

# Feasibility studies on newly identified $\text{LiCrP}_2\text{O}_7$ compound for lithium insertion behavior

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**Abstract** A new category of lithium intercalating cathode candidates, namely  $\text{LiCrP}_2\text{O}_7$ , was synthesized at  $800^\circ\text{C}$  using a citric acid assisted modified (CAM) sol–gel method and examined for possible lithium insertion behavior. The formation of a phase pure and monoclinic  $\text{LiCrP}_2\text{O}_7$  compound with finer crystallite size was confirmed from the X-ray diffraction patterns. The presence of nano-sized particles as observed from a transmittance electron microscope image of  $\text{LiCrP}_2\text{O}_7$  and the presence of a preferred local cation environment, evidenced from Fourier transform infra-red and  $^7\text{Li}$  nuclear magnetic resonance studies, are the added advantages of the present study. Further, cyclic voltametry study performed on 2016 coin cells consisting of the synthesized  $\text{LiCrP}_2\text{O}_7$  cathode revealed an excellent cycling reversibility and structural stability. Hence, CAM sol–gel synthesized  $\text{LiCrP}_2\text{O}_7$  is found to possess desirable physical as well as electrochemical properties, leading one to consider the same as a possible lithium intercalating cathode material.

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## 1 Introduction

Lithium batteries are smaller, lighter, more powerful and long lasting batteries that address the growing needs of portable, ever-more-wireless world of laptops, cell phones, medical devices, and other modern e-commodities. One of

the limitations of present day commercial lithium batteries is the toxic and costly nature of  $\text{LiCoO}_2$  cathode, which promotes the search for a suitable and an alternative cathode material. Towards this direction, currently  $\text{ABPO}_4$  olivines with a prime focus on  $\text{LiFePO}_4$  cathode [1] is widely being studied. Here again, the inherent poor electronic conductivity and stringent synthesis methodology of  $\text{LiFePO}_4$  are the hampering issues working against its commercial acceptance [1, 2]. As a result, research focus on other possible phosphates and derivative of phosphates, viz., pyrophosphates with various transition metals, gains importance. Since phosphates in general are popularly known for their low cost, high voltage and inherent structural and thermal stability, such a study on phosphate related compounds for lithium battery applications is mandatory to combat the toxic and thermal instability issues of existing lithium battery cathodes.

Among the various  $\text{ABPO}_4$  cathodes of known type, only  $\text{LiFePO}_4$  is widely studied [1, 3] and the  $\text{LiCoPO}_4$  and  $\text{LiNiPO}_4$  cathodes [4–6] seem to be less attractive, due to the known toxic and costly nature of Co and Ni counterparts. On the other hand, very few and arguably interesting controversial reports on the synthesis and electrochemical properties of  $\text{LiMnPO}_4$  are available in the literature [7]. Hence, basic understanding on the synthesis-structure-property relationship of  $\text{ABPO}_4$  or  $\text{ABP}_2\text{O}_7$  category compounds becomes mandatory, which in turn emphasizes the need for an extensive study of the same. Ultimately, such a study would pave the way to address the known and unknown issues of phosphate related cathodes and hence the search for a new category of  $\text{ABPO}_4$  or  $\text{ABP}_2\text{O}_7$  cathodes with a suitable transition metal gains importance.

Consequent to  $\text{ABPO}_4$  cathodes, it is well known that the performance characteristics of any pyrophosphate with the general formula  $\text{ABP}_2\text{O}_7$  depends upon the size of A and

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B cations and the conformations of the  $(\text{P}_2\text{O}_7)^{4-}$  polyanions. Rissouli et al. [8, 9] have studied the structural and magnetic properties of Co and Ni based pyrophosphates and recently a Fe based pyrophosphate [10, 11] is reported to deliver a capacity of  $\sim 100$  mAh/g. On the other hand, with regard to  $\text{LiCrP}_2\text{O}_7$  compound, only reports on the X-ray crystallographic data [12] are available and no results on the lithium intercalation and deintercalation behavior of  $\text{LiCrP}_2\text{O}_7$  are available in the literature. In other words, the presence of  $\text{Cr}^{3+}$  in a distorted  $O_h$  environment and the formation of a three dimensional network with the di-phosphate anions along with the filling of channels by lithium cations in  $\text{LiCrP}_2\text{O}_7$  alone is reported [13]. However, reports available for similar pyrophosphates but with selected metals, viz., Ti, Fe and V [11, 13] have led to discussions of the possibility of lithium intercalating cathode behavior. People having intrigued by the same, the newer category  $\text{LiCrP}_2\text{O}_7$  was planned to be subjected for systematic feasibility studies mainly to understand whether the compound could be explored for a lithium intercalation behavior.

Hence, the present study on the deployment of  $\text{LiCrP}_2\text{O}_7$  as cathode for demonstrating the reversible lithium insertion behavior in coin cell assembly is first of its kind and the same is the highlight of the present communication.

Herein, a CAM sol-gel method, based on solution approach is chosen to synthesize the title compound mainly to ensure the uniform distribution and atomic level mixing of reactants and gelling agents. Such an intimate mixing of precursors in a CAM sol-gel method renders phase pure final products with nano-particle size, which has already been demonstrated with respect to the synthesis of a wide variety of oxide and phosphate cathodes [4, 14]. In addition, based on the well known fact that the crystal structure, local cation environment, surface morphology and chemical composition of the materials play a significant role for the electrochemical performance of the same, a series of physical characterization studies were performed on  $\text{LiCrP}_2\text{O}_7$  material so as to understand and to further correlate the physical properties with that of the electrochemical cycling behavior.

With this background, the present study was aimed at the synthesis and systematic characterization of  $\text{LiCrP}_2\text{O}_7$  compound along with an investigation for the lithium intercalation and de-intercalation process of  $\text{LiCrP}_2\text{O}_7$  cathode.

## 2 Experimental details

### 2.1 Synthesis procedure

The  $\text{LiCrP}_2\text{O}_7$  material was synthesized by adopting the citric acid modified sol-gel (CAM sol-gel) method, as described elsewhere [4].

### 2.2 Physical and electrochemical characterizations

The compound formation temperature was confirmed by thermogravimetry and differential thermal analysis (TG/DTA) with a thermo balance, model STA 409 PC, in the temperature range 25–800°C, using alumina crucibles with 20 mg of samples, under air with a heating rate at 20°C/min. Phase characterization was done by a powder X-ray diffraction technique on a Philips 1830 X-ray diffractometer using Ni-filtered  $\text{Cu K}\alpha$  radiation ( $\lambda = 1.5406 \text{ \AA}$ ) in the  $2\theta$  range 10–70° at a scan rate of 0.04°/s. A Fourier transform infrared spectroscopic (FTIR) study was performed on a Perkin-Elmer paragon –500 FTIR spectrophotometer using a pellet containing a mixture of KBr and the active materials in the region 400–2000  $\text{cm}^{-1}$ , and  $^7\text{Li}$  NMR measurement was carried out with a Bruker MSL-400 spectrometer employing a 5 mm Bruker VT-MAS probe operating at a  $^7\text{Li}$  frequency of 14 MHz. The electrochemical cyclic behavior was investigated using a cyclic voltametry (CV) measurement that was performed using an Auto lab electrochemical workstation, wherein the CV scan rate was fixed at 1 mV/s.

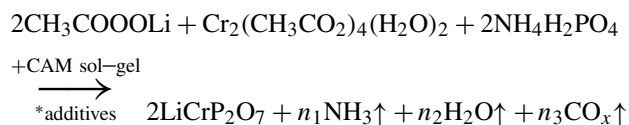
### 2.3 Electrode preparation and coin cell fabrication

Details pertaining to the electrode fabrication and the subsequent 2016 coin cell assembly are reported elsewhere [4]. CV characterization was carried out on freshly fabricated 2016 coin cells consisting of a lithium anode, a synthesized  $\text{LiCrP}_2\text{O}_7$  cathode and a non-aqueous electrolyte containing 1M  $\text{LiPF}_6$  dissolved in 1:1 v/v EC:PC with a polypropylene separator.

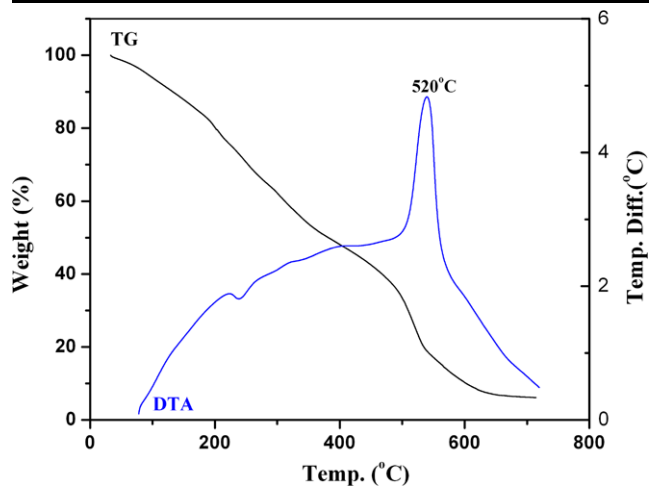
## 3 Results and discussion

### 3.1 Thermal analysis

Figure 1 exhibits the result of simultaneous thermogravimetric-differential thermal analysis (TG-DTA) of a mixture containing the precursors of  $\text{LiCrP}_2\text{O}_7$ , wherein the TG curve presents a two step weight loss behavior. The initial weight loss observed up to 400°C is assigned to the evaporation of ammonia and water from the precursor mix. The second weight loss observed between 400–610°C is due to the pyrolysis of citric acid along with the in-situ formed metastable chelated complex and other organic compounds. Based on this, a reaction of the following type is expected to take place:



\*Citric acid + Acrylamide + *N,N'*-methylene-bis-acrylamide.

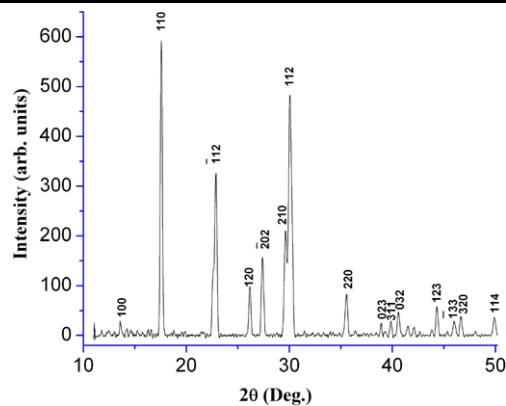


**Fig. 1** Thermal studies of ground precursors of  $\text{LiCrP}_2\text{O}_7$

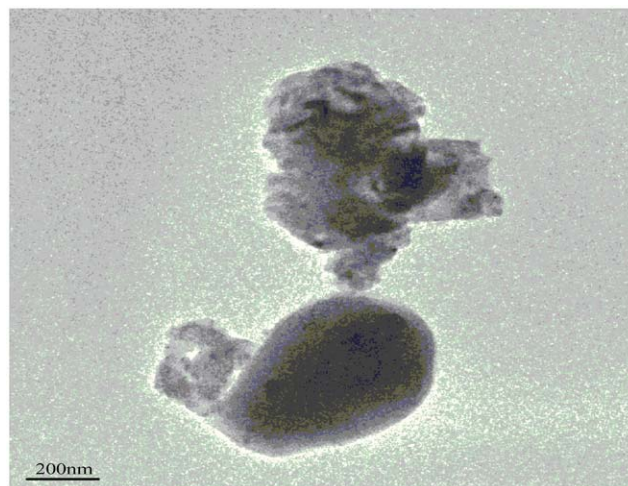
The same is obvious from the appearance of larger exothermic peak at  $520^\circ\text{C}$  in the DTA curve. When the calcination temperature goes beyond  $610^\circ\text{C}$ , the weight loss becomes insignificant until the temperature reaches  $720^\circ\text{C}$ . Hence,  $\text{LiCrP}_2\text{O}_7$  compound formation is believed to take place at a temperature well below  $650^\circ\text{C}$ . However the compound preparation was carried out at  $800^\circ\text{C}$  to improve the phase purity and a better crystallinity of  $\text{LiCrP}_2\text{O}_7$ .

### 3.2 Phase characterization

Figure 2 shows the PXRD (Powder X-ray diffraction) pattern of  $\text{LiCrP}_2\text{O}_7$  material synthesized at  $800^\circ\text{C}$  by a CAM sol-gel method. The existence of well defined and characteristic peaks of high intensity nature demonstrates the presence of a phase pure and highly crystalline product. Basically, the XRD pattern of the title compound matches well with that of the reported pattern of  $\text{LiCrP}_2\text{O}_7$  in the literature [12], thus confirming the monoclinic lattice structure with a  $P_21$  space group. Using the indexed  $h$ ,  $k$ ,  $l$  values [11], the lattice parameter values were calculated, which are as follows:  $a = 7.01$ ,  $b = 9.26$  and  $c = 7.1$ . The absence of extra peaks do confirm the absence of undesirable impurities related to Li or Cr based derivatives. The average crystallite size of  $\text{LiCrP}_2\text{O}_7$ , calculated using Scherer's formula [15], was found to be 300 nm, which was further evidenced by TEM study. Similarly, the strain value calculated using Stokes' formula [16] was found to be very small (0.34), thereby ensuring the formation and existence of strain free crystal lattice of  $\text{LiCrP}_2\text{O}_7$ . Further, the slight broadening of XRD peaks observed in Fig. 2 is correlated to the finite crystallite size of ultrafine powders of the  $\text{LiCrP}_2\text{O}_7$  sample, which is the significance of the CAM sol-gel synthesis method.



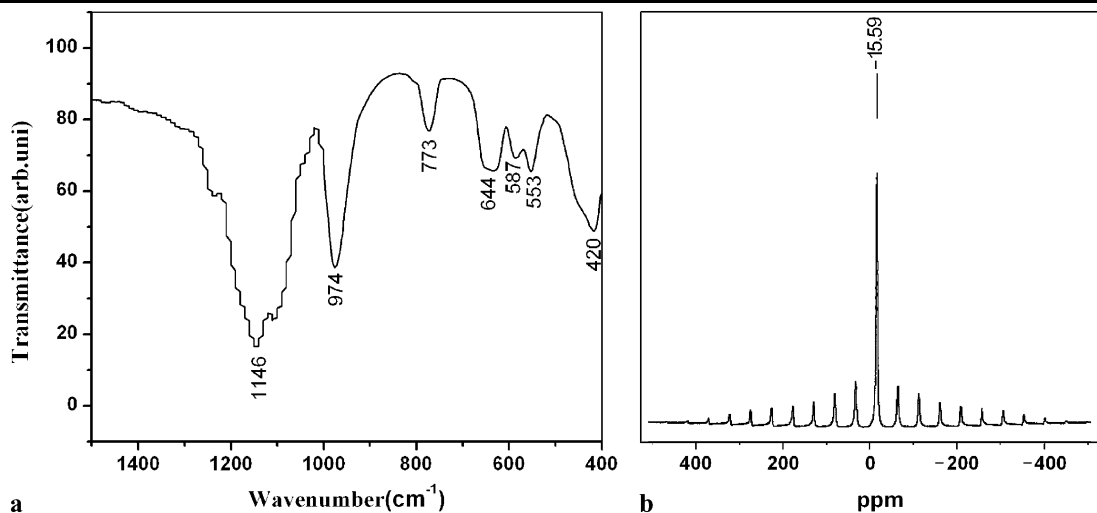
**Fig. 2** X-ray diffraction pattern of  $\text{LiCrP}_2\text{O}_7$  synthesized by the CAM sol-gel method



**Fig. 3** TEM image of  $\text{LiCrP}_2\text{O}_7$  synthesized by the CAM sol-gel method

### 3.3 Transmittance electron microscope (TEM) study

Figure 3 shows the TEM image of  $\text{LiCrP}_2\text{O}_7$ , wherein a particle size of 200 nm is clearly seen. Hence the nanometric grain sizes of  $\text{LiCrP}_2\text{O}_7$ , deduced from XRD results, are substantiated from TEM studies. Herein, the particle size of  $\text{LiCrP}_2\text{O}_7$  is less than the reported value corresponding to pyrophosphates [10]; it justified that the intrinsic nature of pyrophosphates grown by wet-chemical process may lead to agglomeration of crystalline particles to result in the formation of micro-crystalline particles. However, the present study claims the possibility of the formation of nanometric particle size in the range of 200 nm by adopting a CAM sol-gel method. Hence the reduced particle size of  $\text{LiCrP}_2\text{O}_7$  is mainly due to the significance of the presently adopted CAM sol-gel method, wherein compound formation takes place via a metastable chelated complex, and the entire processes is aided by the added citric acid. Hence, it is confirmed from TEM studies that the presence of nanometric  $\text{LiCrP}_2\text{O}_7$  par-



**Fig. 4** Local cation environment of the  $\text{LiCrP}_2\text{O}_7$  compound from (a) FTIR spectra and (b)  $^7\text{Li}$  NMR spectra

ticles, which is desirable for a lithium intercalation compound, is obtained by deploying a CAM sol–gel synthesis methodology.

### 3.4 Local cation environment by FTIR and $^7\text{Li}$ NMR

It is well known that FTIR study is sensitive to the short-range environment of oxygen coordination around the cations in the oxide lattice. Figure 4a shows the FTIR pattern recorded for CAM sol–gel synthesized  $\text{LiCrP}_2\text{O}_7$ . The vibrational features in the lower wavenumber region ( $400\text{--}1000\text{ cm}^{-1}$ ) are similar to that of  $\text{PO}_4^{3-}$  based compounds and the additional signatures that are observed at  $773$  and  $974\text{ cm}^{-1}$  may be attributed to the antisymmetric  $\nu_{\text{as}}$  and symmetric  $\nu_{\text{s}}$  stretching modes of P–O–P bridges. In the higher wavenumber region, IR bands are well resolved with the highest component at  $1146\text{ cm}^{-1}$ . This in turn may be assigned to the terminal stretching mode of  $\text{P}_2\text{O}_7^{4-}$  ions, because the terminal stretching modes of  $\text{P}_2\text{O}_7^{4-}$  ions usually occur in the region  $1250\text{--}975\text{ cm}^{-1}$  [17]. Similarly, the broad band with a hump at  $644\text{ cm}^{-1}$  is attributed to the presence of a Cr–O group. The resonant frequencies of  $\text{LiO}_6$  are not reported in the present study, as the same will appear in the frequency range of  $200\text{--}400\text{ cm}^{-1}$  [18, 19]. Since the FTIR study of the present work is restricted between  $400\text{--}1600\text{ cm}^{-1}$ , an elaborate discussion regarding the presence of  $\text{LiO}_6$  octahedra is not applicable to the present case.

To confirm the Li ion site occupancy, a  $^7\text{Li}$  NMR (Nuclear Magnetic Resonance) study was carried out and the corresponding spectral data recorded for  $\text{LiCrP}_2\text{O}_7$  are shown in Fig. 4b. The appearance of a large single isotropic peak at  $-15\text{ ppm}$  indicates the presence and tetrahedral site occupation of Li in  $\text{LiCrP}_2\text{O}_7$  and the negative shift is corroborated by the hyperfine interaction between the nucleus of  $^7\text{Li}$  ( $I = 3/2$ ) and the transition metal  $\text{Cr}^{3+}$  unpaired

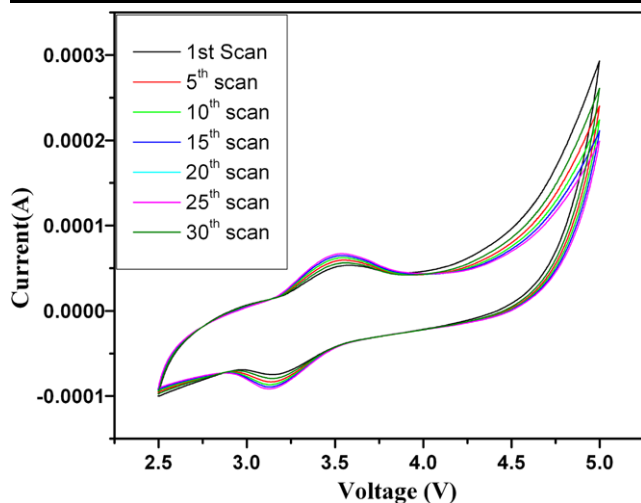
electrons [20]. Thus the possible crystal defects due to the cation distribution, off-stoichiometry, disordered arrangements of crystal lattice etc. are ruled out in the currently synthesized  $\text{LiCrP}_2\text{O}_7$  compound. Hence, the  $^7\text{Li}$  NMR study confirms the orderly formed monoclinic  $\text{LiCrP}_2\text{O}_7$  from our CAM sol–gel method.

### 3.5 Electrochemical study of $\text{LiCrP}_2\text{O}_7$

In order to qualify the CAM sol–gel synthesized  $\text{LiCrP}_2\text{O}_7$  as a possible lithium intercalation material for lithium battery applications, the electrochemical cycling performance was studied by cyclic voltammetry analysis. Figure 5 shows the representative cyclic voltammogram of the  $\text{LiCrP}_2\text{O}_7$  cathode, prepared from the synthesized title compound and the CV was recorded at room temperature under a scan rate of  $1\text{ mV s}^{-1}$  in the potential range of  $2.5\text{--}5.0\text{ V}$  versus  $\text{Li/Li}^+$ .

The CV features a prominent anodic peak at  $3.51\text{ V}$  and a corresponding cathodic peak at  $3.12\text{ V}$ , thus confirming the cyclic reversibility of the newly synthesized  $\text{LiCrP}_2\text{O}_7$  cathode. It is reported that  $\text{Cr}^{3+}$  is capable of undergoing three electron transfer process via the familiar  $\text{Cr}^{\text{III}}/\text{Cr}^{\text{VI}}$  redox couple formed through a possible intermediate  $\text{Cr}^{4+}$  state. Herein, the presence of an anodic peak at  $3.51\text{ V}$  and a corresponding cathodic peak pair at  $3.12\text{ V}$  corresponds to the formation of the  $\text{Cr}^{3+}/\text{Cr}^{4+}$  redox couple, and hence the perfect electrochemical reversibility of  $\text{Cr}^{3+}$  in the  $\text{LiCrP}_2\text{O}_7$  cathode, which is essential for lithium battery applications, is demonstrated through the present study.

Further, the CV pattern upon extended CV scans up to 30 cycles has registered perfect overlap of both anodic and cathodic peak pairs in the respective positions, thereby confirming the excellent cycling reversibility of the synthesized  $\text{LiCrP}_2\text{O}_7$  cathode upon extended cycling. The absence of



**Fig. 5** Representative cyclic voltammogram of a  $\text{LiCrP}_2\text{O}_7$  cathode sintered at  $800^\circ\text{C}$  (3 h)

even minimal deviation from the anodic/cathodic peak positions upon extended cycling confirms the presence of orderly arranged crystal lattices of  $\text{LiCrP}_2\text{O}_7$  and the absence of crystal imperfection or structural degradation problems as derived already from XRD and  $^7\text{Li}$  NMR studies. Hence, it is obvious that the CAM sol–gel synthesized  $\text{LiCrP}_2\text{O}_7$  qualities itself for consideration as a new category of lithium inserting electrode material.

#### 4 Conclusion

In an attempt to explore the less studied pyrophosphate compound viz.,  $\text{LiCrP}_2\text{O}_7$  as a cathode for rechargeable lithium batteries, a CAM sol–gel method has been chosen for synthesizing the same at  $800^\circ\text{C}$ . The presence of nanometric particle size and the highly crystalline nature of  $\text{LiCrP}_2\text{O}_7$  are confirmed from TEM images and XRD patterns, respectively. The local cation environments as determined from FTIR and  $^7\text{Li}$  NMR studies are in favor of an orderly arranged crystal structure of  $\text{LiCrP}_2\text{O}_7$  in the as-synthesized form. Further, the  $\text{LiCrP}_2\text{O}_7$  compound is found to exhibit reversible lithium intercalation/de-intercalation behavior when deployed as cathode in 2016 coin cells. Thus, the

study recommends that the  $\text{LiCrP}_2\text{O}_7$  compound could be considered as yet another lithium insertion electrode material for use in next generation lithium batteries.

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