Improved electrochemical performance of the Cr doped cathode materials for energy storage/conversion devices

Sangeeta, Shruti Agnihotri, Anil Arya, and A. L. Sharma

Citation: AIP Conference Proceedings **1728**, 020380 (2016); doi: 10.1063/1.4946431
View online: http://dx.doi.org/10.1063/1.4946431
View Table of Contents: http://scitation.aip.org/content/aip/proceeding/aipcp/1728?ver=pdfcov
Published by the AIP Publishing

Improved Electrochemical Performance of the Cr Doped Cathode Materials for Energy Storage/Conversion Devices

Sangeeta, Shruti Agnihotri, Anil Arya and A.L. Sharma*

Centre for Physical Sciences, Central University of Punjab, Mansa Road Bathinda-151001, Punjab, India
*alsharmaiitkgp@gmail.com

Abstract. Successful synthesis of a nanostructured Cr-doped $LiFePO_4$ cathode material has been prepared by a sol–gel technique followed by a single step thermal treatment at 750° C for 12 hours. As olivine type $LiFePO_4$ has already gained much attention due to its advantages over other cathode materials, doping of metal ion is done in the paper to improve its drawback of lower conductivity. FESEM couples with EDX were done to characterize the morphology and particle size of the materials. $LiFe_{(1-x)}Cr_xPO_4$ (x=0.1, 0.2, 0.3) materials have average particle size of 30 to 50 nm. EDX analysis confirmed the precursor used and also confirmed the presence of carbon which is in good agreement with chemical analysis result. Electrical conductivity of the prepared cathode materials is estimated of the order of 10^{-5} Scm^{-1} by AC impedance analysis. The energy density and power density of the cathode materials is improved drastically after addition of Cr as dopant. The estimated parameters appear at desirable value for use of materials as cathode in energy storage/conversion devices.

INTRODUCTION

In the 21st century, energy shortage and environmental based issues has been directly linked to technological development and hence search on energy sources continues. In this regard, olivine structured $LiFePO_4$ is renowned as a powerful cathode material to be used in batteries for energy storage/conversion devices. The olivine type Lithium iron phosphate has additional advantage of being thermally stable, non-toxic and inexpensive over the conventional used $LiCoO_2$ cathode material. Also, the high stability of the $LiFePO_4$ cathode material with little changes in unit cell parameters during the $LiFePO_4$ / $FePO_4$ phase transition was spotlighted as the beneficial factors for good cycle life of the battery. However, low intrinsic electronic conductivity (10^{-8} to 10^{-10} Scm^{-1}) of $LiFePO_4$ restrains its use for commercial applications. This limitation has been accomplished by optimizing synthetic conditions which include in situ carbon coating on particles and doping of metal ions with super valent cations such as Zr, Nb, Mg, V, Zn and Cr [1,2]. In this paper, we reported a citric acid assisted sol-gel approach to synthesize a series of Cr-doped $LiFe_{1-x}Cr_xPO_4/C$ (x = 0.1, 0.2, 0.3) cathode materials. Citric acid was used as the carbon precursor[3] because the carbon coating helps to retard undesirable particle growth during thermal treatment and also significantly enhance the electrochemical performance of the olivine cathode materials. The varied concentration of x in $LiFe_{1-x}Cr_xPO_4$ can be used to study its properties for the formation of a novel cathode material. There is a general interest in the effect of chromium as a dopant in $LiFePO_4$ because of the smaller ionic radius of Cr^{3+}(62 pm) than that of Fe^{2+} (78 pm) or Li^+ (76 pm). It results in decreased unit–cell volume and hence improves the kinetics of cathode material in terms of power density, energy density and better cycle life. Many studies have reported that $LiFe_{1-x}Cr_xPO_4$ composites have been synthesized by the ball-milling technique. Sung Bin Park et al.[4] suggested that metal doping by ball–milling technique improved rate capability rather than enhancing the capacity. Nanosized powders synthesized by sol-gel technique exhibits better structural and microstructural parameters and thus increase kinetics of cathode materials.

LFP cathode materials synthesized via a single–step thermal treatment at 750° C possesses a large surface area and porous structure. Porous structure is a necessary condition for unhindered transport of electrolyte into the particles exterior [5,6]. The structural morphological properties are studied and detailed in next sections.

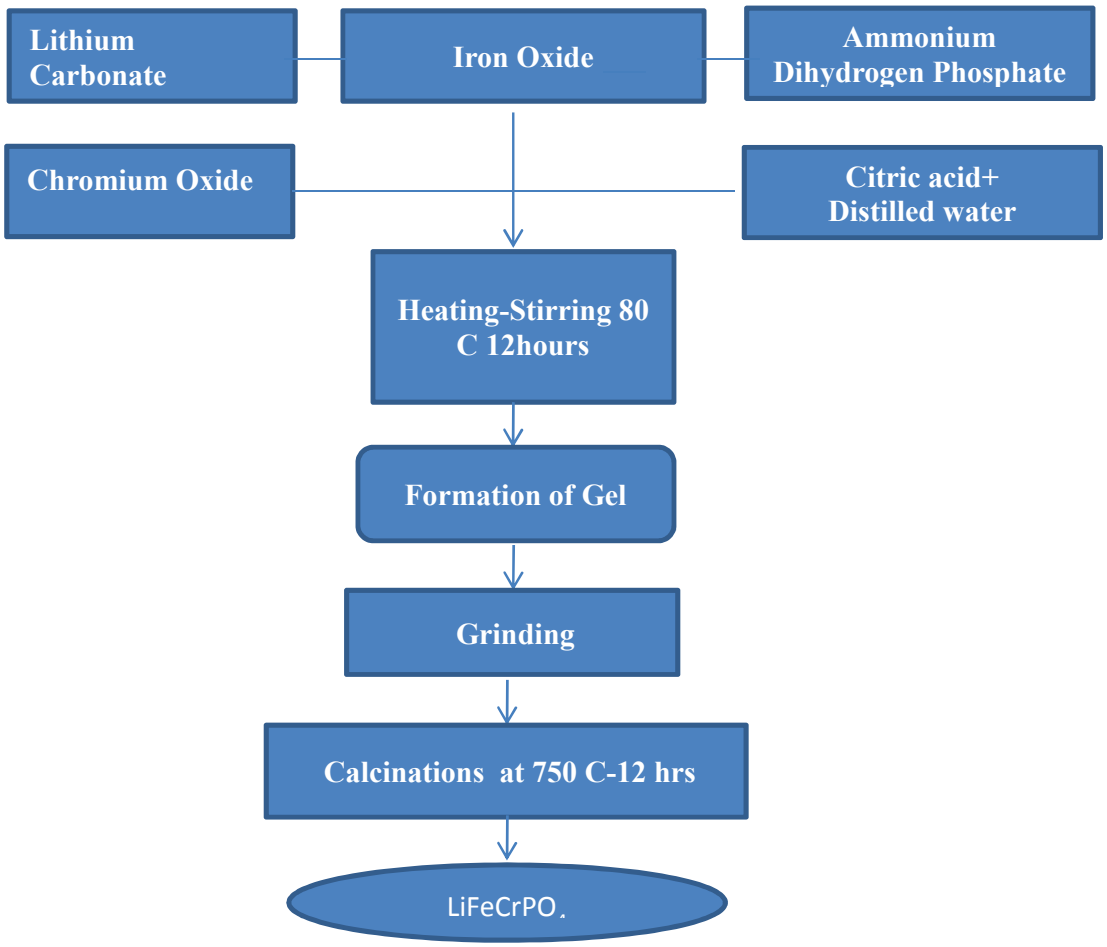
International Conference on Condensed Matter and Applied Physics (ICC 2015)
AIP Conf. Proc. 1728, 020380-1–020380-5; doi: 10.1063/1.4946431
Published by AIP Publishing. 978-0-7354-1375-7/$30.00

Material and Experimental work

Chemicals used-Lithium carbonate (Li_2CO_3), Iron oxide (Fe_2O_3), Chromium oxide (Cr_2O_3), Ammonium dihydrogen phosphate ($(NH_4)_2HPO_4$), Citric acid.

Preparation of $LiFe_{1-x}Cr_xPO_4$ (x=0.1, 0.2, 0.3) materials by SOL-GEL method.

Cr doped $LiFe_{1-x}Cr_xPO_4$ (LFCP) materials were synthesized by sol-gel method. Li_2CO_3, Fe_2O_3, $(NH_4)_2HPO_4$ were dissolved in distilled water. Then the desired amount of doping material Cr_2O_3 was added.
Cr doped $LiFePO_4$ – C composited were synthesized at different concentration of x=0.1,0.2,0.3 with proper amount of citric acid added as chelation agent. The aqueous solution was continuously stirred at 60^o C until it produced a homogeneous suspension. Then the mixture was placed at 200^o C in vacuum oven for about 2 hours to remove water. The powder obtained was grounded for 3 hours. Finally, the resulting slurry was heat treated at 750^o C for 12 hours.

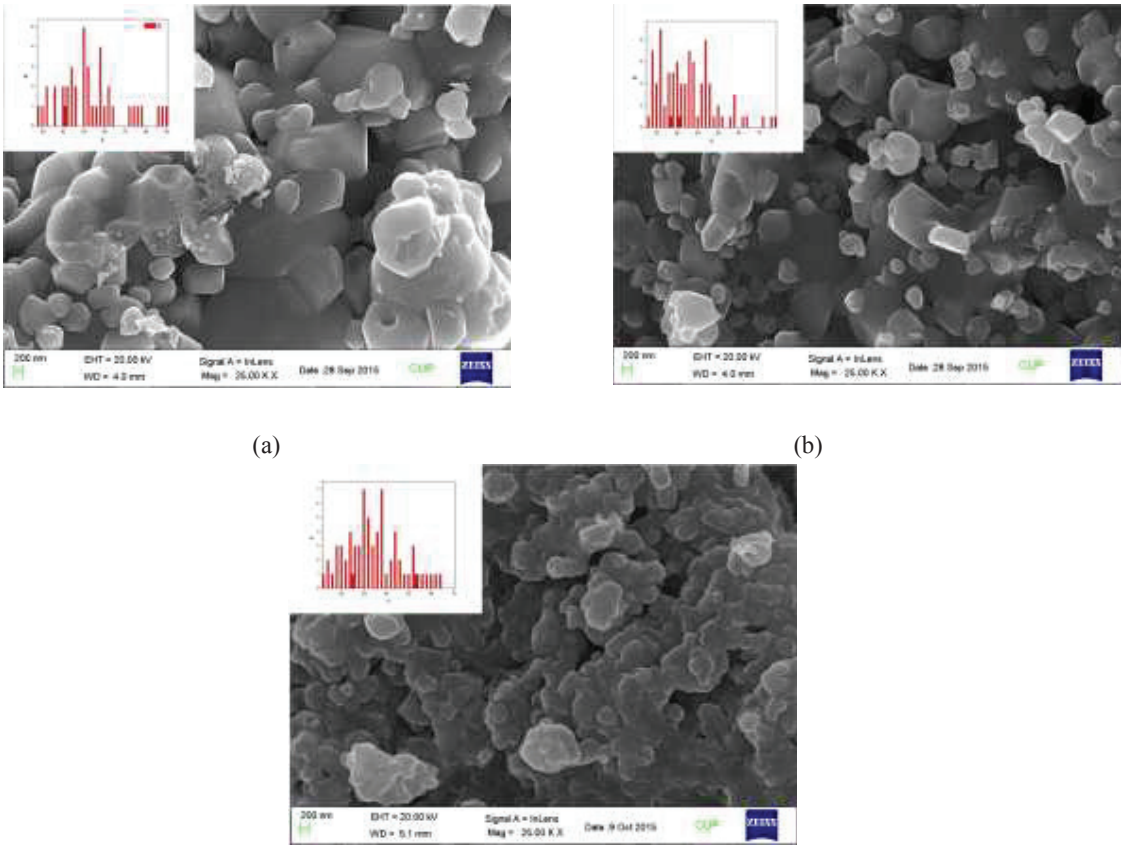


Characterization tools- FESEM was used to observe particle sizes and morphological properties of the materials. Electrochemical impedance spectroscopy (EIS) measurements were performed by a CH instrument (Model: 760) by placing a sample between two stainless steel electrodes.

RESULT AND DISCUSSION

FESEM Analysis

The electrochemical performance of the cathode material is greatly impressed by the particle size and the morphology of the particles. SEM images of the $LiFe_{0.9}Cr_{0.1}PO_4$, $LiFe_{0.8}Cr_{0.2}PO_4$ and $LiFe_{0.7}Cr_{0.3}PO_4$ are shown in Fig. 1. Samples show impressive particle size with an average particle size of 30 to 50 nm. With the increasing content of Cr, there is impactful reduction in particle size because Cr^{2+} can occupy the Fe^{2+} via doping, which induced the lattice deformity of olivine crystal. This lattice distortion could reduce the surface energy of $LiFePO_4$ crystal and then inhibit the enlargement of $LiFePO_4$ crystal [9].



(a) (b)

(c)

FIGURE 1. FESEM images of LFCP particles at (a) x=0.1 (b) x=0.2 (c) x=0.3

Electrical Conductivity Analysis

The electric conductivity of the cathode material has been estimated using the expression $\sigma = \frac{\ell}{R_b A}$ where R_b is the bulk resistance, ℓ is the thickness of electrode material and A is the contact area of electrode. The electrical conductivity of prepared cathode materials has been evaluated by intercept of high frequency small semi-circular arc on real axis of all the three concentration. According to Fig. 2, we concluded that proper amount of Cr doping in $LiFePO_4$/C composites leads to the improvement of electrochemical performance of $LiFePO_4$/C composites because

of the formation of semiconducting amorphous carbon which is formed by a single step thermal treatment at 750° C and thus exhibits conductivity of the order of 10^{-5} Scm^{-1}.

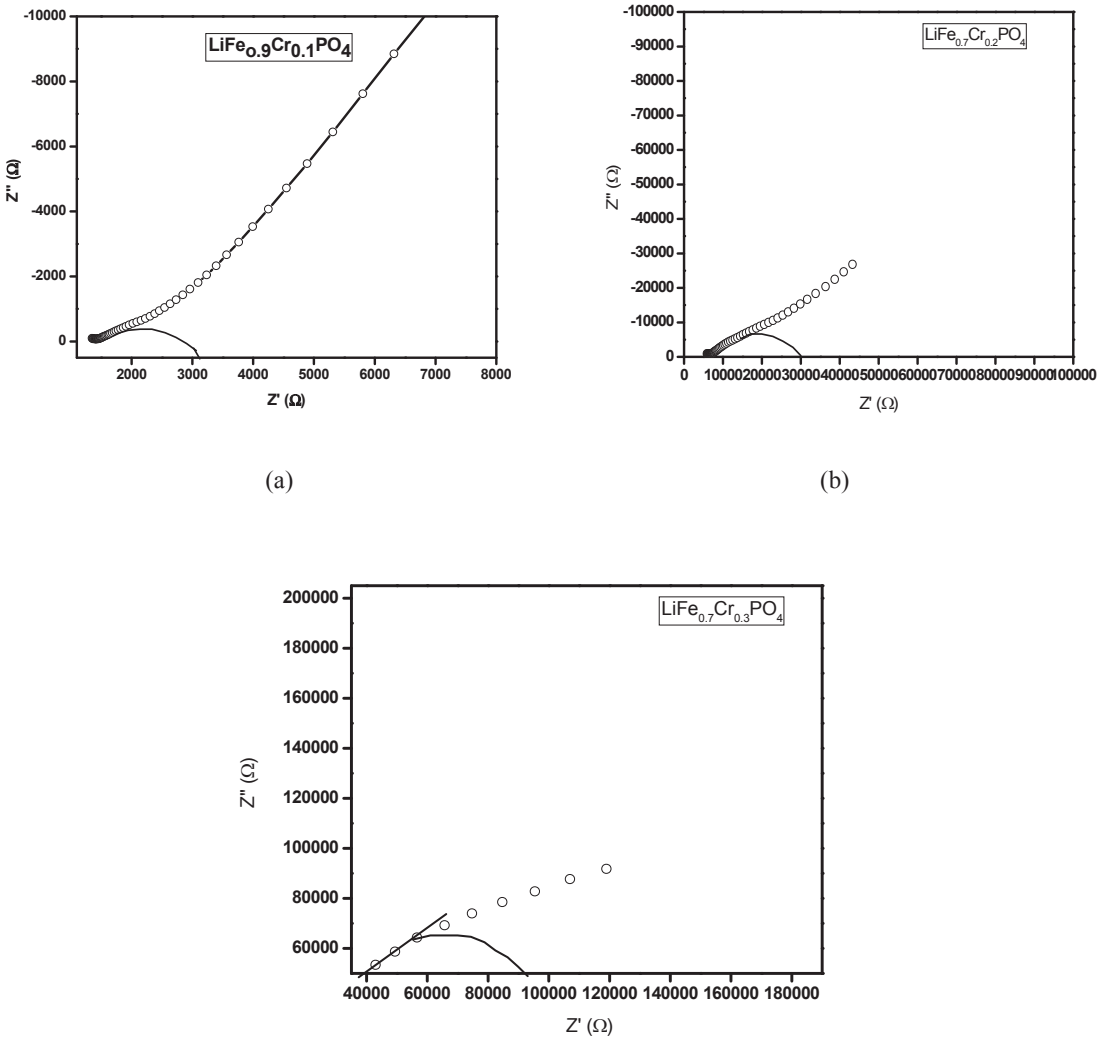


FIGURE 2. Nyquist plots of LFCP at (a) x=0.1 (b) x=0.2 (c) x=0.3

Along with the carbon amount, cation doping and particle size are directly related to the formation of Fe_2P impurity phase and excess amount of iron phosphide will lower the electrochemical performance of the electrode [7,8].

Table 1 shows calculated value of electric conductivity of cathode material

concentration (x)	**Thickness (cm)**	**Contact Area (cm^2)**	**Bulk resistance(Ω)**	**Electric conductivity (Scm^{-1})**
0.1	0.2	1.47	3074	4.42×10^{-5}
0.2	0.2	1.47	29711	4.58×10^{-6}
0.3	0.2	1.47	93050	1.46×10^{-6}

In this paper, low level doping (x=0.1) shows better electrical conductivity having estimated value of 8.2 x 10^{-5} Scm^{-1}. Thus increase in doping level of Cr^{2+} for $LiFe_{1-x}Cr_xPO_4$-C samples have Fe_2P impurity phase.

CONCLUSION

Nanoparticle $LiFeCrPO_4$ powder was prepared by a sol-gel method using citric acid as a carbon precursor. The composites were characterized by FESEM, elemental analysis and their electrochemical properties were also studied by CIS. FESEM reveal that average particle size of the synthesized $LiFeCrPO_4$-C sample has been found to be in the range of 30-50 nm.The prepared $LiFe_{0.9}Cr_{0.1}PO_4$-C sample exhibits conductivity of the order of 10^{-5} Scm^{-1}.

Acknowledgement

Author is thankful to the Central University of Punjab for providing facility, infrastructure and financial support for the current Research Work.

REFERENCES

1. S.Y. Chung,J.Blocking,and Y.M. Chiang,*J.Nature Mater*.**1**,123(2002).
2. H.Liu,Q.Cao,L.J.Fu,C.Li,Y.P.Wu,and H.Q. Wu,*J.Electrochem.Commun*.**8**,1553(2006).
3. R.Dominko,M.Bele,M.Gaberseck,M.Remskar,D.Hanzel,J.M.Goupil,S.Pejovnik,J.Jamnik,*J.Power Sources*.**153**,274(2006).
4. Sung Bin Park,ChangKyooPark,Jin Tae Hwang,WonIICho,and Ho Jang,*J.Met.Mater*.**17**,729-732(2011).
5. R.Dominko,J.M.Goupil,M.Bele,M.Gaberseek,M.Remskar,D.Hanzel,J.Jamnik,*J.Electrochem.Soc*.**152,**A843-A858(2005)
6. M.Takahashi,S.Tobishima,K.Takei,Y.Sakurai,*J.Power Sources*.**146**,521-524(2005).
7. R.Young-Ho,L.F.Nazar,L.Perry,D.Ryan,*J.Electrochem.Soc*.**154**,A283(2007).
8. Y.G. Yin,H.Pan,L.Shen,X.Ye,y.F.Liu,P.S. Fedkiw,X.Zhang,*J.Power sources* .**199**,256(2012).
9. J.K. Kim,G. Cheruvally,J.H. Ahn,*J. Solid State Electrochem*.**12,**799(2008)
10. W.X. Peng,L.F. Jiao,H.Y. Gao,*J.Power Sources*. **196,**2841(2011).
11. A.Kumar,R. Thomas,N.K. Karan,J.J. Saavedra-Arias,*J. Nanotechnology*.**2009,**10(2009).
12. Y. Zhu,C. Wang,*J.Phys.Chem.C*.**2830**,114(2010).