EnviroESCA™

AP-XPS investigations of a commercial lithium-based electrolyte

In this note we present first AP-XPS results from a commercial liquid electrolyte for lithium ion battery production recorded at 10 mbar in the EnviroESCA. The solution is $LiPF_6$ in EC/DMC as a common battery electrolyte. First we analyzed the $LiPF_6$ solution in its vapor and liquid phase. In a second step we immersed V_2O_5, a typical cathode material, in this solution. Photoelectron spectra show significant chemical differences on the studied surfaces. This proof of principle study shows the enormous potential of the EnviroESCA for AP-XPS investigations of solid-liquid interfaces and the simplicity of the experimental setup.

Motivation

X-ray Photoelectron Spectroscopy (XPS) is a powerful and non-destructive technique for material and surface analysis, which provides quantitative elemental and chemical information. (Near) Ambient pressure (N)AP XPS has been developed to enable routine analysis of real world samples. The transformation of XPS from a UHV-based method towards environmental conditions has revolutionized XPS dramatically, and opens up completely new application areas. (N)AP XPS is used extensively for in situ measurements and operando studies of industrial relevant (electro) chemical reactions and catalytic processes, especially at gas-liquid, gas-solid, and liquid-solid interfaces.

V_2O_5 is a model cathode material, not because of its ultimate performance or cycling stability, but because of its stability in completely de-lithiathed (=charged) state, giving easy access to the first discharge by spontaneous intercalation of lithium even without electrodes and potentials. Lithium can originate from any source, in this case from commercial liquid electrolyte solution, producing the classical electrolyte-cathode interface. A detailed understanding of the interface reactions here and at the electrolyte-anode interface in its elementary steps is still missing. It would allow for materials optimization of the electrode materials and the electrolyte, but it would also help to improve performance, durability and safety of the complete lithium ion battery.

Fig. 1 Typical set-up with a solid sample in solution for solid-liquid interface studies using the EnviroESCA.

Method

EnviroESCA utilizes X-ray Photoelectron Spectroscopy (XPS) as analytical technique, cf. Fig. 2. Here an electron beam is generated inside the X-ray source and focused on an aluminum X-ray anode. The deceleration of electrons on the anode generates X-rays. This X-ray beam is monochromated and focused on the sample.

X-ray photons impinging the sample excite electrons in the material which are subsequently emitted with a specific kinetic energy that is determined by their binding energy and the photon energy of the X-rays. In case of solid samples only electrons from atoms down to a depth of about 10 nm are able to leave the surface.
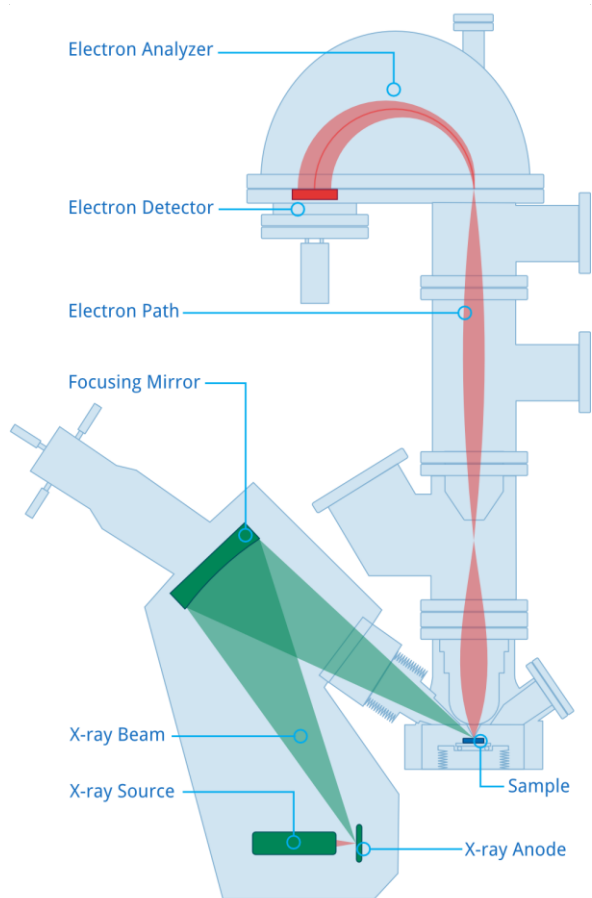
Fig. 2 XPS with EnviroESCA

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 intensity in counts per second. A photoelectron spectrum is recorded by sweeping the voltage of the spherical capacitor while measuring the number of electrons per second on the detector. Then a quantitative analysis of the sample surface - giving the elemental composition - can be extracted from these spectra.

Experimental Section

EnviroESCA can work under vacuum as well as (near) ambient pressure (N)AP conditions up to several dozens of mbar. Thus, it is very well suited for in situ and operando studies of electrochemical reactions at

gas–solid or liquid–solid interfaces, e.g., in battery materials.

EnviroESCA comes with an intrinsic charge compensation which we call *Environmental Charge Compensation* that makes additional low energy electron or ion sources unnecessary. As shown schematically in Fig. 3 illumination of the surrounding gas atmosphere with soft X-rays generates free charges, which compensate potential surface charging on the sample.
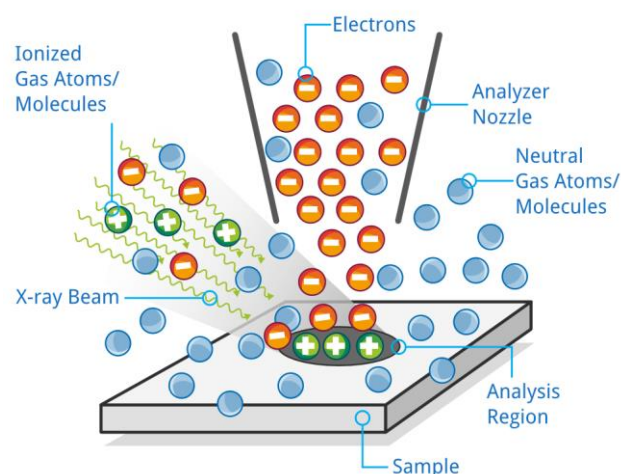

Fig. 3 Environmental Charge Compensation

Here, we present first results of a surface chemical analysis of a commercial electrolyte solution containing 1 M $LiPF_6$ in a 1:1 mixture of EC/DMC. The liquid electrolyte was transferred from a glovebox in a sealed container into the load lock chamber of the EnviroESCA and filled in a watch glass under a flow of argon. Then the pressure was stabilized to 10 mbar and the electrolyte was analyzed as received and in contact with a V_2O_5 single crystal using the EnviroESCA.

In the following section XPS data will be presented that have been obtained from the:

1. electrolyte, as vapor and in liquid phase
2. V_2O_5 single crystal in the electrolyte, and
3. cleaned V_2O_5 single crystal after drying in air.

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Results

Pure electrolyte, as vapor and in liquid phase

At first we analyzed the vapor above the as purchased LiPF$_6$ electrolyte at a pressure of 10 mbar to evaluate contributions originating from the gas phase. The corresponding C 1s and O 1s detail spectra are shown in Fig. 4 and 5. The C 1s of the vapor consist of two peaks in a 2:1 ratio that can be assigned to $\underline{C}$-O and $\underline{C}$O$_3$ moieties of ethylene carbonate (EC) and dimethyl carbonate (DMC) (see inset in Fig. 4). This explicit correlation to solvent-related carbon atoms will help for later assignments of solution based C 1s spectra.

Also the O 1s spectrum of the gas phase shows oxygen atoms ($\underline{O}$=C, $\underline{O}$-C) from the solvents as well as additional contributions from molecular oxygen (O$_2$) and water, which results in three main features at binding energies of 534 eV, 536 eV, and 540 eV originating from $\underline{O}$=C, $\underline{O}$-C (and H$_2$O), and O$_2$, respectively.[1-2]

A bit more complexity is observed in C 1s and O 1s spectra of the liquid phase of LiPF$_6$ solution in EC/DMC. Figure 4b and 5b show these liquid spectra and with the knowledge of the gas phase composition the C 1s and O 1s spectra can be interpreted very well.

The C 1s in Fig. 4b also contains two components from $\underline{C}$-O and $\underline{C}$O$_3$ moieties but compared to the vapor phase spectra those liquid peaks are shifted by ~1.0 eV to lower binding energy. Additionally a third component caused by adventitious hydrocarbons ($\underline{C}$C/$\underline{C}$H) is now present at 285.5 eV.

The O 1s core-level spectrum of the electrolyte solution (*cf*. Fig. 5b) also shows two main components at 533 eV and 535 eV due to $\underline{O}$=C and $\underline{O}$-C moieties from the liquid phase of the organic solvent mix. In comparison to the vapor phase those peaks are also shifted to lower binding energy.
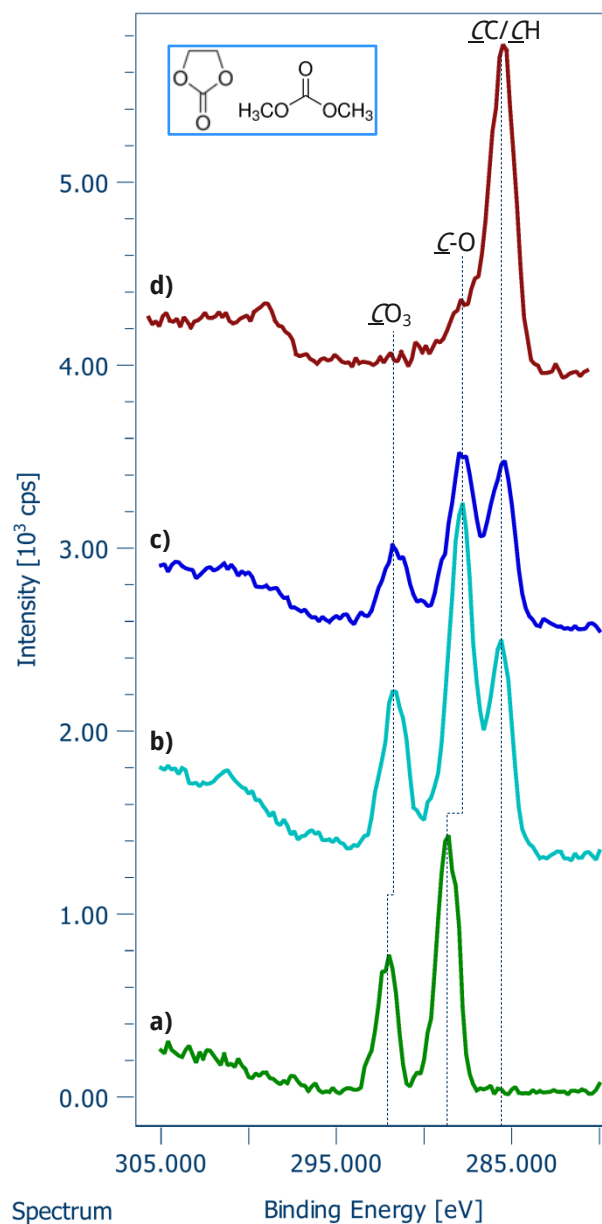

Fig. 4 C 1s core-level spectra taken at 10 mbar from a) the vapor above LiPF$_6$ in EC/DMC electrolyte, b) the liquid electrolyte, c) a V$_2$O$_5$ single crystal immersed in the electrolyte, and d) the same crystal after immersion, EtOH cleaning, and drying. (Inset shows chemical structures of the solvent mixture.)

V$_2$O$_5$ single crystal in electrolyte

Immersion of a V$_2$O$_5$ single crystal into the LiPF$_6$ electrolyte was done to simulate a typical cathode material and study the consequences of this addition. There has been no potential applied but a spontaneous Li-intercalation into the cathode can be expected.[3]
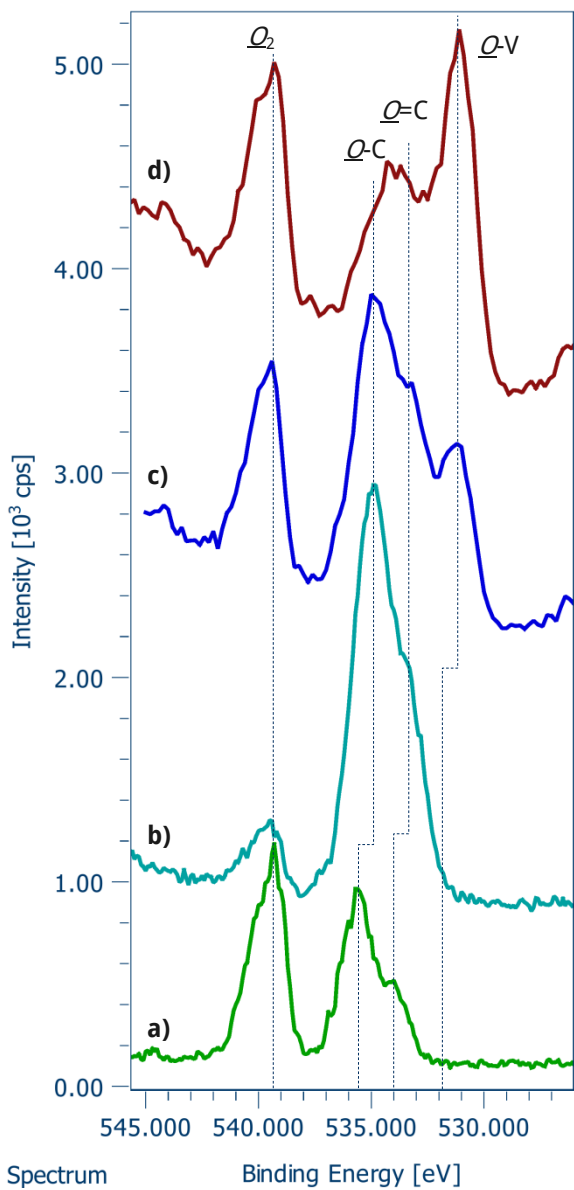
Fig. 5 O 1s core-level spectra taken at 10 mbar from a) vapor above LiPF$_6$ in EC/DMC electrolyte, b) liquid electrolyte, c) a V$_2$O$_5$ single crystal immersed in electrolyte, and c) the same crystal after immersion, EtOH cleaning, and drying.

Figures 4–7 exhibit the spectra obtained in a region where a film of liquid electrolyte covered the V$_2$O$_5$ crystal that was thin enough to probe both the electrolyte and the crystal's surface.

Now additional peaks originating from the V$_2$O$_5$ crystal are needed to describe the measured spectra. In the C 1s core-level the $\underline{C}$C/$\underline{C}$H related component rises to 36 % (cf. Fig. 6) compared to 27 % in the electrolyte.

Compared to the pure electrolyte the O 1s spectrum changes significantly due to an additional vanadium oxide related component ($\underline{O}$-V) located around 531 eV, cf. Fig. 5 and 7. Additionally V$_2$O$_5$ related V 2p components with V 2p$_{3/2}$ at 518 eV and V 2p$_{1/2}$ at 525 eV could be observed, as shown in Fig. 7.[4]

Fig. 7 also includes the O 1s, F 1s, and P 2p detail spectra of the V$_2$O$_5$ crystal in contact with the electrolyte solution. P 2p and F 1s spectra exhibit single peaks at 687 eV and 137 eV that correspond well with earlier reported data of liquid LiPF$_6$ electrolytes.[5-8] Absence of other F 1s and P 2p peaks related to LiF or phosphates indicate a mostly intact LiPF$_6$ solution. Moreover, a small and broad Li 1s peak is observed at around 56 eV indicating the presence of lithium in the analyzed solid-liquid interface region.[5-8]
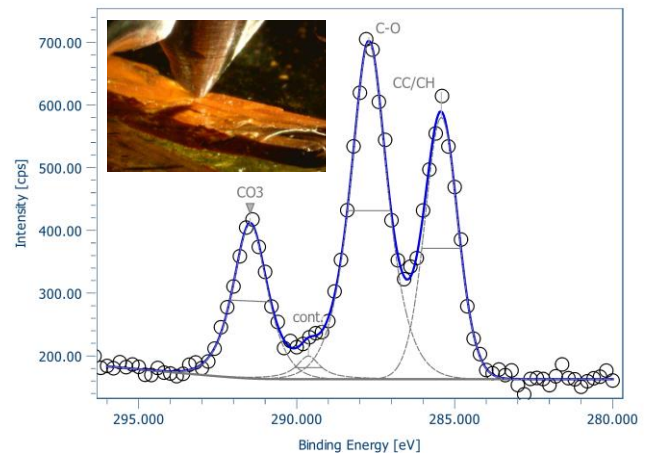

Fig. 6 Fit of the C 1s core-level spectrum taken at 10 mbar from a V$_2$O$_5$ single crystal immersed in the electrolyte. (Inset shows V$_2$O$_5$ sample in liquid electrolyte under the nozzle)

V$_2$O$_5$ dry after cleaning

Finally, the dry crystal was investigated after a short ethanol cleaning to determine which components from the electrolyte remain on the surface after immersion. The corresponding C 1s and O 1s core-level spectra are presented in Fig. 4d and 5d. Apparently EC/DMC-related carbon components in the C 1s are lost almost completely and the main species originates now from $\underline{C}$C/$\underline{C}$H together with minor contributions from $\underline{C}$-O, $\underline{C}$=O and/or $\underline{C}$OO species.
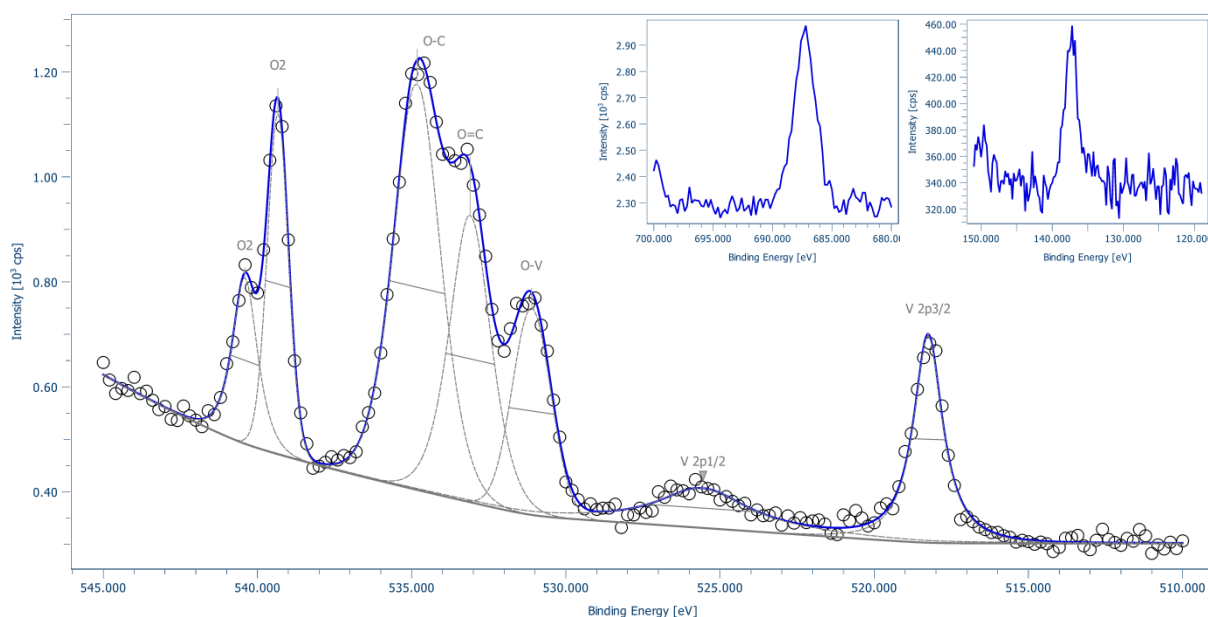
Fig. 7 Fit of the O 1s and V 2p core-level spectrum taken at 10 mbar from a V_2O_5 single crystal immersed in $LiPF_6$ in EC/DMC electrolyte. Insets show the corresponding F 1s and P 2p spectra.

The O 1s spectrum also shows some differences when compared to the spectra of the immersed crystal. Now the vanadium-related components are more intense and additional contributions from oxidized Li species located in the binding energy region from 532-535 eV are also possible, e.g., $LiPO_2F_2$, Li_xO_y, Li_2CO_3. Additional information could be obtained from the fit of V $2p_{3/2}$ core-level spectra which indicate reduction from V^{5+} to V^{4+} during intercalation and an enrichment of V^{4+} species on the crystal surface after cleaning and drying.

Alkali intercalation in V_2O_5 leads to a charge transfer of the outer shell Li 2s electron to unoccupied V 3d-derived conduction band states that split-off due to localization effects. Exposure of such an intercalated $Li_xV_2O_5$ leads to surface reactions of the lithium with the water vapor, forming Li oxides, hydroxides, peroxides and superoxides. Part of the oxygen needed for this comes from the V_2O_5 structure itself, leaving behind oxygen vacancies. This reaction transfers electrons back to the V ions, filling unoccupied V 3d states, increasing the reductions. Thus the contribution of the V^{4+} peak component to the total V $2p_{3/2}$ peak area increases from 4.4% when in solution to 9.3% on the dry crystal. From the dried-out $LiPF_6$ also P- and F-containing reaction products were found on the crystal surface after drying.

Conclusion

We have demonstrated the possibility of studying commercial Li-based electrolytes at elevated pressures using the EnviroESCA. With that proof-op-principle experiment we were able to show how in situ or operando investigations of interfacial electrochemical reactions could be done in a very easy and effective way. Further work is currently in progress to study lithium ion batteries under working conditions and get deeper insight into the real nature of the solid-electrolyte interfaces.

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