✚ IJESRT

INTERNATIONAL JOURNAL OF ENGINEERING SCIENCES & RESEARCH TECHNOLOGY

STRUCTURAL AND ELECTROCHEMICAL PROPERTIES OF LITHIUM TITANIUM FLUOROPHOSPHATE CATHODE MATERIAL FOR LITHIUM ION RECHARGEABLE BATTERIES

Dr.-Ing. Madhav Singh*, Dr.-Ing. Bhawana Singh, Prof. Dr. Monika Willert-Porada
*Chair of Materials Processing, Faculty of Engineering Sciences,
University f Bayreuth, 95440 Bayreuth, Germany
(_Dedicated to late Prof. Dr. Monika Willert-Porada_)

ABSTRACT

As a new approach, three-dimensional flower-like $LiTiPO_4F$ nano-structured particles were successfully synthesized in a single step by chemical solution deposition method. Each flower-like structure consists of petal like assembly, which might be helpful to enhance the electrochemical performance of $LiTiPO_4F$. The obtained powder was characterized by X-ray diffraction and scanning electron microscopy. The lithium storage properties of the nanostructured $LiTiPO_4F$ were investigated as a cathode material for lithium ion batteries. The electrochemical evaluation of the $LiTiPO_4F$ exhibits a reversible specific capacity of around 150 mAh/g (94% of theoretical capacity) at C/10.

KEYWORDS: Chemical solution deposition, nanostructured $LiTiPO_4F$, cathode material, flower morphology.

INTRODUCTION

Among the several cathode materials for lithium ion batteries, the phosphor olivine $LiFePO_4$ is one of the most interesting material due to its low cost, environmental friendliness and thermal stability during the charging-discharging with a theoretical capacity of 170 mAh/g and a constant open circuit voltage of 3.4 V[1]. In the search of promising materials, phosphates have become more attractive due to good electrochemical performances at useful redox potential and safer than the commonly used metal oxides. However, olivine has some drawbacks like one-dimensional Li-ion transport and two phase redox reaction [2-4], thus introduction into large applications, like hybrid electric vehicles batteries is difficult. As Li-ion batteries continue to improve, lithium metal fluorophosphates and sodium metal fluorophosphates are also emerged as promising cathode materials instead of lithium metal phosphates for Li-ion and Na-ion batteries because of their advantages such as two-dimensional Li-ion transport and negligible structural changes during the reduction-oxidation process [5, 6]. Ramzan et al. have reported the charge distribution, electronic structure, magnetism, and crystal structure of lithium and sodium iron fluorophosphate[7]. Few other lithium transition metal fluorophosphate ($LiVPO_4F$, Li_2NiFPO_4) have also been reported so far [8, 9]. However, these materials have not yet been studied in detail in the literature so far.

Generally, Fluorophosphate cathode materials are synthesized via solid state and hydrothermal process at high temperature. However, these materials have yielded good storage performances but at the same time these methods suffers from the problems of complicated producing process including ball milling and subsequent heat treatment for a long time[5, 10]. Therefore, the demand of large amount of energy along with the complexity of the ceramic methods motivates the development of a cheaper and faster method for preparing lithium titanium fluorophosphate nanoparticles without any post heat treatment. In this paper, we report the synthesis of $LiTiPO_4F$ nanoparticles with high crystallinity via a chemical solution deposition process without any post heat treatment.

MATERIALS AND METHODS

A Stoichiometric amount of titanium (III) fluoride (TiF_3, Sigma Aldrich) and lithium phosphate (Li_3PO_4, Sigma Aldrich) was employed as precursors. All chemicals were directly used without any further purification. The precursors were dissolved in tetraethylene glycol (TEG, purity 99%, Sigma Aldrich) in a three-neck round bottom flask equipped with both the refluxing unit and a magnetic stirring unit. The flask is purged with argon during the whole experiment. In order to fully dissolve the chemicals in TEG, temperature was kept at 150 °C for 30 minutes. The solution was then heated and refluxed at 300 °C for 28 h. After cooling to room temperature, the precipitate was separated from the solvent by centrifugation (2500 rpm) and washed with acetone a couple of times. Finally the precipitate is dried at 150 °C for 5 h under Ar atmosphere.

The solid material was characterized by X-ray diffractometry (XRD, Phillips X'Pert PW 3040) with CuK_α radiation. The morphology was examined by scanning electron microscopy (SEM, Leo 1530 Gemini). The cathode was prepared by mixing active material, carbon black and polyvinylidene fluoride in a 65:25:10 weight ratio. The slurry was casted onto an Al foil and dried under argon atmosphere at 120 °C for 3 hour. The electrochemical performance was evaluated using BASYTEC CTS-lab (BASYTEC GmbH Germany), using a lithium metal anode and $LiPF_6$ based EC-DMC electrolyte. A Whatman GF-C binder free glass fibre cloth was used as a separator. Room temperature galvanostatic cycling was carried out between 1.5 and 4.0 V corresponding to a C/10 rate. The cyclic voltammetry cycling tests were carried out versus Li/Li$^+$ at ambient temperature using a Solatron Potentiostat 1285.

RESULTS AND DISCUSSION

The phase purity and crystal structure of the product synthesized by chemical solution deposition was examined by XRD. Fig.1. shows the XRD pattern (Fig.1.) of $LiTiPO_4F$ and it is comparable with the data reported elsewhere for the material made by solid state synthesis method [11]. The $LiTiPO_4F$ powder pattern is indexed in a triclinic cell (space group: $P\bar{1}$). The structure is refined using the Rietveld analysis, starting with atomic coordinates calculated in reference [12]. The final results of the structural refinements for the sample $LiTiPO_4F$ by Reitveld analysis are shown in table 1 and table 2.
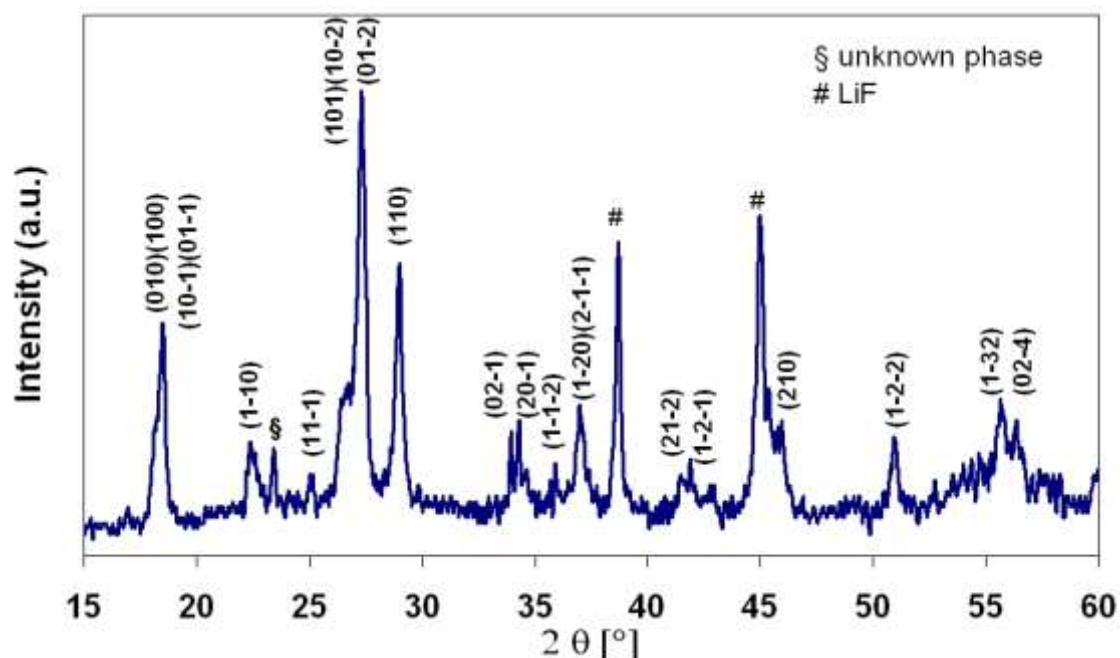

Fig. 1. X-ray diffraction patterns of LiTiPO₄F powder prepared by chemical solution deposition method

Table 1. Crystallographic data and atomic coordinates for LiTiPO₄F

Chemical formula	Molecular weight	Space group	Crystal system	
LiTiPO₄F	168.78	$P\bar{1}$	Triclinic	

Unit cell parameters				
a(Å) = 5.2459	b(Å) = 5.2767	c(Å) = 7.1911	V(Å³) = 175.11	
α[°] = 107.419	β[°] = 108.348	γ[°] = 97.259		
Density calculated = 3.34 g/cm³		Primary particle size = 35 nm		

Atom	Oxidation state	Wyckoff position	x	y	z
Li1	+1	2i	0.1008	0.6306	0.7583
Li2	+1	2i	0.1345	0.8475	0.5823
Ti1	+3	1a	0	0	0
Ti2	+3	1b	0	0	0.5
P	+5	2i	0.3363	0.6268	0.2319
O1	-2	2i	0.6639	0.7647	0.4034
O2	-2	2i	0.1036	0.6913	0.3623
O3	-2	2i	0.3068	0.3033	0.1774
O4	-2	2i	0.2359	0.7986	0.1051
F	-1	2i	0.0958	0.9214	0.7361

Table 2. Selected bond lengths (Å) and angles (°) in LiTiPO₄F

Li1—O1	2.266	Li2—O1	2.030
Li1—O2	2.181	Li2—O2	1.815
Li1—O3	1.941	Li2—O2	2.211
Li1—O4	2.230	Li2—O3	2.294
(Li1—O)average	2.154	(Li2—O)average	2.087
Li1—F	1.885	Li2—F	2.079
Ti1—O3	2.100	P—O1	1.529
Ti1—O4	1.981	P—O2	1.575
Ti1—F	1.908	P—O3	1.465
Ti2—O1	1.980	P—O4	1.480
Ti2—O2	2.012	(P—O)average	1.512
Ti2—F	1.991		
O1—F—O2	62.999°	O3—F—O4	60.694°
O1—F—Ti2	45.359°	O3—F—Ti1	42.515°
O2—F—Ti2	46.264°	O4—F—Ti1	41.639°
O2—Ti2—O1	43.415°	O3—Ti1—O4	43.941°

Tavorite crystal structure view along the [100] direction is shown in fig. 2. In this framework, the TiO₄F₂ octahedra, each coordinated with four oxygen and two fluorine ion per titanium metal ion, form corner sharing one-dimensional chains along the [010] channel (b-axis) with alternating tilted octahedra bridged by the F atoms. These chains are further joined together by PO₄ tetrahedra by sharing corners involving oxygen ions to form TiPO₄F layers. The lithium ions are co-ordinated by either oxygen or fluorine ions and resides in the largest tunnels located along the [100] channels. Lithium ions are surrounded by four oxygen ions and one fluorine ion and forming strongly distorted polyhedra.
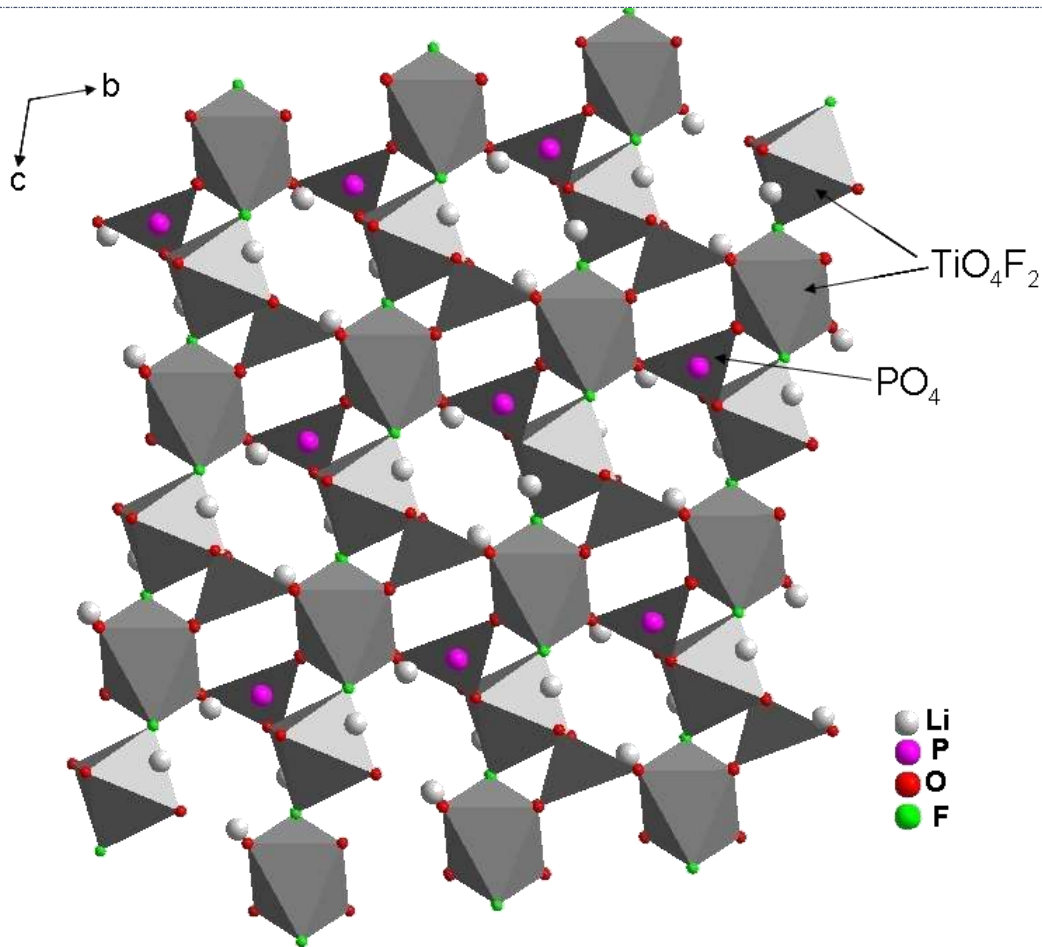
Fig. 2. LiTiPO₄F crystal structure view along the [100] direction: Titanium octahedra are shown in light gray, phosphate tetrahedral in dark gray and the Li sites is creamy white (colour online).

The size and morphology of the $LiTiPO_4F$ product was examined by scanning electron microscopy (SEM). Fig. 3(a) shows that almost all the $LiTiPO_4F$ sample consists of monodispersed flowerlike texture. The diameter of the hierarchical flowerlike texture is 300-500 nm. It can be visibly seen that flower like morphology are composed of many nanoplate and irregular shape of nanoparticle petals with an average width of about 30-80 nm. These nanoplate and nanoparticles connect together in one particular direction forming flowerlike structure. Such a well-ordered morphology might be favourable to facilitate sufficient amount of electrolyte penetration into the electrode particles from open structure, thus providing more interface area between the electrode and electrolyte and enhancing the electrochemical performance. Furthermore, this unique morphology with high interconnection among the nearest neighbouring particles in comparison to conventional particles, might be beneficial for diffusion of Li-ions.

It can be assumed that the dissolution and precipitation have caused the formation of flowerlike structure with inter-grown nanoplates. The glycol medium acts not as a solvent in the process, but also as a stabilizer to limit particle growth and prohibit agglomeration [13]. By comparison (not included here), the products obtained in the absence of tetraethylene glycol shows various peaks of impurities in the XRD pattern, indicating pure and well crystalline $LiTiPO_4F$ is not obtainable in experiments replacing tetraethylene glycol by lower boiling point glycols such as diethylene glycol, diethylene glycol monoethyl ether. Therefore, in order to synthesize $LiTiPO_4F$ with high purity and crystallinity, the solvent has a significant effect on morphology and crystal growth during the chemical solution deposition method.
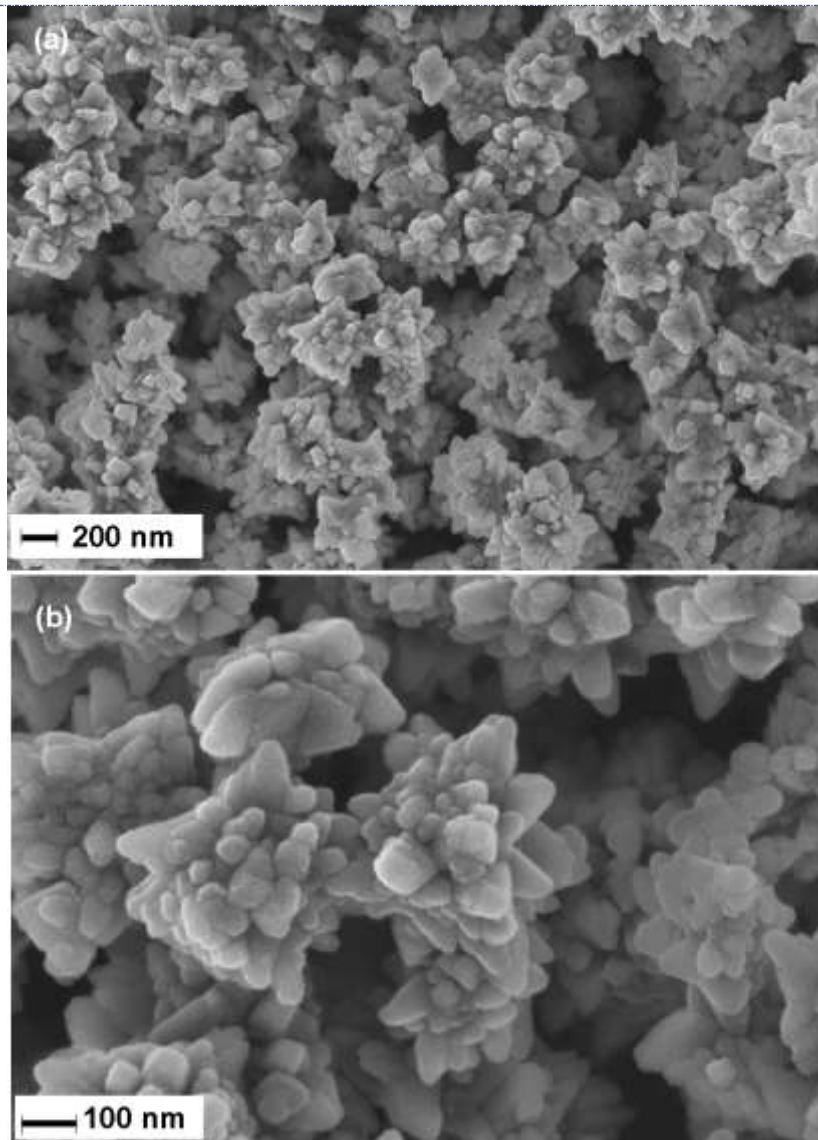
Fig. 3. Representative SEM images of the flowerlike texture: (a) overall morphology of the product; (b) high magnification image, revealing constituent details of the nanoplatelets.

On the basis of experimental results and investigations, the assumed formation mechanism of the flower-like $LiTiPO_4F$ structures is given in scheme 1. Initially, the inorganic precursors (TiF_3 and Li_3PO_4) dissociates into ions such as Ti^{3+}, Li^+, F^- and PO_4^{3-}. After this stage, nucleation, dissolution and complexation take place. As temperature increased, $LiTiPO_4F$ nanoparticles have a tendency to grow into petal-like structures. Besides, TEG molecules might be attached on the surface of these petal-like structures, which can be helpful for further growth. These petal-like structures aggregate into uniform larger flower like particles.

Electrode prepared from this material was examined in Swagelok–type cells, using lithium metal as a counter electrode. The cell was cycled at a C/10 current rate equivalent to fully charging the theoretical capacity (~159 mAh/g) of the material in 10h over the 1.5–4.0V voltage range, using the active material loading about 5 mg/cm². The carbon black and active materials were mixed in N-methyl pyrrolidone in a Thinky mixer for 2 min to maintain the flowerlike morphology of the active material. The voltage charge-discharge curves for the first five cycles in Fig. 4 reveals two flat plateaus located at around 2.8 V (oxidation of Ti^{3+} into Ti^{4+}) and 1.7 V (reduction of Ti^{3+} into Ti^{2+}).
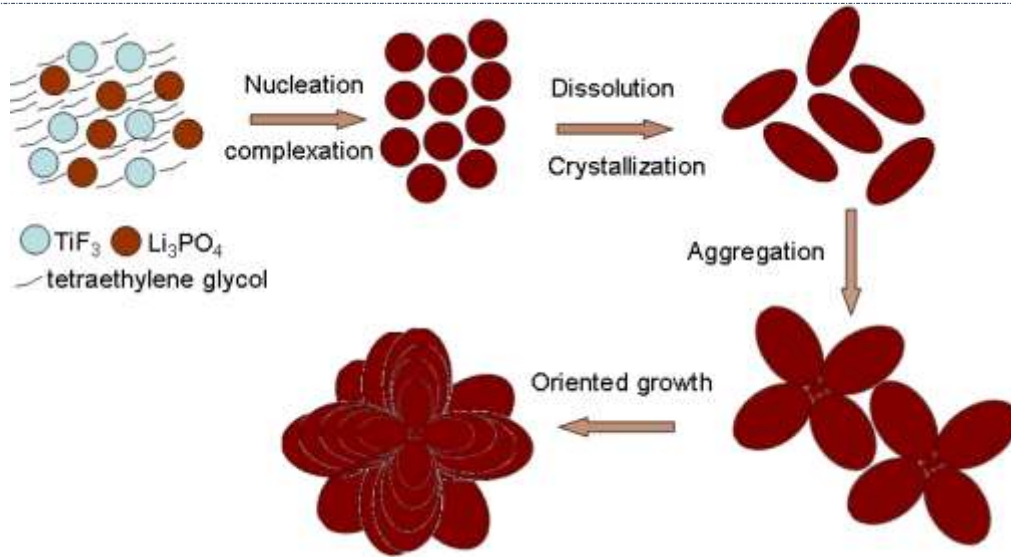
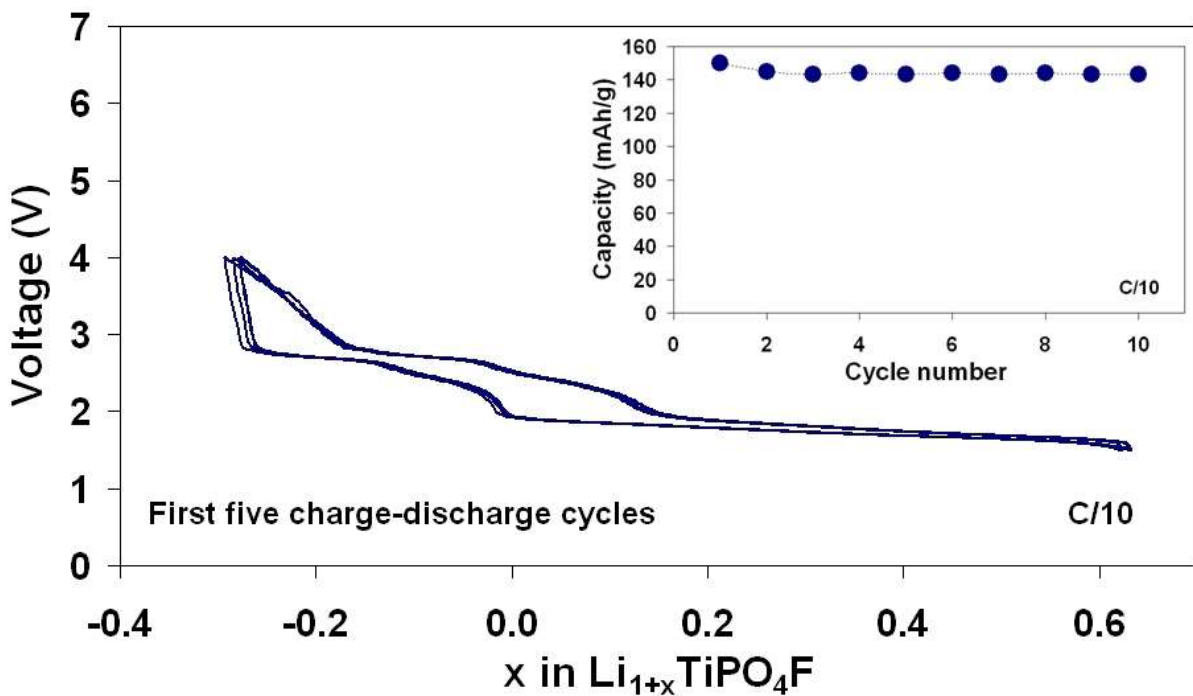*Scheme 1. Schematic illustration of the growth mechanism of flower-like LiTiPO₄F structure.*

Fig. 4. Voltage charge-discharge curves of LiTiPO₄F versus lithium metal at C/10 rate.

Li/LiTiPO$_4$F exhibited an electrochemical transformation to TiPO$_4$F and Li$_2$TiPO$_4$F at different potentials with a reversible capacity of 0.94 Li corresponding to a specific gravimetric capacity of 150 mAh/g. In addition, flower-like particles showed an excellent cyclability with no noticeable fade.

CONCLUSION

Novel flower-like LiTiPO$_4$F nano-structured particles with triclinic crystal structure were synthesized at low temperature in one step by a chemical solution deposition method and applied as cathode material. In this article, we describe the structural, morphological and electrochemical properties of novel flower-like nano-structured LiTiPO$_4$F cathode material. This flower-like morphology with interconnected open network allows electrolyte penetration and thus enhancing the electrochemical performance.

ACKNOWLEDGEMENTS

REFERENCES

[1] A. K. Padhi, K. S. Nanjundaswamy, and J. B. Goodenough. Phospho-olivines as positive-electrode materials for rechargeable lithium batteries. J. Electrochem. Soc., 144:1188-1194, 1997.

[2] D. Morgan, A. Van der ven, and G. Ceder. Li conductivity in Li_xMPO_4(M = Mn, Fe, Co, Ni) olivine materials. Electrochem. Solid State Lett., 7:A30-A32, 2004.

[3] T. Maxisch, F. Zhou, and G. Ceder. Ab initio study of the migration of small polarons in olivine Li_xFePO_4 and their association with lithium ions and vacancies. Phy. Rev. B, 73:104301{104306, 2006.

[4] C. Delacourt, P. Poizot, J.-M. Tarascon, and C. Masquelier. The existence of a temperature-driven solid solution in Li_xFePO_4 for $0 \leq x \leq 1$. Nature, 4:254-260, 2005.

[5] B. L. Ellis, W.R. M. Makahnouk, Y. Makimura, K. Toghill, and L.F. Nazar. A multifunctional 3.5 V iron-based phopphate cathode for rechargeable batteries. Nat. Mater., 6:749-753, 2007.

[6] J.-M. Tarascon, N. Recham, M. Armand, J.-N. Chotard, P. Barpanda, W. Walker, and L. Dupont. Hunting for better Li-based electrode materials via low temperature inorganic synthesis. Chem. Mater., 22:724-739, 2010.

[7] M.Ramzan, S. Lebegue, and R. Ahuja. Ab initio study of lithium and sodium iron fluorophosphate cathodes for rechargeable batteries. App. Phy. Lett., 94:151904-151906, 2009.

[8] J. Barker, R.K.B. Gover, P. Burns, A. Bryan, M.Y. Saidi, and J.L. Swoyer. Structural and electrochemical properties of lithium vanadium fluorophosphate, $LiVPO_4F$. J. Power Souces, 146:516-520, 2005.

[9] M. Dutreilh, C. Chevalier, M. El-Ghozzi, D. Avignant, and J. M. Montel. Synthesis and crystal structure of a new lithium nickel Li_2NiFPO_4 with an ordered mixed anionic framework. J. Solid State Chem., 142(1):1-5, 1999.

[10] B.L. Ellis, W.R.M. Makahnouk, W.N. Rowan-Weetaluktuk, D.H. Ryan, and L.F.Nazar. Crystal structure and electrochemical properties of A_2MPO_4F fluorophosphates (A = Na, Li; M = Fe, Mn, Co, Ni). Chem. Mater., 22:1059-1070, 2010.

[11] J. Barker, M.Y. Saidi, and J. Swoyer. Lithium metal materials and preparation thereof, US 6387568 B1, 2002.

[12] N. Recham, J.-N. Chotard, J.-C. Jumas, L. Laffont, J.-M. Tarascon and M. Armand. Ionothermal synthesis of Li-based fluorophosphates electrodes. Chem. Mater., 22:1142-1148, 2010.

[13] F. Fievet, J.P. Lagier, and B. Blin. homogeneous and heterogeneous nucleations in the polyol process for the preparation of micron and sub micron size metal particles. Solid State Ionics, 32-33:198-205, 1989.