



KeyWords

NAP XPS, Ionic Liquids,
Measurements, Surface Analysis,
Liquid-Gas Interface

XPS surface analysis of an ionic liquid with EnviroESCA

This application note presents how EnviroESCA can be used to analyze the surface of an ionic liquid under ambient conditions. Such investigations of the interface between an ionic liquid and a gas in near ambient pressure regions is of great interest for their potential usage in catalysis, batteries, gas handling, or carbon capture and storage.

Motivation

Ionic liquids are salts, made of cations and anions, with melting points below 100°C. The combination of a vast structural diversity and their special physicochemical properties is the base for their (potential) application in electrochemistry, catalysis, organic synthesis, gas handling, separation technologies, or carbon capture. [1]

From a scientific perspective a detailed analysis of the ionic liquid surface is of enormous interest, especially when the ionic liquid comes in contact with adsorbents, catalysts, gases or other potential reactants in such multiphasic reactions.

Many XPS studies of ionic liquids and their surface and interfacial properties have been limited to ultra-high vacuum conditions. However, many potential applications of ionic liquids include gaseous reactants in contact with the ionic liquid (bulk or thin film) under environmental conditions which makes the gas-liquid interface under ambient pressures very important.

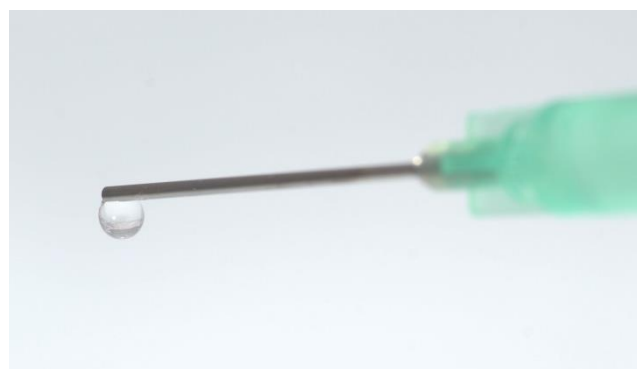


Fig. 1 Single drop of the investigated ionic liquid *1-propyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide* ($[C_3C_1Im][NTf_2]$).

Method

EnviroESCA utilizes X-ray Photoelectron Spectroscopy (XPS) as its main analytical technique. Hereby an electron beam is generated inside the X-ray source and focused onto an X-ray anode made of aluminum. The deceleration of the electrons on the anode leads to the production of X-rays. This X-ray beam is monochromated and focused onto the sample.

X-ray photons impinging the sample excite electrons in the material which are subsequently emitted with specific kinetic energy determined by their binding energy and the photon energy of the x-rays. Thereby only electrons from atoms up to a depth of approx. 10nm are able to leave the surface. These electrons propagate through the lens system of the Electron Analyzer into the hemisphere which acts as a spherical capacitor forcing the electrons onto circular paths with radii depending on their kinetic energy. The path of photoelectrons ends at an electron sensitive detector where the electrons are amplified and measured as an intensity in counts per second. Sweeping the voltage of the spherical capacitor while measuring the number of electrons per second on the detector results in a photoelectron spectrum. From these spectra a quantitative analysis of the atomic composition of the sample surface can be done.

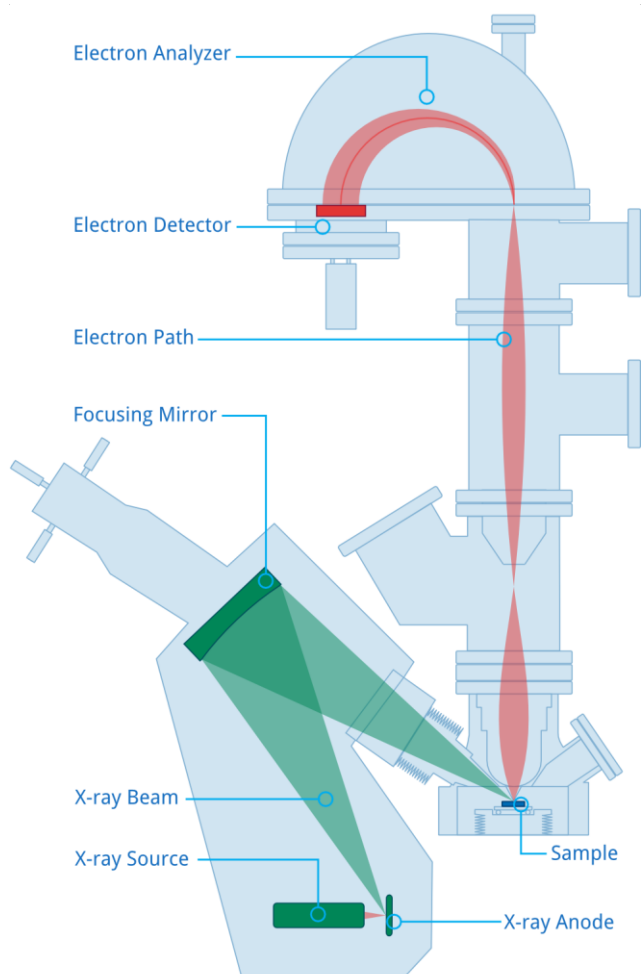


Fig. 2 XPS with EnviroESCA

Experimental Section

The ionic liquid $[C_3C_1Im][NTf_2]$ was filled in a 0.2 mm deep cavity of a customized stainless steel sample holder as shown in Figure 3. That sample holder was introduced directly in the Sample Environment of the EnviroESCA by placing it on one of the sample plates. And $[C_3C_1Im][NTf_2]$ was analyzed in the EnviroESCA without any further treatments after pumping down the Sample Environment to a pressure of 1 mbar.

Results

In the following section we are presenting unmodified raw data taken with EnviroESCA which was not smoothed or shifted on the energy scale.

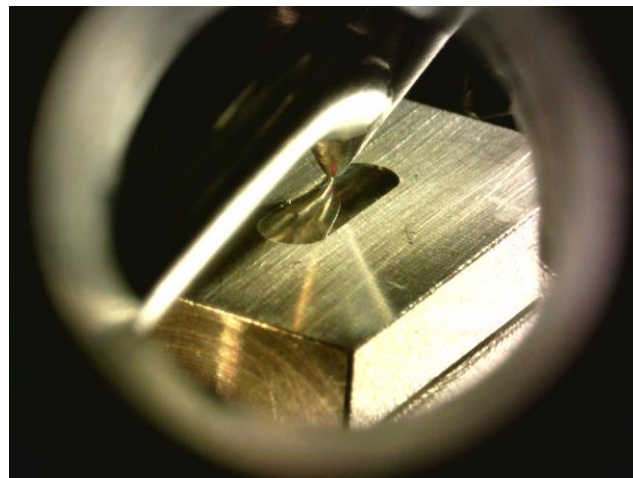


Fig. 3 Camera view onto the analyzed area of $[C_3C_1Im][NTf_2]$ which was placed in a 0.2 mm deep cavity of a stainless steel sample holder.

A first survey spectrum (2 Scans, 1 eV step width) was acquired in less than three minutes after starting to evacuate the Sample Environment to 1 mbar (cf. Fig. 4).

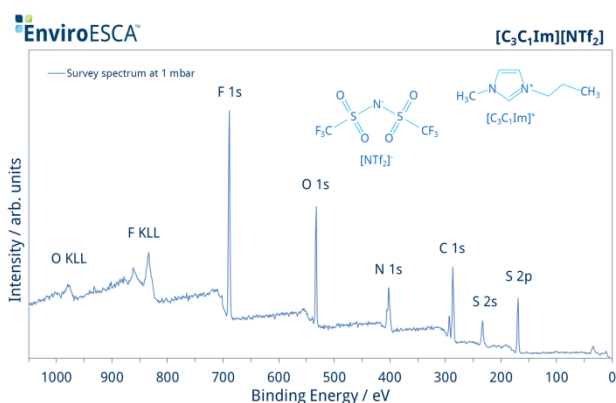


Fig. 4 XPS survey spectrum of $[C_3C_1Im][NTf_2]$ at a working pressure of 1 mbar. The inset shows the chemical structure of the ionic liquid.

That survey spectrum shows the following elements fluorine, oxygen, nitrogen, carbon, and sulfur as indicated by the chemical structure (cf. inset Fig. 4). No other unexpected elements or contaminations were detected.

Figure 5 shows a detail spectrum of the C 1s core-level region with its peak maximum located around 286.5 eV.

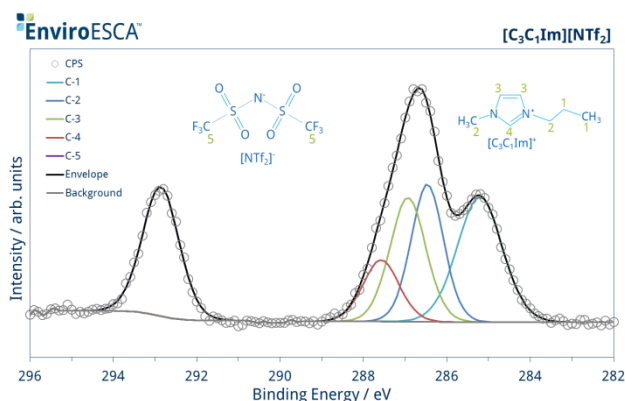


Fig. 5 C 1s core-level spectrum of the ionic liquid $[C_3C_1Im][NTf_2]$ measured at 1 mbar. The open circles represent experimental data and the solid black line shows the fitted curve. The colored lines correlate with different carbon moieties: C-C aliphatic (C-1), C-N aliphatic (C-2), imidazolic C-C-N (C-3), imidazolic N-C-N (C-4), and CF_3 (C-5) (cf. numbering of C's in the chemical structure).

That spectrum was fitted with five components located at 285.2 eV (C-1), 286.5 eV (C-2), 286.9 eV (C-3), 287.6 eV (C-4), and 292.9 eV (C-5). These five components can be assigned to the following carbon species: C-C aliphatic (C-1), C-N aliphatic (C-2), imidazolic C-C-N (C-3), imidazolic N-C-N (C-4), and CF_3 (C-5) as indicated by the black numbers on the different carbon atoms in the chemical structure of Fig. 5. The experimental area ratio of those carbon peak components (2.6 : 2.1 : 2.1 : 1.0 : 2.2) is close to the theoretical ratio of 2 : 2 : 2 : 1 : 2. The slightly increased area of the aliphatic component (C-1) indicates the presence of some adventitious carbon.

The high-resolution N 1s spectrum shown in Fig. 6 exhibits three different species. The nitrogen atom N-1 of the bis(trifluoromethylsulfonyl)imide anion $[NTf_2]^-$ is assigned to the peak component located at the lowest binding energy position (399.4 eV). The second component at 402.1 eV originates from the two nitrogen atoms N-2 of the aromatic imidazole ring. And the third component at 405.2 eV in the N 1s core-level spectrum is caused by residual nitrogen gas used for venting the instrument.

The S 2p core-level spectrum shows a doublet at 168.9 eV that can be assigned to the two sulfonic groups of the $[NTf_2]^-$ anion (cf. Fig. 7).

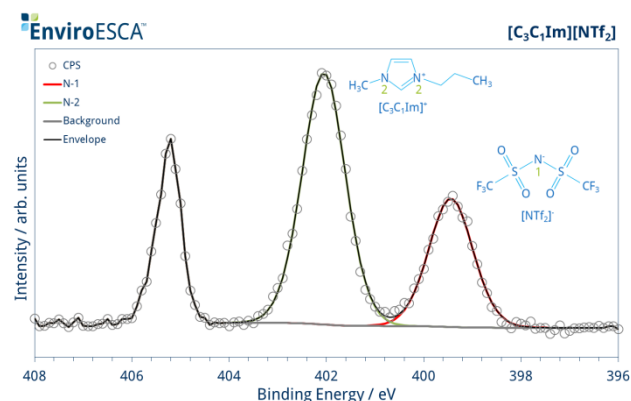


Fig. 6 N 1s core-level spectrum of $[C_3C_1Im][NTf_2]$ measured at 1 mbar. The open circles are experimental data and the solid black line shows the fitted curve. The colored lines correlate with the different nitrogen species: N-S imidic (N-1), N-C imidazolic (N-2). The third N component located at 405.2 eV originates from residual nitrogen gas used for venting.

The oxygen located in the S=O moieties of the sulfonic groups gives a single peak at 532.7 eV. And the organic fluorine located in the CF_3 groups of the $[NTf_2]^-$ anion can be correlated with the single component located at 688.9 eV in the F 1s core-level spectrum (not shown).

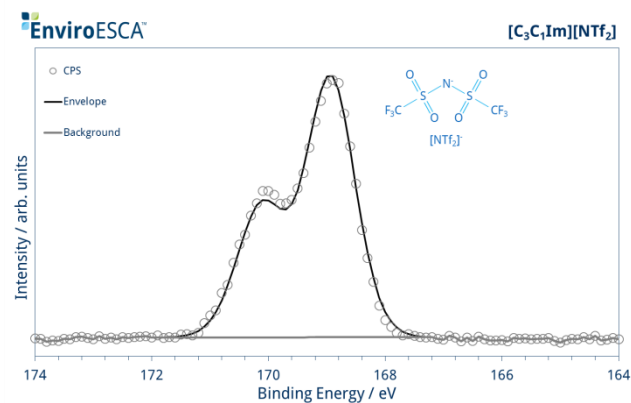


Fig. 7 S 2p core-level spectrum of $[C_3C_1Im][NTf_2]$ at 1 mbar.

Conclusion

EnviroESCA has proven to be a powerful tool to investigate with XPS the surface of ionic liquids especially when in contact with gases under application relevant conditions in the near ambient pressure region.

[1] Ionic Liquids: Applications and Perspectives, Intech, 2011, ISBN 978-953-307-248-7. DOI: 10.5772/1782

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