



# Multiple redox couples cathode material for Li-ion battery: Lithium chromium phosphate

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## ABSTRACT

Carbon coated  $\text{Li}_3\text{Cr}_2(\text{PO}_4)_3/\text{C}$  model materials were synthesized by a sol-gel route and a solid state route with calcination at  $800^\circ\text{C}$  under an inert atmosphere. The model materials were characterized by X-ray diffraction (XRD), neutron powder diffraction (NPD), scanning electron microscopy (SEM), laser diffraction analysis (granulometry) and thermogravimetric analysis (TGA). The electrochemical signatures obtained for the solid state (carbon coated) route synthesized compounds revealed the presence of two redox couples,  $\text{Cr}^{3+}/\text{Cr}^{2+}$  and  $\text{Cr}^{4+}/\text{Cr}^{3+}$ , between 1.5–2.5 V and 4.0–4.9 V vs.  $\text{Li}^+/\text{Li}$ , respectively. The model materials show an initial specific charge (for lithiation) of  $131 \text{ mAh g}^{-1}$  (sol-gel, carbon coated) and  $119 \text{ mAh g}^{-1}$  (solid state, carbon coated), which decreases to  $90 \text{ mAh g}^{-1}$  and  $46 \text{ mAh g}^{-1}$ , respectively, after 100 cycles. Operando XRD measurements revealed reversible structural changes in the crystal structure upon cycling, leading to the conclusion of an insertion reaction mechanism.

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## 1. Introduction

Lithium-ion batteries are widely used to power mobile electronic devices like smartphones and notebooks but their energy density needs to be further improved to fulfil the requirements of electric cars. Apart from good performance over reasonable cell lifetime, the cost and safety aspects also need to be considered [1].

In commercial Li-ion batteries, the electroactive materials used as positive electrodes are based on single electron exchange reactions per metal atom (such as  $\text{LiFePO}_4$  or  $\text{LiCoO}_2$ ). The rather low specific charge of the positive electrode (e.g.  $170 \text{ mAh g}^{-1}$  for  $\text{LiFePO}_4$ ) when compared to the negative electrode (generally graphite,  $372 \text{ mAh g}^{-1}$ ), is one of the factors that limits the energy density of the Li-ion batteries [2,3]. Different strategies have been proposed to increase their energy density. One of these is based on the development of 5 V-cathode materials like  $\text{LiMn}_{1.5}\text{Ni}_{0.5}\text{O}_4$  (LMNO) or Li-rich nickel-cobalt-manganese oxide (HE-NCM) [4–8]. Alternatives can be found with lithium metal phosphate materials with high voltage potential plateaus e.g.  $\text{LiVPO}_4\text{F}$  [9–11]. While a significant gain in energy density was obtained with these

materials, they presented several disadvantages such as transition metal leaching and voltage decay during cycling, that makes their commercialization challenging to date [12–16].

Thus, an alternative strategy based on cathode materials with multiple redox couples was developed, i.e. to increase the number of electrons involved to obtain specific charge superior to current commercial materials. Sun et al. investigated  $\text{Li}_2\text{Cu}_2\text{O}(\text{SO}_4)_2$ , a material with two redox couples –  $\text{Cu}^{3+}/\text{Cu}^{2+}$  and  $\text{Cu}^{2+}/\text{Cu}^+$ . While the specific charge delivered was very low ( $20 \text{ mAh g}^{-1}$  at 4.7 V vs.  $\text{Li}^+/\text{Li}$ ), the concept of multiple redox materials was proven to be a suitable alternative [17]. Other materials were investigated as well, such as  $\text{Li}_2\text{FeSiO}_4$  with an initial specific discharge capacity of  $220 \text{ mAh g}^{-1}$  [18]. In the case of  $\text{LiVP}_2\text{O}_7$ ,  $\text{V}^{3+}/\text{V}^{2+}$  (2.0 V vs.  $\text{Li}^+/\text{Li}$ ) and  $\text{V}^{4+}/\text{V}^{3+}$  (4.3 V vs.  $\text{Li}^+/\text{Li}$ ) redox couples are cycled, yielding a discharge capacity of  $140 \text{ mAh g}^{-1}$  for both redox couples [19]. Interestingly, the  $\text{V}^{2+}/\text{V}^{1+}$  (1.2 V vs.  $\text{Li}^+/\text{Li}$ ) redox couple could also be cycled, as shown recently by Mani et al., who obtained an initial discharge capacity of  $600 \text{ mAh g}^{-1}$  by cycling  $\text{V}^{2+}/\text{V}^{1+}$  and  $\text{V}^{3+}/\text{V}^{2+}$  redox couple [20].

This concept can also be applied to anode materials, with  $\text{Li}_3\text{VO}_4$  delivering more than  $400 \text{ mAh g}^{-1}$  after 200 cycles (however in a large potential window from 3 V to 5 mV vs.  $\text{Li}^+/\text{Li}$ ), assuming that the oxidation state of vanadium in the pristine phase ( $\text{V}^{5+}$ ) is reduced down to  $\text{V}^{2+}$  [21,22].

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However, all these materials suffer from various disadvantages.  $\text{Li}_2\text{Cu}_2\text{O}(\text{SO}_4)_2$  presents a limited specific charge whereas  $\text{Li}_2\text{FeSiO}_4$  suffers from specific charge fading, as well as a relatively high hysteresis of the discharge–charge galvanostatic profiles leading to a partial  $\text{Fe}^{4+}$ -formation when cycled up to 4.8 V vs.  $\text{Li}^+/\text{Li}$ . Finally,  $\text{LiVP}_2\text{O}_7$  shows a low rate capability as well as a specific charge fading when it is used as anode/cathode material [19,20,23].

Cr-based polyanion materials  $\text{Li}_y\text{CrX}$  (X is the anion) can theoretically overcome the one-electron limitation. Based on DFT calculations, the first material investigated,  $\text{LiCrP}_2\text{O}_7$ , was expected to present an energy density of  $\sim 900 \text{ Wh kg}^{-1}$  based on two redox couples,  $\text{Cr}^{3+}/\text{Cr}^{2+}$  ( $\sim 2.2$  vs.  $\text{Li}^+/\text{Li}$ ) and  $\text{Cr}^{4+}/\text{Cr}^{3+}$  ( $\sim 5.0$  vs.  $\text{Li}^+/\text{Li}$ ) and assuming a Li counter electrode with negligible mass [24]. However, our previous study showed that its electrochemical properties are highly dependent on the synthesis method [25]. While  $\text{LiCrP}_2\text{O}_7/\text{C}$  can be reversibly cycled with a stable specific charge up to  $100 \text{ mAh g}^{-1}$ , only one redox couple was found to be active at  $\sim 2.0 \text{ V}$  vs.  $\text{Li}^+/\text{Li}$ .

Recently, Herklotz et al. showed that  $\text{Li}_3\text{Cr}_2(\text{PO}_4)_3$  can be obtained by solid state synthesis and can be cycled in a reversible manner, at least partially, between 4.6–4.9 V vs.  $\text{Li}^+/\text{Li}$  ( $\text{Cr}^{4+}/\text{Cr}^{3+}$ ). Unfortunately, no electrochemical activity was observed at lower potentials for the second redox couple [26]. Thus, we optimized the synthesis of  $\text{Li}_3\text{Cr}_2(\text{PO}_4)_3$  by i) using a sol-gel route to obtain small crystallites and, ii) adding “in situ carbon coating” which was followed by a post-synthesis treatment (ball-milling to decrease the particle size). Prior to the electrochemical investigations, the model material was characterized by different techniques such as scanning electron microscopy (SEM), X-ray diffraction (XRD) and neutron diffraction (ND). In the part of the manuscript and for better readability, the term “material” is used instead of “model material”. Then, we investigated the electrochemical properties of these materials by capacity retention studies, cyclic voltammetry (CV) and galvanostatic cycling (GC). Finally, the reaction mechanism was assessed by operando X-ray diffraction experiments.

## 2. Experimental

### 2.1. Synthesis

$\text{Li}_3\text{Cr}_2(\text{PO}_4)_3/\text{C}$  was synthesized by two routes: a sol-gel (carbon coated) synthesis, adapted from a previous work, and a solid state (carbon coated) synthesis, based on the study performed by Herklotz et al. [25,26].

#### 2.1.1. Sol-gel (carbon coated) synthesis

The precursors for the sol-gel (carbon coated) synthesis,  $\text{Li}(\text{CH}_3\text{COO})\cdot 2\text{H}_2\text{O}$  (Alfa Aesar),  $\text{Cr}_3(\text{CH}_3\text{COO})_7(\text{OH})_2$  (Sigma-Aldrich),  $\text{NH}_4\text{H}_2\text{PO}_4$  (Alfa Aesar) and citric acid (Sigma-Aldrich) were dissolved in demineralized water at a molar ratio of 3.6:1:6:10 (1.2:1.0:2.0 atomic ratio of Li:Cr:P). The solution was heated at  $160^\circ\text{C}$  for 12 h, leading to the decomposition of the precursors and the formation of greenish foam. The material was then calcined in two steps, first at  $300^\circ\text{C}$  for 6 h in air, and afterwards in a tubular oven under argon atmosphere at  $800^\circ\text{C}$  for 5 h. The remaining amount of carbon in the final product is 13 wt% (measured by TGA, see part 2.2.4). For sake of clarity, even if the material synthesized by sol-gel is carbon coated, it will hereafter be called only sol-gel.

#### 2.1.2. Solid state (carbon coated) synthesis

The precursors used [ $\text{Li}_2\text{CO}_3$  (Sigma-Aldrich),  $\text{Cr}(\text{NO}_3)_3$  (Alfa Aesar),  $(\text{NH}_4)_2\text{HPO}_4$  (Fluka) and citric acid (Sigma-Aldrich)] were dissolved in  $\text{HNO}_3$  (30 wt%) at a molar ratio of 6:8:12:5 or 6:8:12:10 (3:2:3 atomic ratio of Li:Cr:P) to study the impact of carbon content on the electrochemical performance. The solution was heated at  $110^\circ\text{C}$  until a viscous gel was obtained. This gel was dried at  $160^\circ\text{C}$

in air to obtain a pitch-black powder. The final calcination at  $800^\circ\text{C}$  was carried out in a tubular oven under an atmosphere composed of 5 %  $\text{H}_2$ : 95 % Ar for 5 h. The amount of carbon that remained in the final product was 2.9 and 5.0 wt%, respectively, for the two solid state syntheses samples (determined by TGA, see part 2.2.4).

For both synthesis routes, the heating rate used was  $5^\circ\text{C min}^{-1}$ . The materials were ground carefully in a mortar between all the drying and calcination steps. Finally, in order to reduce and homogenize the particle size, all synthesized powders were ball-milled in a ceramic vessel using a Fritsch ball milling machine, Pulverisette 7 (300 rpm for 4 h).

### 2.2. Characterization

#### 2.2.1. Laser diffraction analysis

The particle size distribution (PSD) was measured using a laser diffraction particle analyzer LA-950 from Horiba Company with the powder dispersed in water.

#### 2.2.2. Scanning electron microscopy

SEM images of the pristine powders were taken on a Carl Zeiss Ultra 55 microscope. The accelerating voltage was 3 kV. Prior to the measurement, the samples were Au-sputtered with a Leica EM ACE 200 instrument. EDX measurements were conducted with an Apollo XV SDD detector, using an accelerating voltage of 10 kV. TEM images were measured under the following conditions: A suspension of each material in ethanol was prepared under ultrasonication and then a droplet was deposited on a carbon coated copper grid. After drying overnight, the samples were inserted in a JEOL-2010 microscope and the measurement was performed at an accelerating voltage of 200 kV.

#### 2.2.3. X-ray diffraction (XRD)

XRD experiments were performed with a PANalytical Empyrean diffractometer using  $\text{Cu-K}\alpha$  radiation. Operando experiments were performed with an in-house operando XRD cell developed by Bleith et al. [27] XRD patterns were measured with 0.5 h data acquisition in the range  $2\theta = 23\text{--}32^\circ$  with a step size of  $0.033^\circ$ .

High resolution XRD experiments were carried out on the pristine samples using a capillary setup with a wavelength of  $0.775865 \text{ \AA}$  at the MS-powder beamline in the Swiss Light Source (SLS) synchrotron facility of the Paul Scherrer Institute.

#### 2.2.4. Neutron powder diffraction (NPD)

Neutron powder diffraction (NPD) data of the pristine sample were recorded with the high resolution powder neutron diffractometer HRPT at the SINQ neutron source of the Paul Scherrer Institute. Le Bail refinements were performed using the FullProf Suite software [28,29].

#### 2.2.5. Thermogravimetric analysis (TGA)

The percentage by weight of the carbon coating was determined by thermogravimetric analysis (TGA) with a Mettler Toledo TGA/DSC 1 Star<sup>c</sup> system using two different atmospheres (2%  $\text{H}_2$ /98% Ar atmosphere or air). The calcinations were conducted in aluminum metal crucibles with a heating rate of  $5 \text{ K min}^{-1}$  until  $600^\circ\text{C}$ .

#### 2.2.6. Electrochemistry

Electrodes for cyclic voltammetry and galvanostatic cycling were prepared using 80 wt%  $\text{Li}_3\text{Cr}_2(\text{PO}_4)_3/\text{C}$ , 10 wt% Super C65 carbon additive (Imerys) and 10 wt% PVDF binder (Kynar, Solvay) dissolved in N-methyl-2-pyrrolidone (Alfa Aesar). The dispersion was deposited on an Al-foil used as current collector by doctor blading and then dried at  $80^\circ\text{C}$  under vacuum. For operando XRD measurements, the composition of the electrode film was 70 wt%

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