Electronic Supplementary Information

Free-standing LiFePO$_4$-carbon paper hybrid cathode for flexible Lithium-ion batteries

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Table 1: GEM Commodity prices of wood pulp and aluminium from 2010 to 2014.[1]

<table>
<thead>
<tr>
<th></th>
<th>2010</th>
<th>2011</th>
<th>2012</th>
<th>2013</th>
<th>2014</th>
</tr>
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<tbody>
<tr>
<td>Wood pulp [US$/t]</td>
<td>866.79</td>
<td>899.65</td>
<td>762.84</td>
<td>823.08</td>
<td>876.91</td>
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<tr>
<td>Aluminium [US$/t]</td>
<td>2173.12</td>
<td>2401.39</td>
<td>2023.28</td>
<td>1846.67</td>
<td>1867.42</td>
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</tbody>
</table>
Figure S1: Digital photograph of the free-standing LiFePO$_4$@CP hybrid electrode.
Figure S2: Measured XRD pattern of purified paper towel matching the standard XRD pattern of microcrystalline cellulose.\textsuperscript{[2,3]}
Electrode preparation process: For the impregnation with solution 1 (STEP 1 in Scheme 1 main article) consisting of the phosphate and lithium precursor salts, it is important to understand the precipitation mechanism of LiOH·H₂O and NH₄H₂PO₄ and the subsequent acid-assisted dissolution of Li₃PO₄. This allows validating the weight gain as an accurate marker to calculate the amount of solution 2, which contains the iron and carbon precursors, needed to generate the correct stoichiometric ratio of LiFePO₄ impregnated into the PT network. The first reaction between the two precursor materials is the precipitation of Li₃PO₄, wherein all Li ions are consumed (1). The residual NH₄H₂PO₄ dissolves to form aqueous phosphoric acid (H₃PO₄) and NH₃ (2). Hydrochloric acid (HCl) then dissolves the Li₃PO₄ precipitate to form LiCl and LiH₂PO₄ (3), wherein LiCl is consumed by H₃PO₄ to form crystalline LiH₂PO₄ upon solvent and HCl evaporation (4). Consequently, the freeze-drying process leaves the PT impregnated with highly crystalline LiH₂PO₄ homogenously dispersed throughout the fibre network.

\[
\begin{align*}
3\text{LiOH} \cdot \text{H}_2\text{O} + \text{NH}_4\text{H}_2\text{PO}_4 & \rightarrow \text{Li}_3\text{PO}_4(s) + \text{NH}_3 + 6\text{H}_2\text{O} \\
(1) \\
\text{NH}_4\text{H}_2\text{PO}_4 & \rightarrow \text{H}_3\text{PO}_4 + \text{NH}_3 \\
(2) \\
\text{Li}_3\text{PO}_4 + 2\text{HCl} & \rightarrow 2\text{LiCl} + \text{LiH}_2\text{PO}_4 \\
(3) \\
\text{LiCl} + \text{H}_3\text{PO}_4 & \rightarrow \text{LiH}_2\text{PO}_4 + \text{HCl} \\
(4)
\end{align*}
\]

The reaction mechanism in solution 1 as described in equation (1) to (4) has been confirmed by the XRD pattern of the dried solution (Figure S3). The traces of LiCl are negligible due to the pure phase XRD pattern of the final product (Figure 1 main article). It can be assumed that this minor Li excess does not result in the formation of impurities, such as Li₃PO₄.[5-6] On the contrary, a slight oversupply of lithium during solid-state preparation methods is considered beneficial to compensate for the loss of the lithium element caused by the evaporation of Li₂O.[7] These residual LiCl crystals are possibly caused by an undersupply of phosphoric acid (H₃PO₄). According to the theoretical assumption of the reaction mechanism during freeze-drying of solution 1, the mass of the Fe(III)Cl₃ solution (solution 2) needed to ensure the appropriate molar ratio Li:Fe:PO₄=1:1:1 can be sufficiently calculated from the mass load of PT. The impregnation of the iron precursor (STEP 2 in Scheme 1 main article) includes the dissolved carbon precursor, which is applied as reducing agent and to generate a conductive carbon coating on the surface of the LiFePO₄ layer, which also serves as structural support. The next stage of the electrode preparation is the two-stage heat treatment (STEP 3 in Scheme 1 main article). The first heat treatment stage at 312 °C was chosen to allow Fe(III)Cl₃ to melt and consequently enable capillary forces to homogenously distribute it through the PT fibre network. The decomposition of all precursor materials, the
crystal formation of LiFePO$_4$, and the carbon network generation takes simultaneously place in the second and final heat treatment stage from 312 °C to 700 °C.

Figure S3: XRD pattern of solution 1 after drying compared with the simulated pattern of LiH$_2$PO$_4$ calculated from JCPDS card number 83-1340 (* marks traces for LiCl·H$_2$O).
Figure S4: SEM energy-dispersive spectroscopy (EDS) characterization of LiFePO₄@CP. (a) SEM image of the selected area for EDS mapping; (b) Integrated Fe-, P-, O-, and C-elemental mapping image; elemental mapping images of (c) carbon C, (d) oxygen O, (e) iron Fe, and (f) phosphorous P.
Figure S5: Digital photograph to visualize the shrinkage of the cellulose substrate (paper towel) to LiFePO$_4$@C after carbonization.
Figure S6: TGA/DTA analysis of PT carbonized in the temperature range from room temperature to 700 °C under nitrogen flow with a heating rate of 5 °C min⁻¹.
Figure S7: High magnification SEM of LiFePO$_4$@CP showing a cavity inside the dense shell
Figure S8: TGA curve of LiFePO$_4$@CP and carbon free LiFePO$_4$ from room temperature to 700 °C in air
Figure S9: Corresponding differential capacity analysis of (a) step one and (b) step three of LiFePO$_4$@CP (Insets: Overpotentials in mV for the current densities 0.1 to 2.5 mA cm$^{-2}$)
**Preparation of LiFePO₄ cathode materials:** LiFePO₄ was prepared by mixing stoichiometric amounts of FeC₂O₄·2H₂O, NH₄H₂PO₄ and Li₂CO₃ (Sigma-Aldrich) via industrial-scale ball milling in deionized water for 6 h. Simultaneously, 5 wt.% sucrose was added to the suspension to encapsulate the precursor materials during spray drying and to serve as a carbon source in the subsequent carbothermal reduction. The solid content of the suspension was fixed at 20 wt.%. The untreated precursor mixture was spray-dried (Mini Spray Dryer B290, Büchi Labortechnik AG, Switzerland) with an inlet temperature of 170 °C and a feed rate of 15 ml min⁻¹. The dried powder was then transferred into a ceramic crucible to thermally decompose in a tubular furnace at 350 °C for 5 h and sintered at 700 °C for 10 h under argon protection. The working electrodes of LiFePO₄@Al for electrochemical testing were prepared by mixing 80 wt.% as-prepared LiFePO₄ with 10 wt.% carbon black and 10 wt.% poly(vinyl difluoride) (PVDF, Sigma-Aldrich) in N-Methyl-2-pyrrolidone (NMP, Sigma-Aldrich). The obtained dispersion was carefully pasted onto aluminium foil, dried in a vacuum at 80 °C for 12 h and pressed before cell assembly. The cell assembly was conducted as described in the experimental section.

![Figure S10](image.png)

**Figure S10:** (a) Rate performance and (b) stability test sequence of a traditional LiFePO₄@Al displayed in areal capacity. The active material mass load of all electrodes is around 2.8 mg cm⁻².
Figure S11: (a) Rate performance and (b) stability test sequence of LiFePO$_4$@CP and a traditional LiFePO$_4$@Al. The capacity is displayed in mAh per gram of electrode (weight including current collector, binder and additives). The active material mass load of all electrodes is around 2.8 mg cm$^{-2}$. 
Figure S12: Rate performance and stability test sequence of LiFePO₄@CP and a traditional LiFePO₄@Al. The capacity is displayed in mAh per gram active material. The active material mass load of all electrodes is around 2.8 mg cm⁻².
References


