Supporting Information

Puzzling out the origin of the electrochemical activity of black P as a negative electrode material for lithium-ion batteries

Marian Cristian Stan†**, Jan von Zamory‡, Stefano Passerini†, Tom Nilges‡ and Martin Winter†*

† Institute of Physical Chemistry, MEET Battery Research Centre, University of Muenster, Corrensstrasse 46, 48149 Muenster, Germany
‡ Chemistry Department, Technische Universitaet Muenchen, Lichtenbergstraße 4, 85737 Garching, Germany

*Corresponding author: martin.winter@uni-muenster.de
**Co-corresponding author: marian.stan@uni-muenster.de

Electrode composition:

To prepare the electrodes for the electrochemical investigations, the active material (i.e. TS-black P, BM-black P, SM-Cu₃P-black P and Cu₃P powders) was mixed with carbon black (Super C65, Timcal) and afterwards with the PVdF (Solef 6020/1001, Solvay) solution in N-methyl-2-pyrrolidone (Sigma Aldrich). To prepare the TS-black P electrodes, the crystalline powder was premixed with the carbon powder in a weight ratio of 60:40. Further the composite powder was mixed with the carbon black powder and the binder to a final composition of 70:15:15 by weight. The amount of TS-black P in the resulted electrodes was of 42% by weight. The SM-Cu₃P-black P electrodes were prepared using a similar procedure, and the resulted amount of SM-Cu₃P-
black P in the electrodes was 41% by weight. Similarly, to prepare the composite powder, the BM-black P powder was additionally ball milled with carbon black in a weight ratio of 70:30 (BM-black P to carbon). Finally this composite powder has been used to prepare the electrodes with the final composition of 70:15:15. The amount of BM-black P active material in the final electrode was 49% by weight. In all these electrodes, the large amount of conductive agent is needed due to the insulating nature of the black P. The electrode preparation procedure and the resulting electrode composition for the Cu3P electrodes have been previously described in ref. 26.

Figure S1. Comparison between the XRD of the pristine (a) and (b) ball milled black P.
Figure S2. Comparison of the XRD patterns of a mixture of copper powder and BM-black P.

Figure S3. XRD pattern of the BM-black P electrodes casted on Ni foil.
Figure S4. Charge-discharge curve of the BM-black P electrode casted on Cu foil and Al-graphite coated foil between 2V and 0.5V using a current of C/10.

Figure S5. SEM pictures of black P (a) before and (b) after ball milling.
Figure S6. Cross section and EDX mapping of the BM-black P electrode.

Figure S7. Morphology of the SM-Cu$_3$P-black P particle after the solvothermal synthesis, indicating the deposit where the EDX elemental analysis has been carried out with the corresponding values indicated in Table S1.
Table S1. EDX element composition of the deposit indicated in Figure S7 by Spectrum 1.

<table>
<thead>
<tr>
<th>Element</th>
<th>App Conc.</th>
<th>Intensity</th>
<th>Weight%</th>
<th>Weight% Sigma</th>
<th>Atomic%</th>
</tr>
</thead>
<tbody>
<tr>
<td>P K</td>
<td>151.30</td>
<td>1.8480</td>
<td>14.17</td>
<td>0.24</td>
<td>25.30</td>
</tr>
<tr>
<td>Cu L</td>
<td>480.56</td>
<td>0.9693</td>
<td>85.83</td>
<td>0.24</td>
<td>74.70</td>
</tr>
<tr>
<td>Totals</td>
<td></td>
<td></td>
<td>100</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Figure S8. Nyquist plot of the (a) BM-black P and (b) TS-black P electrodes during the first cycle. The AC measurements were carried in the frequency range of 1MHz-10mHz with an amplitude of 5 mV using a Solartron Electrochemical Interface 1287/1260 (Solartron Analytical).