

Lithium chromium pyrophosphate (LiCrP_2O_7) as new insertion material for Li-ion batteries

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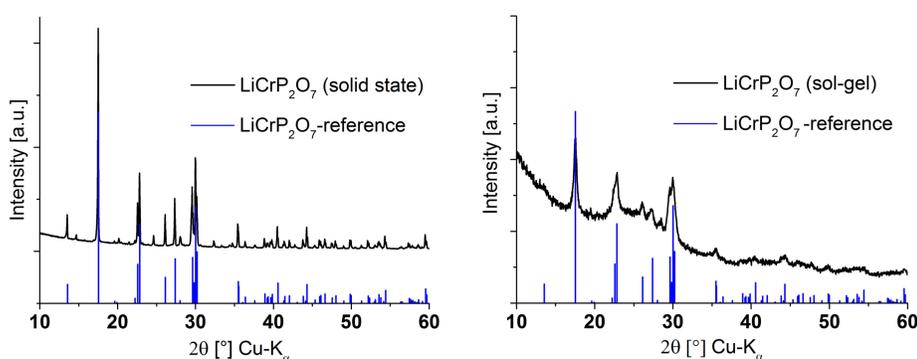
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Motivation

- Chromium oxides Cr_xO_y are electrochemically active materials
- Chromium based polyanions have not been investigated

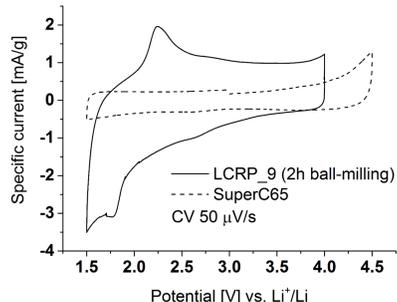
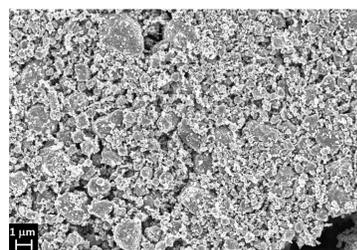
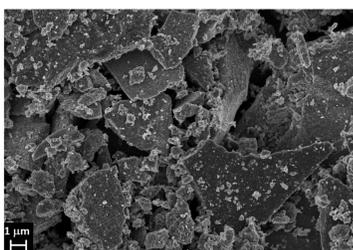
LiCrP_2O_7 (theoretical specific charge = 115 mAh/g) was chosen as **reference material** for a proof of concept.

XRD characterization

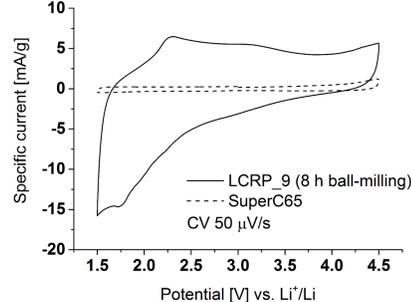


- Solid state synthesis gives more crystalline powder.
- LiCrP_2O_7 obtained by sol-gel synthesis has smaller crystallites.

LiCrP_2O_7 (sol-gel): influence of particle size



Specific charge: 15 mAh/g

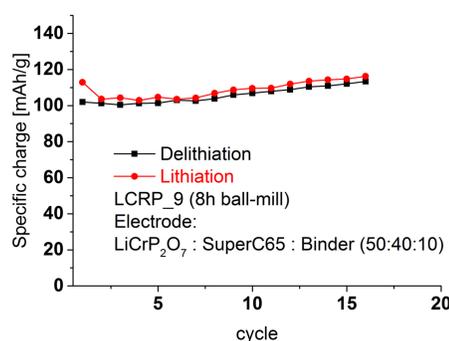


Specific charge: 80 mAh/g

→ Electrochemical activity is particle size dependent.

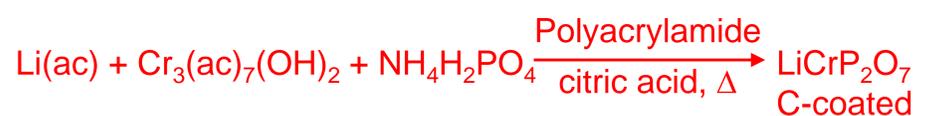
Galvanostatic cycling:
23 mA/g (C/5)
1.5–4.5 V vs. Li^+/Li

Specific charge increases with cycling up to 115 mAh/g.
→ Activation process?



Synthesis

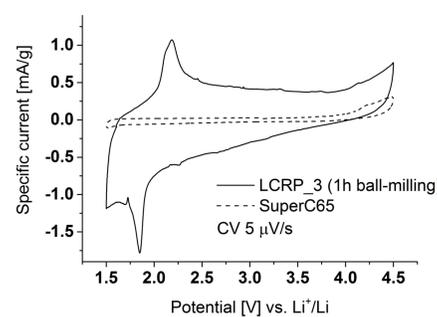
Solid state¹ and sol-gel² synthesis of LiCrP_2O_7 :



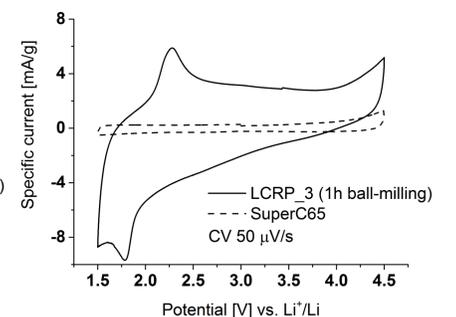
LiCrP_2O_7 (sol-gel): scan-rate dependency

Electrochemical testing:

Coin cells with LiCrP_2O_7 /SuperC65 electrode (50/50 w/w) in 1M LiPF_6 in EC:DMC 1:1 wt. vs. Li^+/Li .



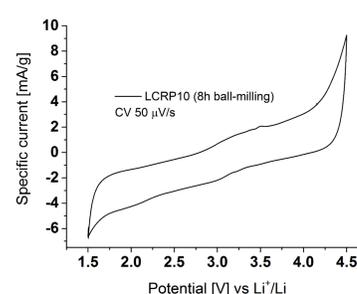
Specific charge 70 mAh/g



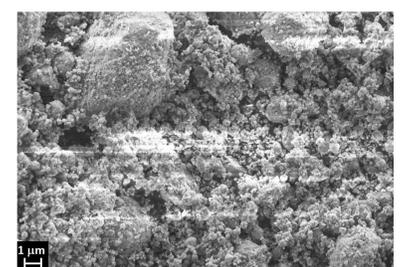
Specific charge 35 mAh/g

- Reduction (1.8 V) and oxidation (2.2 V) peaks attributed to $\text{Cr}^{3+}/\text{Cr}^{2+}$
- Shape of the peaks is rate-dependent

LiCrP_2O_7 by solid state synthesis



Reversible cycling between 1.5 – 4.5 V vs. Li^+/Li
Specific charge: 45 mAh/g



LiCrP_2O_7 (8h ball-milling)

Conclusions

- Reversible electrochemical activity between 1.8 V and 2.2 V vs. Li^+/Li attributed to $\text{Cr}^{3+}/\text{Cr}^{2+}$ redox couple³
- Specific charge stable and close to the theoretical value (115 mAh/g).

[1] L. S. Ivashkevich et al., *Acta Crystallographica Section E* **2007**, 63 (3), i70–i72.
[2] Gangulibabu et al., *Applied Physics A* **2009**, 96, 489–493.
[3] G. Hautier et al., *Chem. Mater.* **2013**, 25, 2064–2074.

