Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Supporting Information

Monitoring the Chemical and Electronic Properties of Electrolyte–Electrode Interfaces in All-Solid-State Batteries Using *Operando* X-ray Photoelectron Spectroscopy

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***Operando* XPS measurement on the WE LCO/LPS/VGCF (45/50/5, w/w/w)**

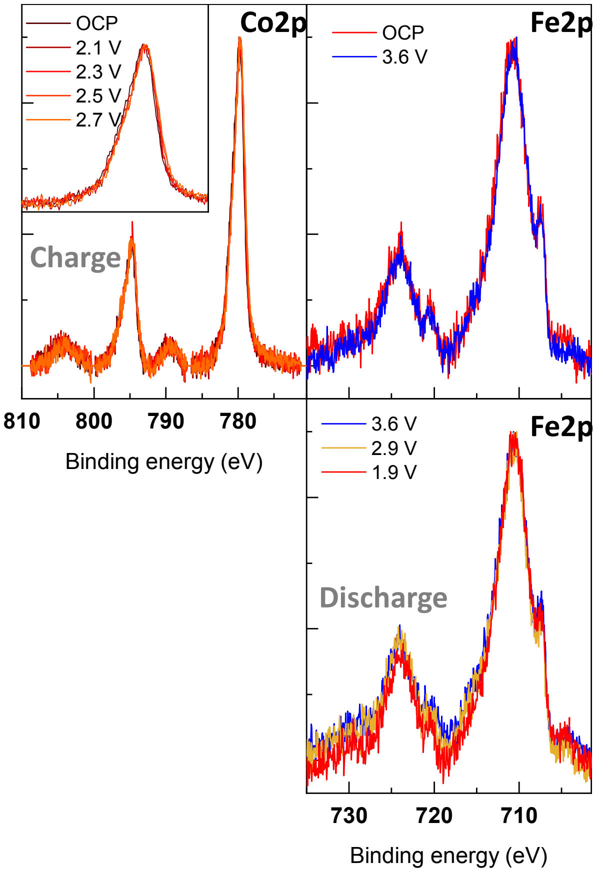
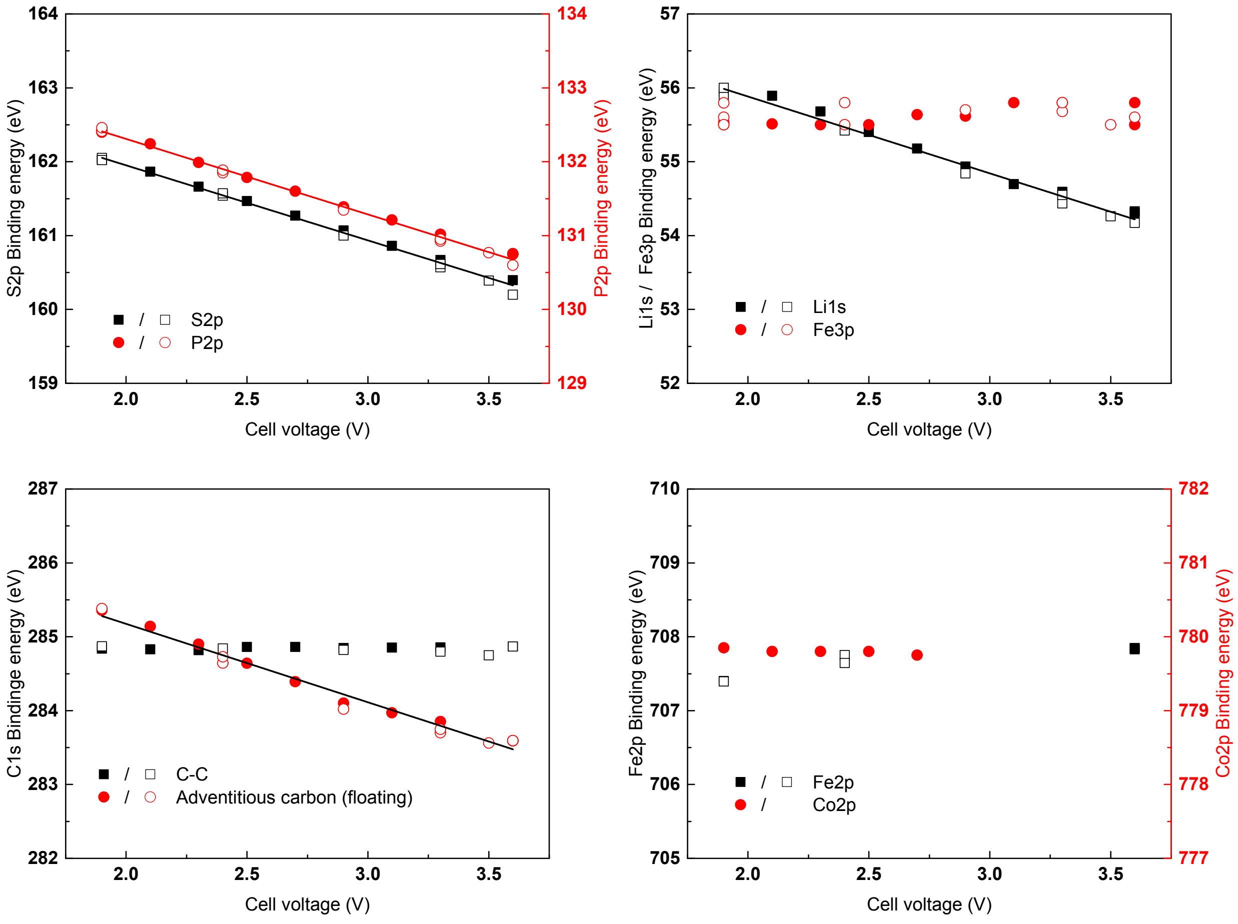


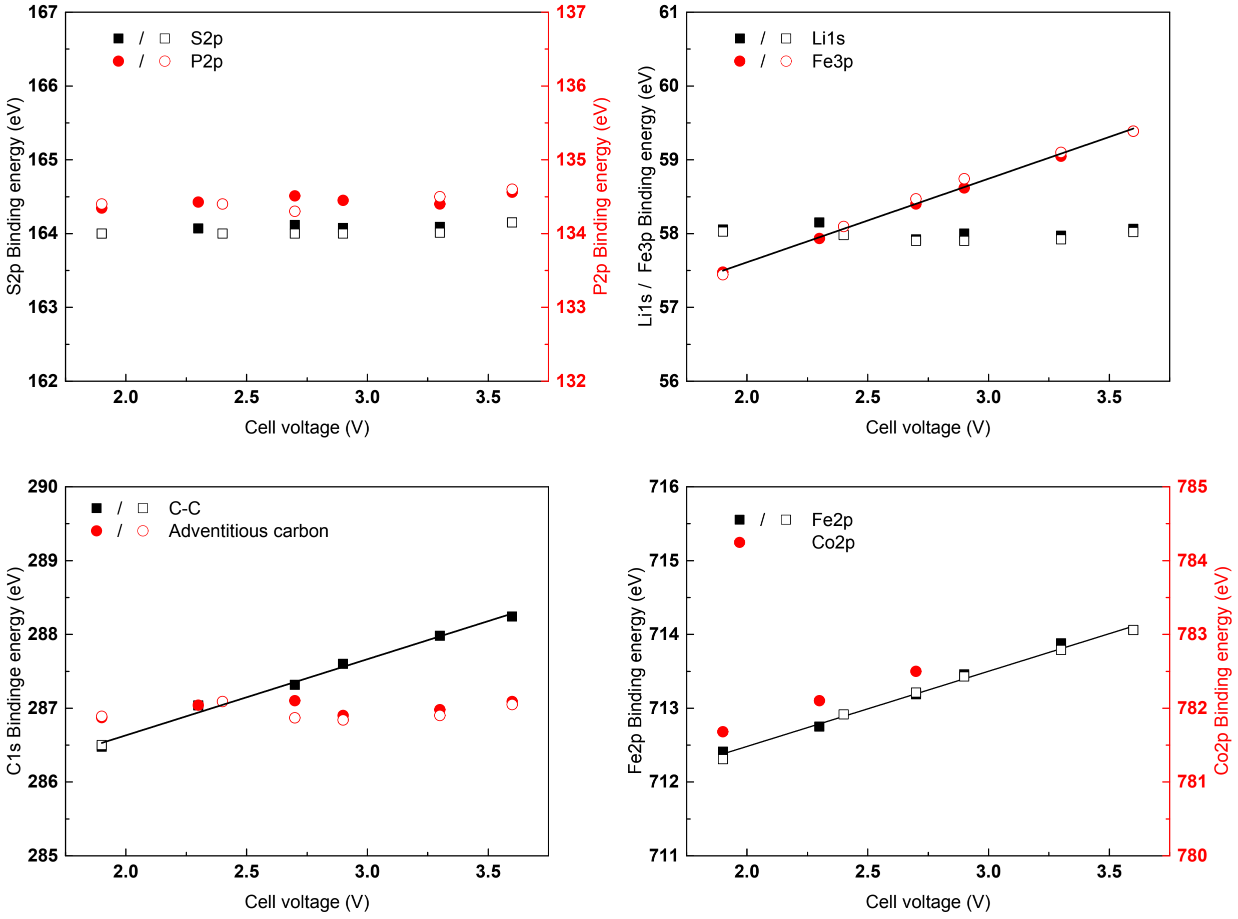
Figure S1. Co2p and Fe2p core levels spectra at selected potential recorded during the *operando* XPS measurement of the WE (45 wt% LCO, 50 wt% LPS and 5 wt% VGCF) cycled vs. $InLi_x$.



Core level	Slope (eV/V)	Adj. R-Square
S2p	-1.02 ± 0.02	0.9950
P2p	-1.02 ± 0.01	0.9961
Li1s	-1.04 ± 0.02	0.9894
C1s (C-H, float.)	-1.06 ± 0.04	0.9775

Core level	Binding energy (eV)
Fe3p	55.6 ± 0.1
Fe2p	710.5 ± 0.1
Co2p	779.8 ± 0.0
C1s (C-C)	284.9 ± 0.1

Figure S2. WE electrode grounded to the analyzer. Apparent binding energy shifts of the main peak in the S2p, P2p, C1s, Fe3p/Fe2p and Co2p spectra as a function of the cell voltage. Solid symbols data were recorded during the delithiation and open symbols data were recorded during lithiation of the WE (45 wt% LCO, 50 wt% LPS and 5 wt% VGCF) cycled vs. $InLi_x$.



Core level	Slope (eV/V)	Adj. R-Square
Fe3p	1.13 ± 0.03	0.9942
Fe2p	1.02 ± 0.02	0.9935
C1s (C-C)	1.03 ± 0.03	0.9911

Core level	Binding energy (eV)
S2p	164.1 ± 0.1
P2p	134.4 ± 0.1
Li1s	58.0 ± 0.1
C1s (float.)	287.0 ± 0.1

Figure S3. CE electrode grounded to the analyzer. Apparent binding energy shifts of the main peak in the S2p, P2p, C1s, Fe3p/Fe2p and Co2p spectra as a function of the cell voltage. Solid symbols data were recorded during the delithiation and open symbols data were recorded during lithiation of the WE (45 wt% LCO, 50 wt% LPS and 5 wt% VGCF) cycled vs. $InLi_x$.

Note 1: Physical model for the observed binding energy shift

Figure S7 illustrates the energy diagram of the sample and the hemispherical analyzer in a XPS measurement.[1, 2] which states the correlation between surface potential and the binding energy shift.

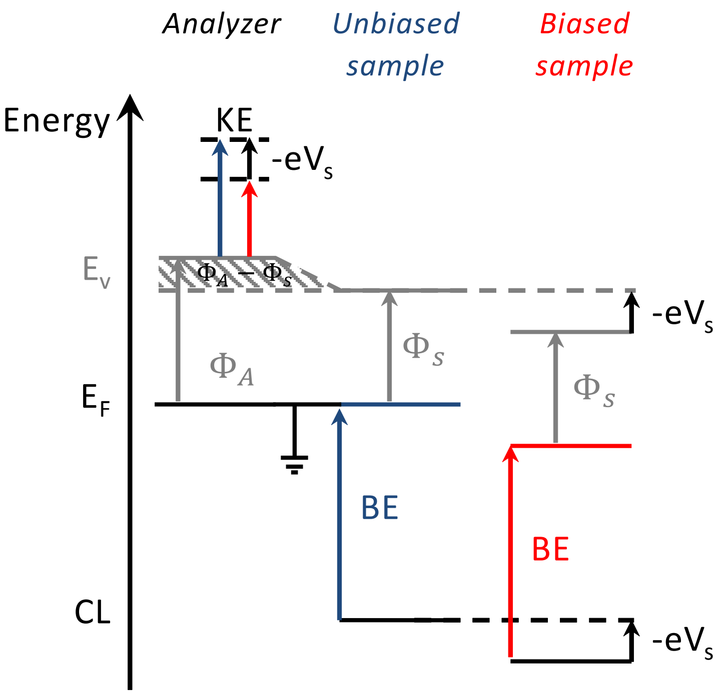


Figure S4. Energy diagram of the XPS measurement for an unbiased and biased sample. E$_V$: vacuum level, E$_F$: Fermi level, CL: core level, Φ: work function, A: hemispherical energy analyzer, s: sample, BE: binding energy and V$_s$: surface potential.

For an unbiased (grounded) sample, as depicted in Figure S7, the kinetic energy of the photo-electrons measured by the analyzer depends on the binding energy (BE) as well as the analyzer work function.[1]

$$KE_A\,(unbiased) = hv - BE - \Phi_s - (\Phi_A - \Phi_s) \qquad \textbf{Equation S1}$$

If the Fermi levels of the analyzer (E_F^A) and the sample E_F^S are aligned, as in the case of a grounded sample, the measured kinetic energy is independent of the sample work function (Φ_s).

The hemispherical energy analyzer measures the kinetic energy (KE) of the emitted photoelectrons from the sample. By calibrating the analyzer work function, it is possible to accurately calculate the BE according to Equation S2, especially if monochromatized source radiation is used.

$$KE_A = hv - BE - \Phi_A \qquad \textbf{Equation S2}$$

In case of external bias voltage on the electrochemical cell, the applied voltage has a direct influence on the position of E_F^S. The measured kinetic energy (KE$_A$) is then dependent on the relative positions between E_F^A and E_F^S. Noting $\Delta E_F = - e\Delta V_s$, the KE energy for a biased sample can be expressed in the following way:

$$KE_A\,(biased) = hv - BE - eV_s - \Phi_A \qquad \textbf{Equation S3}$$

Therefore

$$KE_A\,(biased) - KE_A\,(unbiased) = \Delta KE = - e\Delta V_s$$ **Equation S4**

Taken the fundamental measurement principle of the analyzer into account (Equation S2), which only concludes the BE from KE_A, the measured BE (BE_A) will also shift according to the biased surface potential.

$$BE_A\,(biased) - BE_A\,(unbiased) = \Delta BE = e\Delta V_s$$ **Equation S5**

If the counter electrode in the operando XPS cell is grounded to the analyzer, the relationship in Equation S5 can be directly used to describe the correlation between the observed shift in BE and the surface potential on the particles constituting the WE.

If the WE is grounded to the analyzer, the electronically conductive elements of the WE will exhibit no BE shift due to charge compensation. However, insulating components, such as the SE, will have an apparent BE shift, due to the relative change of their E_F position to the analyzer.

The influence of the cell voltage (V_{cell}) on the E_F of the electrodes is described as follows:

$$V_{cell} = E_{WE} - E_{CE} = -\frac{E_F^{WE} - E_F^{CE}}{e}$$ **Equation S6**

With $E_F^{WE} = E_F^{A}$ and $E_F^{CE} - E_F^{SE} = const.$ (in the case of $InLi_x$ the (de)lithiation process occurs on a electrochemical potential plateau), the relative difference between E_F^{SE} and E_F^{A} is

$$\Delta\left(E_F^{SE} - E_F^{A}\right) = e\Delta V_{cell}$$ **Equation S7**

The change in cell voltage causes a proportional E_F shift of the sample with respect to the analyzer.

Equation S4 is thus further modified as follows:

$$\Delta KE = - e\Delta V_s + e\Delta V_{cell}$$ **Equation S8**

Applying the relationship in Equation S2 analogously as above, the change in binding energy for all insulating and semi-conducting components of the WE is

$$\Delta BE = e(\Delta V_s - \Delta V_{cell})$$ **Equation S9**

Operando XPS measurement on the carbon-free WE LCO/LPS (50/50, w/w)

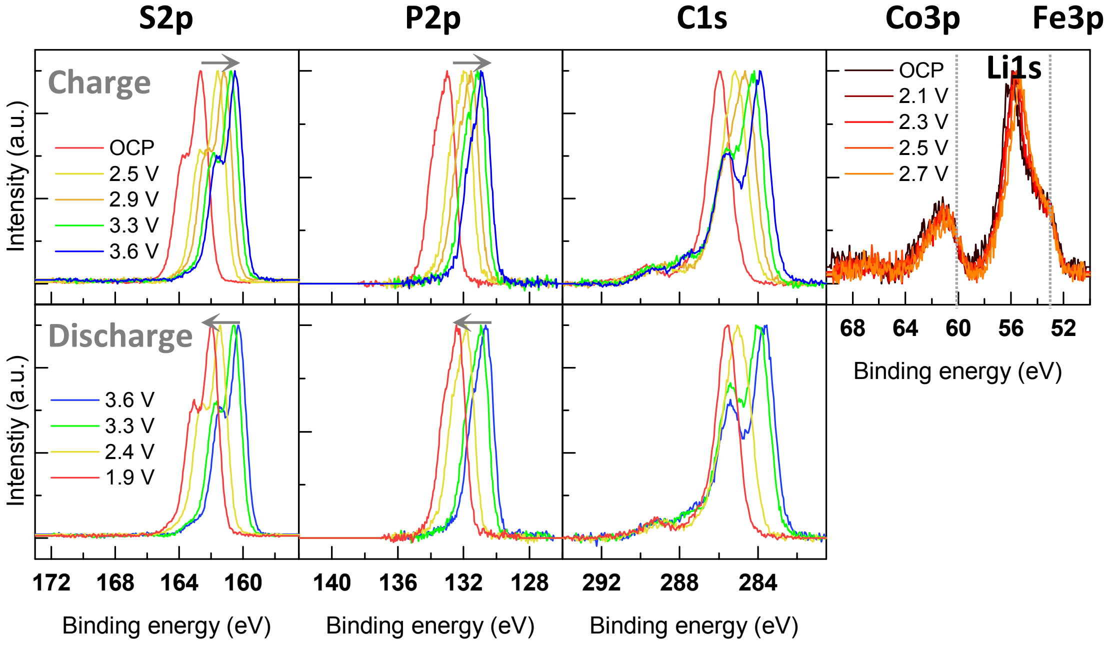


Figure S5. XPS core levels spectra at each potential recorded during the operando XPS measurement of the LCO/LPS (50/50) WE. The arrows indicate the direction of the peak shifts. The WE was grounded to the analyzer during the measurement.

References

1. C. S. Fadley, *Academic, New York*, 1978.
2. M. A. Brown, Z. Abbas, A. Kleibert, R. G. Green, A. Goel, S. May and T. M. Squires, *Phys. Rev. X*, 2016, **6**, 011007.