4f region is expected to be almost linear since the peak area of the doublets corresponding to Au-
metal is non-responsive to external electrical stimuli, whereas ratio between two N1s peaks fluctuate as a function of the applied potential for N1s peaks that undergoes re-orientation. Therefore, the residual sum of squares that describes the overall deviations of the actual data from the predicted model (data fluctuations from the linear regression line in our case), for the graph of peak intensity ratio vs. binding energy (Figure S3) are found to be higher in terms of N1sA/N1sB ratio than the Au4f_{7/2}/Au4f_{5/2} ratio at the same time the slope corresponding to N1s peaks is higher with larger standard deviation as compared to practically linear graph of Au peaks.

![Figure S3](image-url)

**Figure S3.** Evaluated data for Au4f and N1s spectral regions representing the residual sum of squares and slopes together with standard deviations.

**Estimation of the surface voltage developments with electrification**

In order to understand the significance and implications of the 20% intensity change, simple order of magnitude estimates are shown below. Remembering that the 20% is the total intensity ratio change between the negative and positive extreme points, a reasonable charge imbalance could be taken as 10%.

In a given spherical volume of radius r, the electrical potential E is given as:
\[ E = \frac{q}{4\pi\varepsilon_0 \varepsilon} \]

Where \( q \) is the charge, \( \varepsilon \) and \( \varepsilon_0 \) are the dielectric constant (permittivity) of the material and the vacuum, respectively.

In volumes that are non spherical, the potential takes forms that are similar to the above with geometrical corrections that involve large algebraic equations. To calculate orders of magnitude, the above equation will be used. The dielectric constant of the IL medium is taken as 20.3

The density of the ionic liquid is assumed to be 2 g/cm^3 and the molecular weight is 426 g/mol.3 This leads to roughly 2x10^3 mol/cm^3 which is roughly 3x10^21 molecules/cm^3. For estimating the volume, the area under the X-rays are used along with ~6 nm probe depth. This leads to a volume that is on the order of μm^3.

If we have 10% excess charge in a sphere of 1μ diameter:

\[ E = \frac{10\% \times 3 \times 10^{21}/cm^3 \times 1.6 \times 10^{-19}C \times 4/3 \times \pi \times (0.0001cm)^3}{4\pi \times 8.85 \times 10^{-12}F/m} \times 0.0001cm \times 10^{-2}m/cm \approx 5 \times 10^8V \]

Attacking the problem the other way, assuming 2.5V in a sphere of 1μ diameter

\[ 2.5V = \frac{\text{excesscharge}/cm^3 \times 1.6 \times 10^{-19}C \times 4/3 \times \pi \times (0.0001cm)^3}{4\pi \times 8.85 \times 10^{-12}F/m} \times 0.0001cm \times 10^{-2}m/cm \]

Excess charge is roughly 10^{15} units of elementary charge. This will result in only 1 in 10^6 excess charge.

For 10% extra charge to result in a reasonable voltage on the order of volts this simple dielectric picture needs to be amended.4,5 Either simply the charge density is much lower, or the local dielectric constant is much higher, or there are other effects changing the understanding of the system. Ionicity, as mentioned in the paper, can explain the low voltage that is induced by a high charge excess. In that, the structure is such that most of the excess ions are screened by the rest and do not induce extra voltage. This violates the assumption made in the above order of magnitude estimate where excess charges are homogeneously distributed within the volume.

References: