crystals

Supplementary Material

Probing lithium-ion battery electrolytes with laboratory near-ambient pressure XPS

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Supplemental Information

1. *$LiPF_6$ (commercial) electrolyte – additional NAP XPS data*

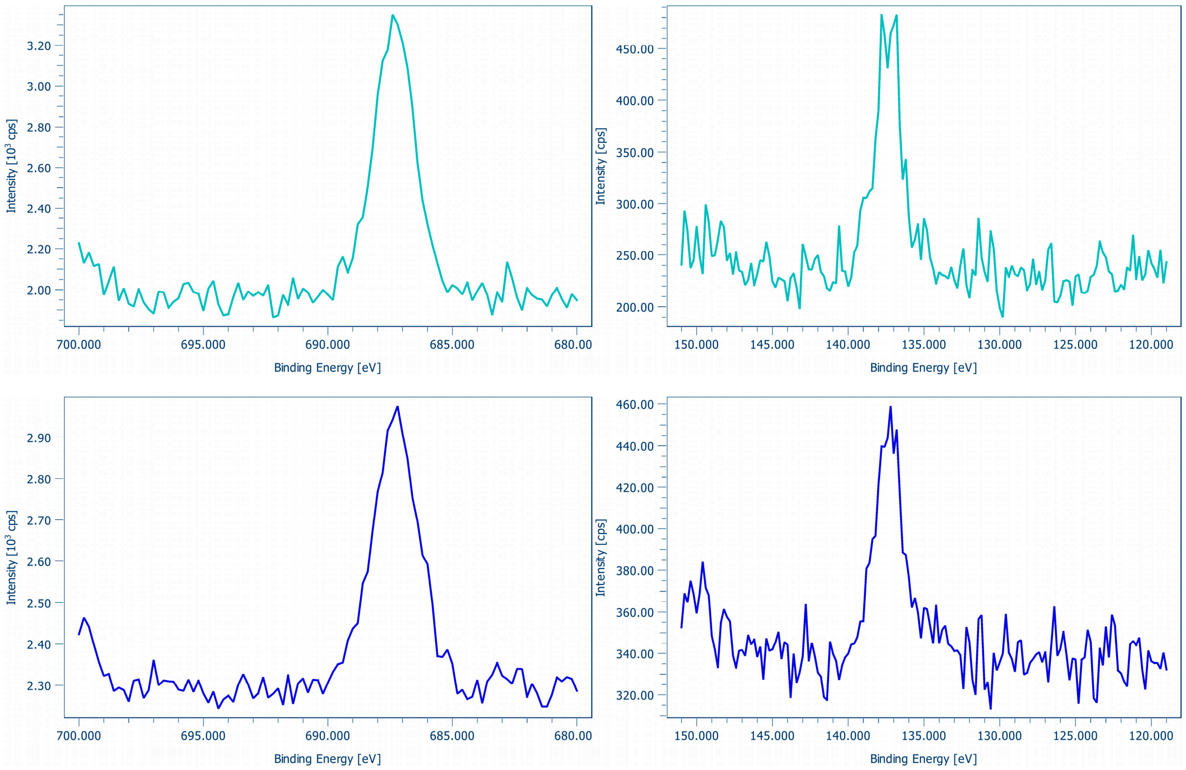


Figure S1. F 1s (left panel) and P 2p (bottom row) core-level spectra of LP30 electrolyte (top row) and in contact with a V_2O_5 single crystal (bottom row) at 10 mbar.

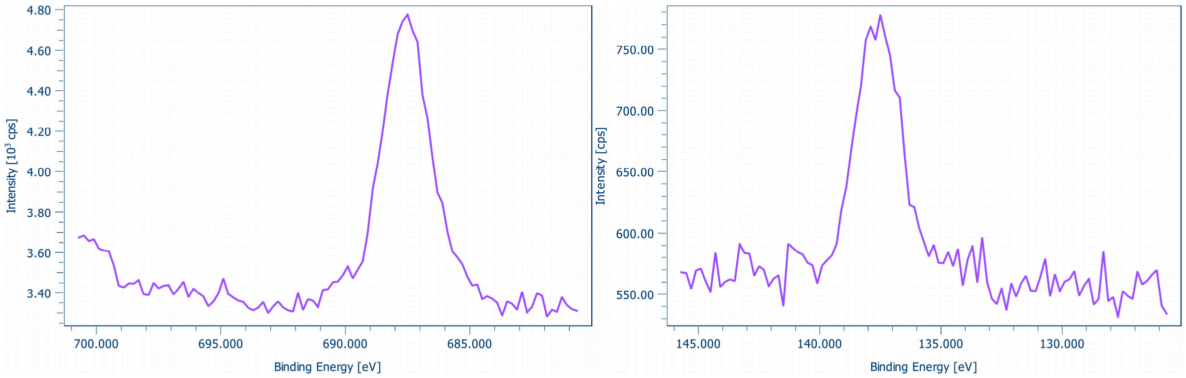


Figure S2. F 1s and P 2p core-level spectra of the immersed V_2O_5 single crystal after cleaning with EtOH.

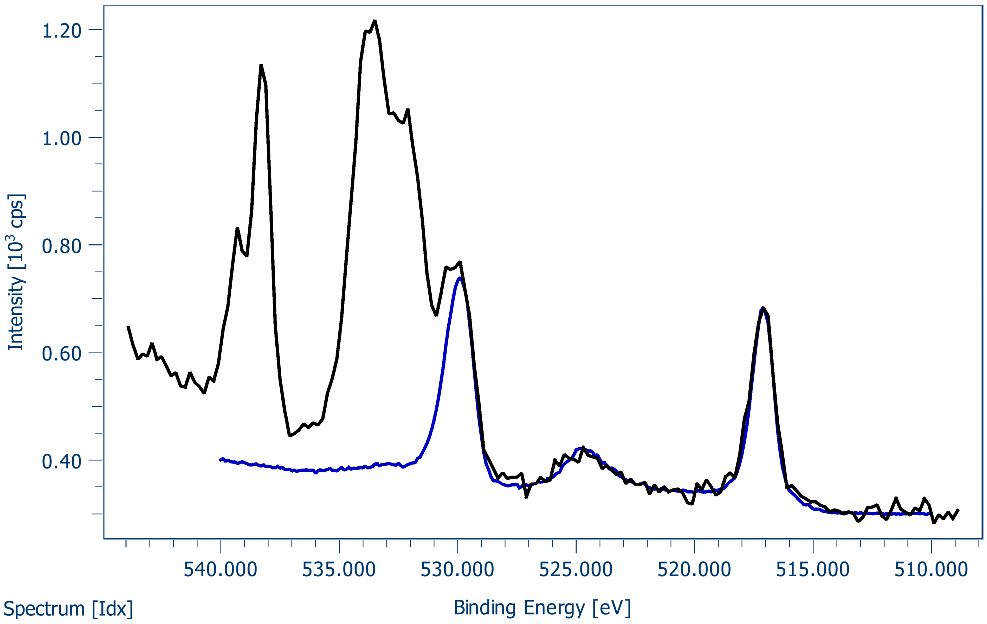


Figure S3. V 2p core-level spectra of a pristine V_2O_5 single crystal (blue curve, x0.1) and in contact with the LP30 electrolyte at 10 mbar (black curve). Relative V^{4+} peak component areas are 4.6% (pristine) and 4.5% (in LP30).

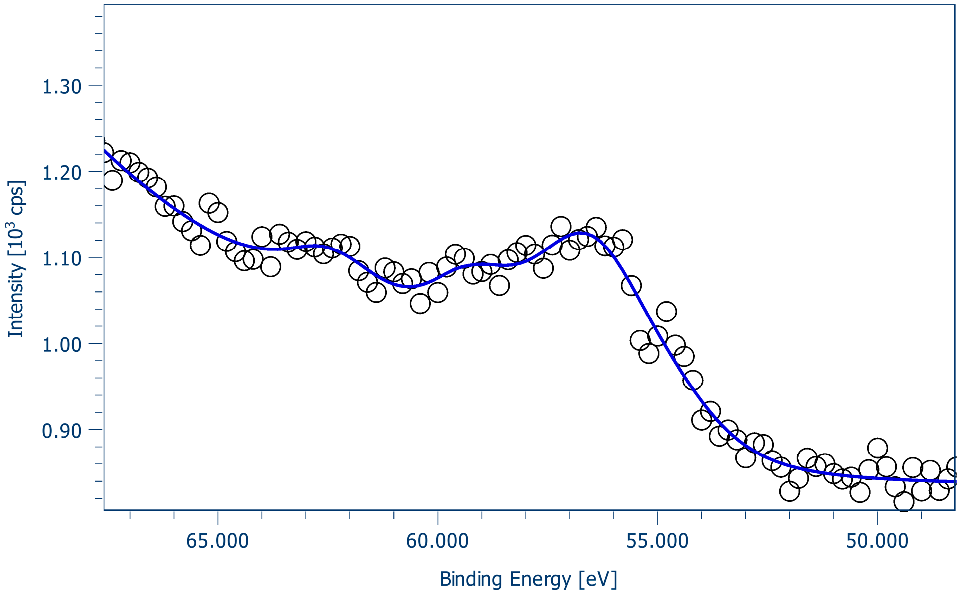


Figure S4. Li 1s core-level spectra of the V_2O_5 single crystal after immersion in LP30 electrolyte and cleaning with EtOH.

2. *Comparison of LiTFSI and LiPF₆ electrolyte– additional NAP XPS data*

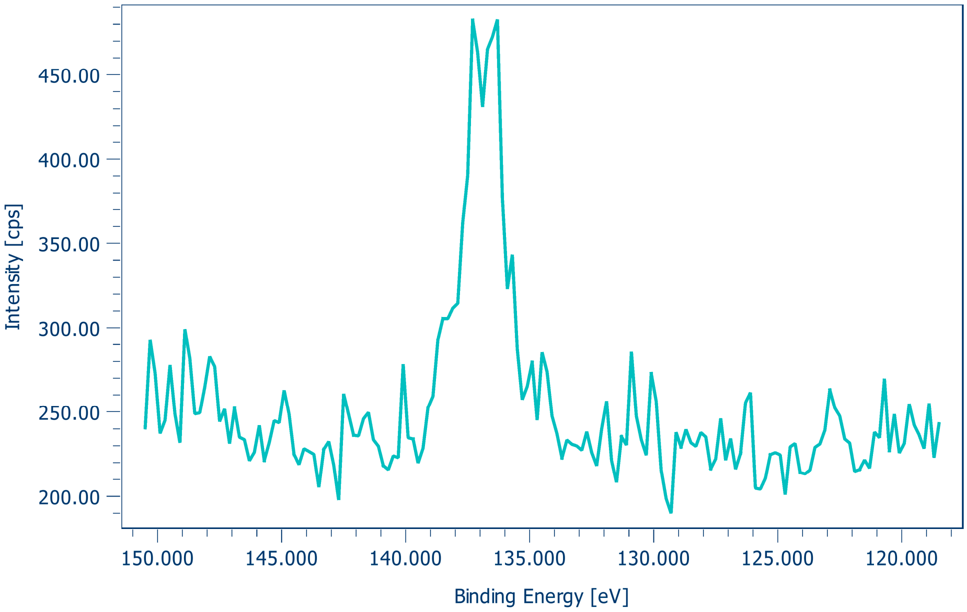


Figure S5. P 2p core-level spectrum of LP30 electrolyte in EC/DMC at 10 mbar (here the BE scale is referenced to C̲C/C̲H = 285.0eV).

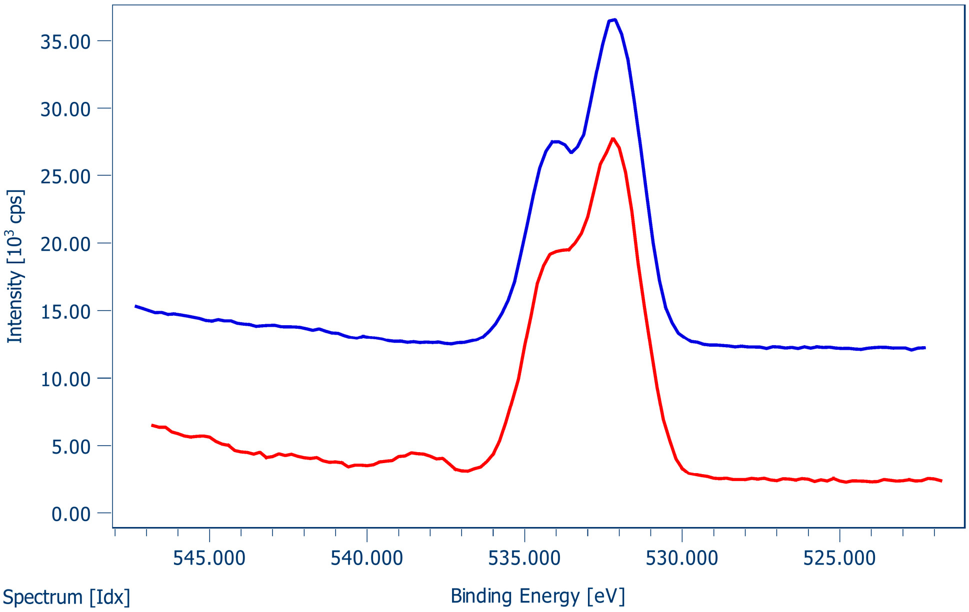


Figure S6. Decrease of the molecular oxygen (O_2) peak at ~538eV in the O 1s core-level spectra of LiTFSI electrolyte, initially (red) and after 40 min at 1 mbar (blue).

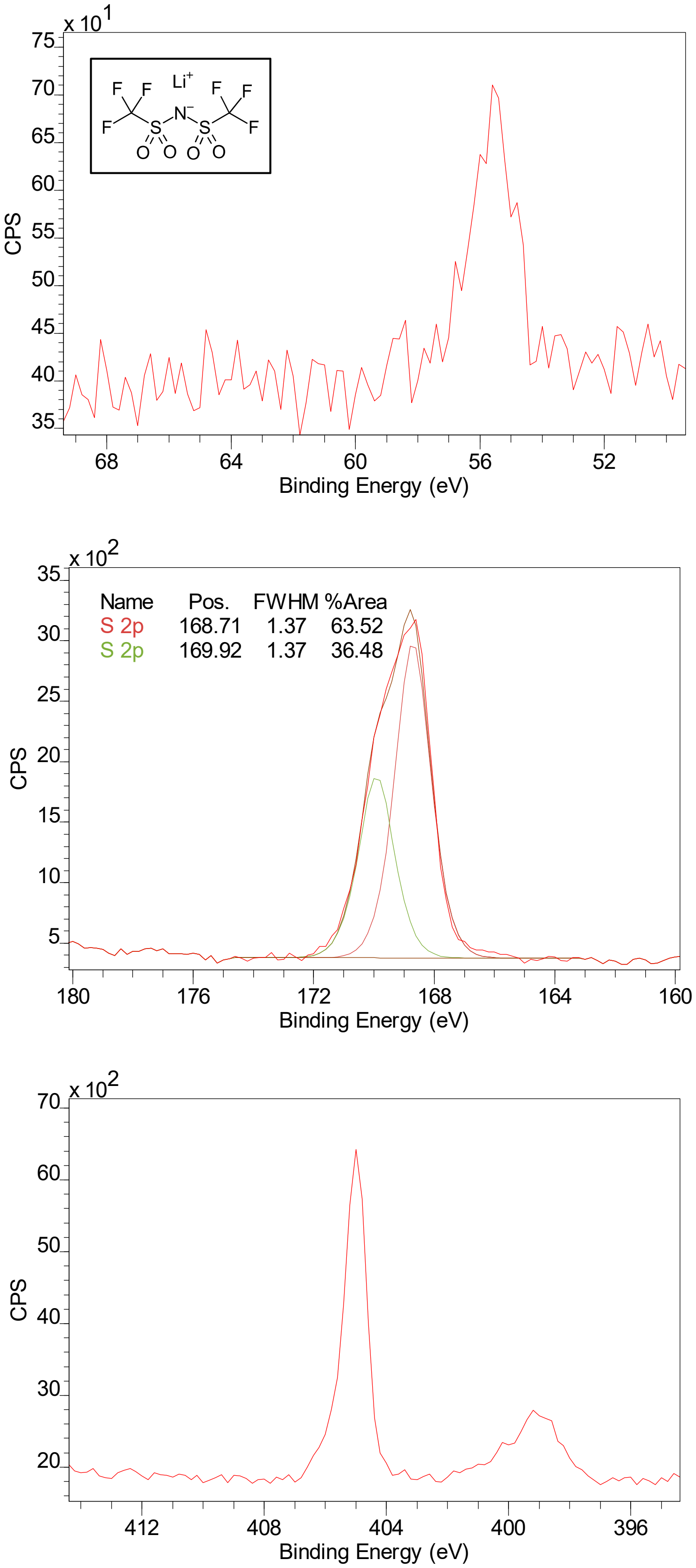


Figure S7. Li 1s (top), S 2p (middle), and N 1s (bottom) core-level spectra of LiTFSI in PC electrolyte at 2 mbar. The chemical structure of LiTFSI is shown in the inset of a.

3. *Contamination layer thickness estimation*

When the detected carbon is entirely attributed to a contamination layer, the quantification result can be corrected with the estimated layer thickness:

$$A_{N,t} = A_{N,t,cont} * \exp(d_{cont.} \,/\, (L_t * cos\theta))$$
$$A_{N,t} = A_{N,t,cont} *(1 - C\% \,/\, 100)\hat{}(-L_{C1s}/\, L_t)$$
$$A_{N,t} = A_{N,t,cont} *(1 - C\% \,/\, 100)\hat{}\ ((-E_{kin,C1s}/\, E_{kin,t})\hat{}0.842$$

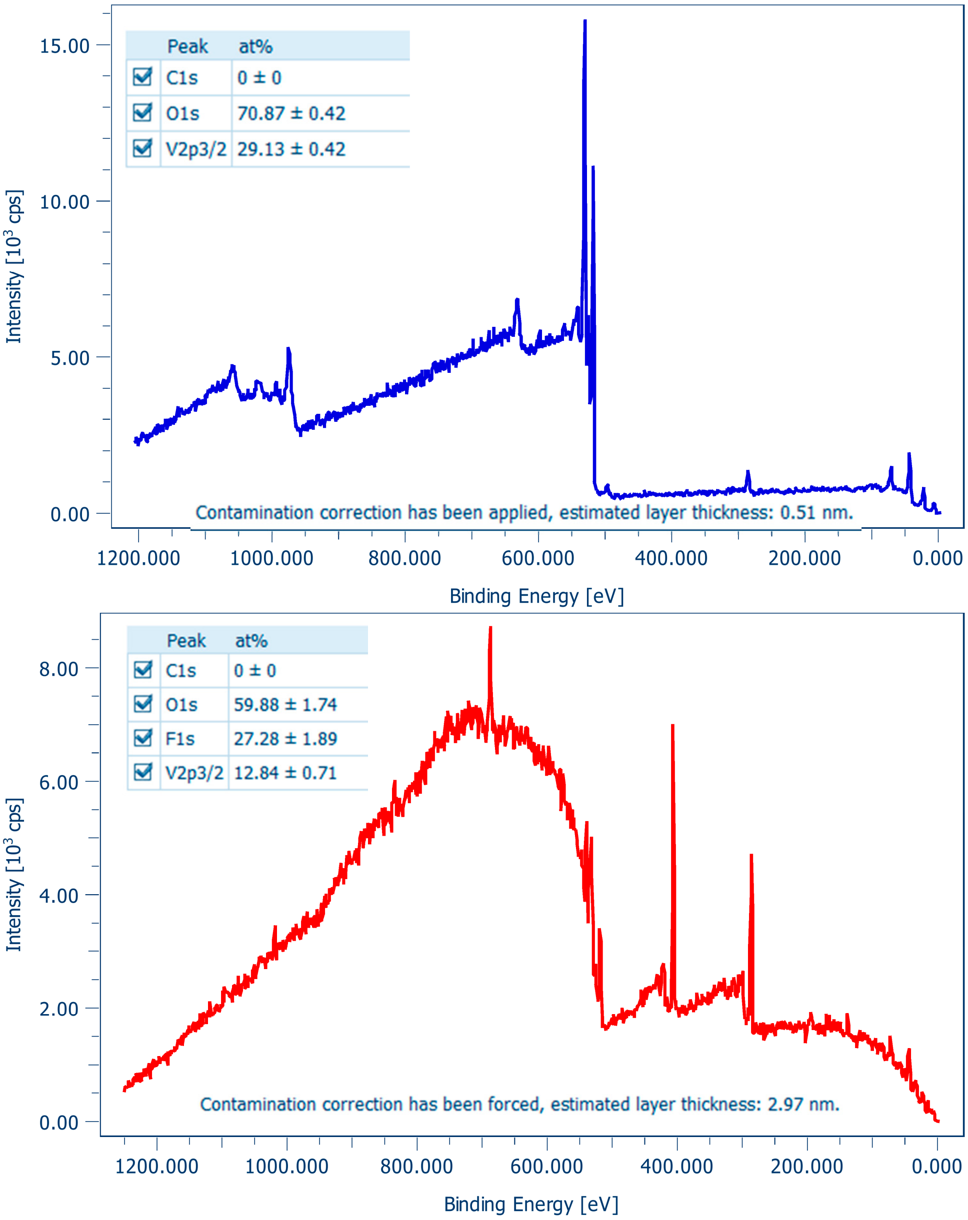
with an estimated contamination layer thickness d

$$d = -L_{C1s} * cos\theta * \ln(1 - C\%/100)$$

and an estimated attenuation length L in nm

$$L_t = 0.00837 * E_{kin,t}^{0.842}$$

Typically, a carbon contamination layer can be expected if the sample has been exposed to air. This correction is only applicable, if the sample does not contain carbon as an integral part of its composition [1-4].



Peak	at%
☑ C1s	0 ± 0
☑ O1s	70.87 ± 0.42
☑ V2p3/2	29.13 ± 0.42

Contamination correction has been applied, estimated layer thickness: 0.51 nm.

Peak	at%
☑ C1s	0 ± 0
☑ O1s	59.88 ± 1.74
☑ F1s	27.28 ± 1.89
☑ V2p3/2	12.84 ± 0.71

Contamination correction has been forced, estimated layer thickness: 2.97 nm.

Figure S8. Survey spectrum of the pristine (top) V_2O_5 single crystal and after immersion in LP30 electrolyte and cleaning with EtOH (bottom). The quantification results after carbon contamination correction and contamination layer thicknesses are shown as insets.

4. References

1. J. E Castle and M.A. Baker, *J. Electron. Spectrosc. Relat. Phenom.*, 105, 245 (1999).
2. J. E. Castle and C. J. Powell, *Surf. Interface Anal*. 36, 225 (2004).
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4. A. S. Lea, K. R. Swanson, J. N. Haack, J. E. Castle, S. Tougaard and D. R. Bear, *J. Electron. Spectrosc. Relat. Phenom.*, 42, 1061(2010).