Supporting Information for

Oxidized Co-Sn Nanoparticles as Long-Lasting Anode Materials for Lithium-Ion Batteries

Marc Walter, a,b Simon Doswald, a,b Frank Krumeich, a Meng He, a,b Roland Widmer, c Nicholas P. Stadie, a,b, d and Maksym V. Kovalenko* a,b

a Department of Chemistry and Applied Biosciences, ETH Zürich – Swiss Federal Institute of Technology Zürich, Vladimir Prelog Weg 1, 8093 Zürich (Switzerland)
b Empa-Swiss Federal Laboratories for Materials Science and Technology, Laboratory for thin films and photovoltaics, Überlandstrasse 129, 8600 Dübendorf (Switzerland)
c Empa-Swiss Federal Laboratories for Materials Science and Technology, Nanotech@surfaces Laboratory, Überlandstrasse 129, 8600 Dübendorf (Switzerland)
d Present address: Department of Chemistry and Biochemistry, Montana State University, 59717 Montana (United States)

[*] Prof. Dr. Maksym V. Kovalenko
E-mail: mvkovalenko@ethz.ch
**Figure S1.** EDX spectrum of amorphous Co NPs. The peak denoted as S (corresponding to ~1 wt% of the sample) could be attributed to residual DMSO, left over after washing.
Figure S2. HR-TEM images along with selected area electron diffraction (SAED) and d-spacing of Co NPs (a, b), Sn NPs (c, d) and CoSn₂ NPs (e, f).
Figure S3. HR-TEM images of CoSn$_2$O$_x$ NPs with d-spacing.
Figure S4. (A) Elemental EDX-STEM maps, (B) HAADF-STEM, and (C) HR-TEM images of CoSn$_2$O$_x$ NPs.
Figure S5. (a) XPS spectra of CoSn$_2$O$_x$ NPs. Survey spectrum assigning the peaks to the elements according to https://srdata.nist.gov/xps/EnergyTypeValSrch.aspx. Detail spectra of (b) C 1s, (c) O 1s, (d) Co 2p and (e) Sn 3d, where oxygen as well as carbon show two components, but more important, cobalt and tin are completely oxidized, most probably forming Co(OH)$_2$ and SnO$_2$ as follows form a ca. 3 eV and 1.7 eV shift of the individual peaks, respectively.
Figure S6. Size-distribution histograms of (a) Co NPs, (b) Sn NPs, (c) CoSn₂ NPs and (d) CoSn₂Oₓ NPs. Mean sizes and standard deviations of nanoparticles were determined using PEBBLES (Mondini et al., *Nanoscale*, 2012, 4, 5356-5372).
Figure S7. XRD pattern of a mixture of bulk Co and Sn powders (molar ratio 1:2) after ball-milling for 4 hours under nitrogen. All reflections can be indexed as belonging to Sn (ICDD PDF entry No.: 00-004-0673) or Co (ICDD PDF entry No.: 00-005-0727).

Figure S8. Galvanostatic charge/discharge curves with full capacity range for (a) Sn NPs, (b) CoSn₂ NPs, and (c) CoSn₂Oₓ NPs measured during 1ˢᵗ, 10ʰ, 100ʰ and 1000ʰ cycle at a current density of 1984 mA g⁻¹.
Figure S9. Cyclic voltammograms of crystalline Sn NPs in a lithium-ion half-cell using a scan rate of 0.1 mV s$^{-1}$ in the potential range of 0.005–1.0 V.

Figure S10. Cyclic voltammograms of CoSn$_2$ NPs in a lithium-ion half-cell using a scan rate of 0.1 mV s$^{-1}$ in the potential range of 0.005–1.0 V.
Figure S11. Cyclic voltammograms of CoSn$_2$O$_x$ NPs in a lithium-ion half-cell using a scan rate of 0.1 mV s$^{-1}$ in the potential range of 0.005–1.0 V.

Figure S12. XRD pattern (with TEM image as inset) of CoSn$_2$ NPs prepared by wet-chemical synthesis. The two unindexed peaks at 30$^\circ$ and 43$^\circ$ might correspond to SnO and CoO. For synthesizing CoSn$_2$ NPs wet-chemically SnCl$_2$ (1.33 mmol) and CoCl$_2$ (0.67 mmol) dissolved in NMP (3 mL) were injected into a solution of NaBH$_4$ in NMP (16 mmol in 17 mL) at 150 $^\circ$C and kept at this temperature for 1 hour.
Figure S13. Cycling stability of CoSn$_2$ NPs prepared by wet-chemical synthesis in lithium-ion half-cells using a current of 1984 mA g$^{-1}$ in the potential range of 0.005–2.0 V.

Figure S14. Rate capability tests for graphite in lithium-ion half-cells within the potential range of 0.005–1.0 V using the same conditions as for Co-Sn-based NPs in Figure 4.
Figure S15. Galvanostatic charge/discharge curves for a CoSn$_2$O$_x$/LiCoO$_2$ full-cell. Cells were cycled with a current of 500 mA g$^{-1}$ in the potential range of 2.0–3.9 V. The specific capacities and currents correspond to the mass of the CoSn$_2$O$_x$ NPs.

Table S1. Comparison of the electrochemical performance of CoSn$_2$O$_x$ NPs (present work) with other reported systems as anode materials for LIBs.

<table>
<thead>
<tr>
<th>Anode material</th>
<th>Current density (mAg$^{-1}$)</th>
<th>Initial capacity (mAhg$^{-1}$)</th>
<th>Retained capacity (mAhg$^{-1}$)</th>
<th>Cycle number</th>
<th>Potential range (V vs. Li$^+$/Li)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CoSn$_2$O$_x$ NPs (present work)</td>
<td>1984</td>
<td>450</td>
<td>525</td>
<td>1500</td>
<td>0.005–1.0 V</td>
</tr>
<tr>
<td></td>
<td></td>
<td>(570 at cycle 100)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>CoSnO$_3$@GN$^1$</td>
<td>2000</td>
<td>~708</td>
<td>566</td>
<td>1500</td>
<td>0.005–3.0 V</td>
</tr>
<tr>
<td>Co–Sn/carbon nanofibers composite$^2$</td>
<td>161</td>
<td>700</td>
<td>560</td>
<td>80</td>
<td>0.02–2.8 V</td>
</tr>
<tr>
<td>SnFeCo alloy composite$^3$</td>
<td>50</td>
<td>585</td>
<td>507</td>
<td>50</td>
<td>0.02–1.5 V</td>
</tr>
<tr>
<td>Co$_3$Sn$_2$@Co/nitrogen doped graphene$^4$</td>
<td>250</td>
<td>1600</td>
<td>1615</td>
<td>100</td>
<td>0.005–3 V</td>
</tr>
</tbody>
</table>
Table S2. Comparison of the theoretical volumetric capacities for graphite or CoSn$_2$O$_x$-based anodes in full-cells with LiCoO$_2$ cathode.

<table>
<thead>
<tr>
<th>System</th>
<th>Capacity [mAh/g]</th>
<th>Density [g/cm$^3$]</th>
<th>Vol. capacity [mAh/cm$^3$]</th>
<th>Vol. cell capacity [mAh/cm$^3$]</th>
<th>Discharge voltage [V]</th>
<th>Vol. energy density [Wh/L]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Graphite/LiCoO$_2$</td>
<td>372/140</td>
<td>2.2/5.1</td>
<td>818/714</td>
<td>381</td>
<td>3.55</td>
<td>1353</td>
</tr>
<tr>
<td>CoSn$_2$O$_x$/LiCoO$_2$</td>
<td>576/140</td>
<td>7.6*/5.1</td>
<td>4378/714</td>
<td>614</td>
<td>3.15</td>
<td>1934</td>
</tr>
</tbody>
</table>

*based on the bulk densities of Sn (7.3 g/cm$^3$) and Co (8.9 g/cm$^3$).
References