

Photoelectron Spectroscopic Evidence for Overlapping Redox Reactions for SnO_2 Electrodes in Lithium-Ion Batteries -Supporting Information-

Solveig Böhme, Bertrand Philippe, Kristina Edström & Leif Nyholm *

1 In-house XPS spectra after storage at open circuit voltage (OCV)

Figures S1 a to d show the in-house XPS spectra (i.e., $h\nu = 1487\text{eV}$) obtained for a SnO_2 electrode that had been stored in an assembled battery at open circuit voltage (OCV) for four hours. The cell was dismantled and the electrode treated as described for the PES measurements in the Experimental part of the main manuscript.

The $\text{C}1\text{s}$ spectra in Figure S1a show a composition very similar to that for the pristine electrodes and the electrodes stopped at 1.2 V vs. Li^+/Li . Carbon Black (CB) is the main component (red line) while $\text{C}-\text{H}$ (yellow line), $\text{C}-\text{O}$ (green line) and $-\text{CO}_2-$ (blue line) species are present as well. The latter three compounds originate from the CMC and SBR binders as well as some surface contaminations.

The $\text{F}1\text{s}$ spectra can be seen in Figure S1b and show $\text{P}-\text{F}$ components (blue line) as well as LiF . No clear $\text{F}1\text{s}$ peaks could be observed for the pristine electrodes and no electrochemical cycling was carried out for the OCV samples. Therefore, the detection of $\text{P}-\text{F}$ and LiF at OCV

*Corresponding author: leif.nyholm@kemi.uu.se

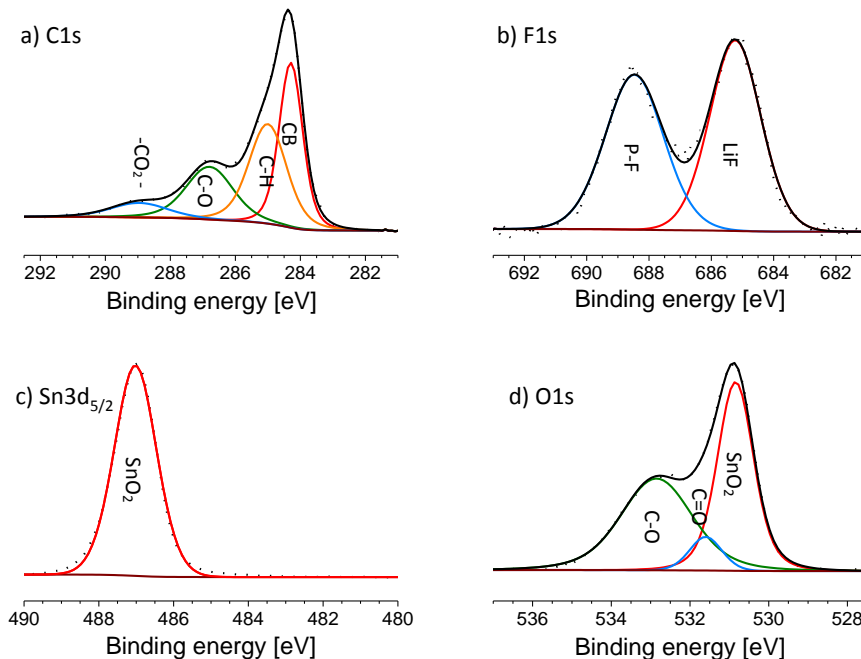


Figure S1: In-house XPS spectra ($h\nu = 1487\text{eV}$) for a SnO_2 electrode that had been stored in a battery for four hours at OCV with a) $\text{C}1\text{s}$; b) $\text{F}1\text{s}$; c) $\text{Sn}3\text{d}_{5/2}$ and d) $\text{O}1\text{s}$.

is evidence that some fluorine containing SEI components were already formed when assembling the battery.

Figures S1c and d display the $\text{Sn}3\text{d}_{5/2}$ and $\text{O}1\text{s}$ spectra, respectively, where SnO_2 could be detected in both spectra (red lines). The $\text{O}1\text{s}$ spectrum further confirms the presence of $\text{C}-\text{O}$ (green line) and $\text{C}=\text{O}$ (blue line) species that originate from the CMC and SBR binders. These components could already be observed in the spectra of the pristine samples as well as for the electrodes stopped at 1.2 V vs. Li^+/Li . They are also seen in the $\text{C}1\text{s}$ spectrum in Figure S1a.

2 $\text{C}1\text{s}$ PES spectra

Tables 1 and 2 show the values of the relative $\text{C}1\text{s}$ peak areas for the different potentials and the excitation energies of 1487 eV (Table 1, in-house XPS) and 2005 eV (Table 2, HAXPES). They provide information about the growth and the main species present in the SEI. The decrease of the CB peak area and the increase of the $\text{C}-\text{H}$ and the CO_3 peak areas during the reductive scan (discharge) are seen. In addition, the data provides further evidence for the partial dissolution of the SEI during the oxidative scan (charge), showing a growth of the CB peak area and a decline

of that for $C - H$ as well as the CO_3 peak areas during the oxidation.

Table S1: Relative peak areas for $C1s$ peaks at different potentials for in-house XPS data ($h\nu = 1487eV$).

Potential	CB [%]	$C - H$ [%]	$C - O$ [%]	$-CO_2-$ [%]	CO_3 [%]
pristine	46.24	10.71	27.71	15.34	0
1.2 V	31.28	17.97	32.43	18.33	0
0.4 V	17.27	38.08	24.33	11.18	9.14
0.05 V	7.29	45.91	28.55	6.91	11.34
1.0 V	11.99	44.91	26.99	7.18	8.93
2.5 V	15.12	27.52	36.8	9.41	11.15

Table S2: Relative peak areas for $C1s$ peaks at different potentials for synchrotron based HAXPES data ($h\nu = 2005eV$).

Potential	CB [%]	$C - H$ [%]	$C - O$ [%]	$-CO_2-$ [%]	CO_3 [%]
pristine	49.17	10.84	28.61	6.29	5.08
1.2	37.48	28.17	20.73	3.5	10.12
0.4 V	29.81	40.06	14.47	11.92	3.74
0.05 V	12.73	33.63	29.31	9.27	15.07
1.0 V	20.16	44.37	17.93	10.03	7.52
2.5 V	23.34	34.64	27.68	9.46	4.87

3 P1s HAXPES spectra

The P1s HAXPES spectra ($h\nu = 6015eV$) (Figure S2) reveal that $P - F$ surface contaminations already were present on the pristine electrode surface. Similar observations could be made for the $F1s$ spectra. The spectra further show the formation of $P - O$ species, i.e., phosphates, during the SEI formation. At lower potentials after continued SEI formation, i.e., 0.4 V and 0.05 V vs. Li^+/Li , even PF_yO_x can be observed. Thus, $P - O$ and PF_yO_x can be added to the compounds present in the SEI on the SnO_2 electrodes. These species are formed by the decomposition of the electrolyte salt during the reductive scan (discharge).

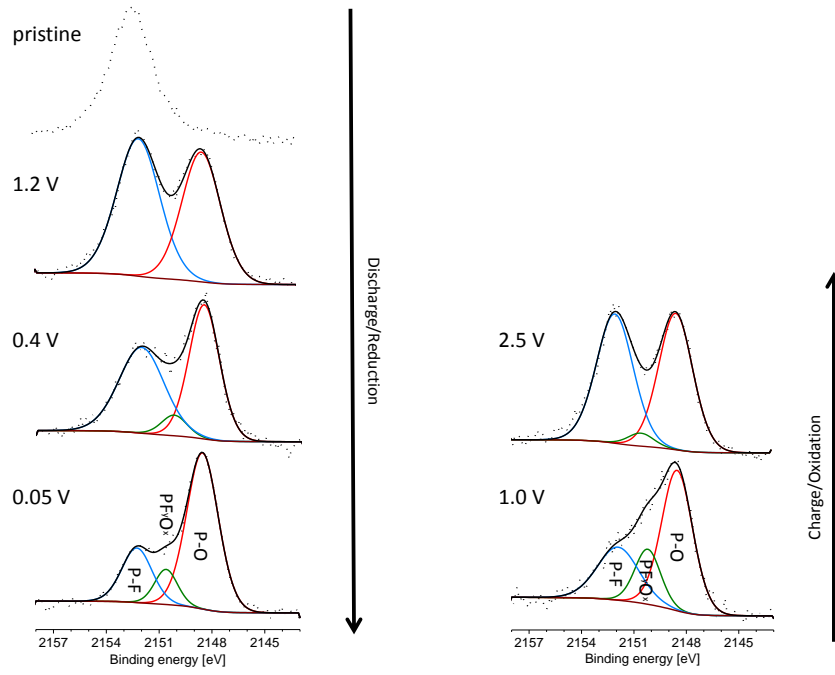


Figure S2: P1s HAXPES spectra ($h\nu = 6015\text{eV}$) measured after stopping batteries at the different potentials marked in the CV, i.e., a) pristine electrode; b) 1.2 V; c) 0.4 V; d) 0.05 V; e) 1.0 V and f) 2.5 V vs. Li^+/Li .

4 Scanning electron microscopy (SEM)

Figures S4 a to f show the SEM images obtained at the different potentials, i.e., a) pristine electrode, b) 1.2 V vs. Li^+Li , c) 0.4 V vs. Li^+Li , d) 0.05 V vs. Li^+Li , e) 1.0 V vs. Li^+Li and f) 2.5 V vs. Li^+Li . It can be seen that an SEI layer was present already at 1.2 V vs. Li^+Li via the presence of LiF and $P - F$ species in the $F1s$ peaks in the main manuscript as well as the growth of $C - O$ and $C - H$ peaks in the $C1s$ spectrum for the electrode stopped at 1.2 V vs. Li^+Li as compared to for the pristine sample. Thus, the SEM images generally confirm the findings as described in the PES spectra seen the main manuscript. Nevertheless, neither the varying SEI thicknesses nor a change in morphology could be observed in the SEM images.

Figure S3 displays the SEM image of a SnO_2 electrode stored in a battery at OCV for four hours. It can be seen that the electrode surface still looks very similar to that for the pristine electrode and no continuous surface layer can be observed. This observation indicates the SEI layer does not form prior to the electrochemical cycling, despite the presence of SEI compounds in the $F1s$ spectra at OCV (Figure S1b).

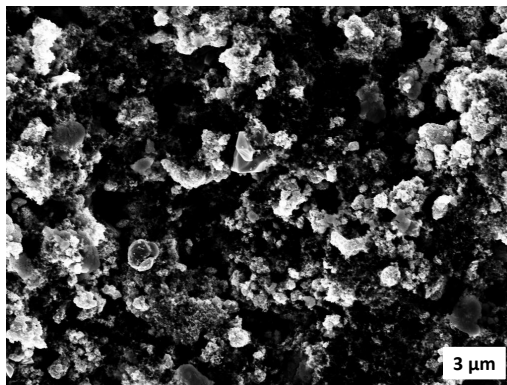


Figure S3: SEM image recorded after storing a SnO_2 electrode in a battery for four hours at OCV.

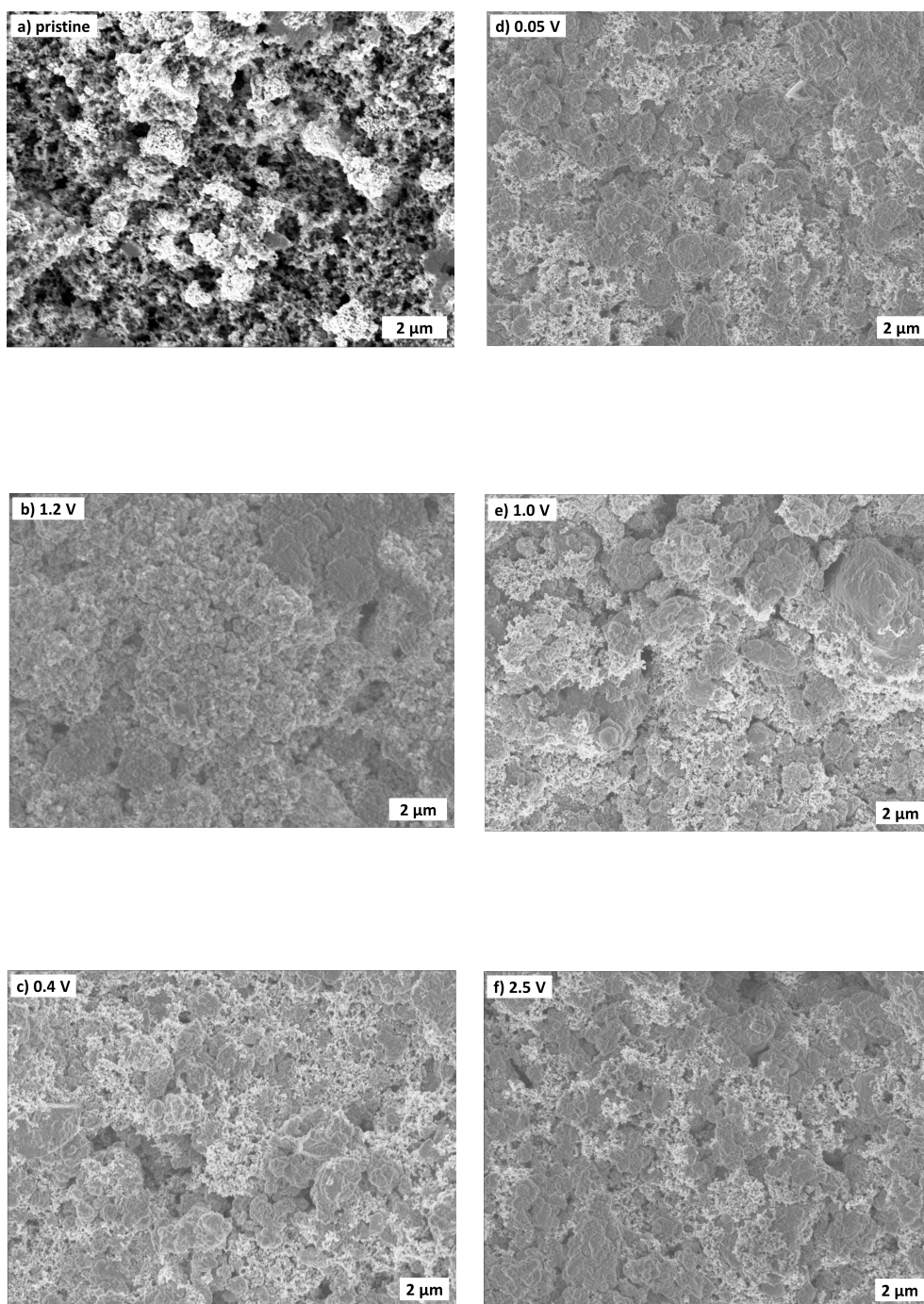


Figure S4: SEM images recorded after stopping batteries at the different potentials marked in the CV, i.e., a) pristine electrode; b) 1.2 V; c) 0.4 V; d) 0.05 V; e) 1.0 V and f) 2.5 V vs. Li^+/Li .

5 Cyclic voltammetry at a scan rate of 0.1 mV/s

Figure S5 features the first cycle voltammogram recorded at a scan rate of 0.1 mV/s. When comparing this CV to the CV collected at 1 mV/s in the main manuscript, sharper peaks, e.g., for the conversion reaction during the reduction, and smaller overpotentials can be observed. Nevertheless, an overlap between conversion and alloying currents can still be seen on the reductive scan, as the current does not reach a value above -0.5 mA between the two visible peaks. This observation suggests that an overlap between conversion and alloying reaction is likewise present at this lower scan rate, at least during the reductive scan.

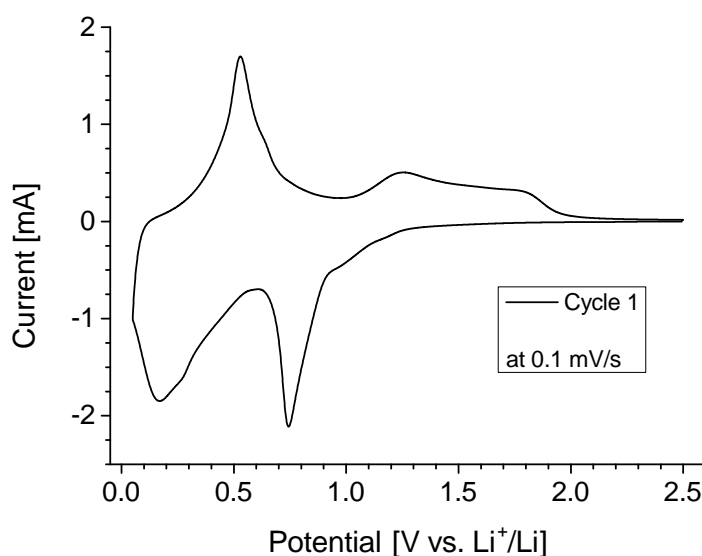


Figure S5: First cycle voltammogram recorded at a scan rate of 0.1 mV/s.