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Improving electrochemical properties of porous iron substituted lithium manganese phosphate in additive addition electrolyte



Jae-Kwang Kim ^{a,*}, Rani Vijaya ^b, Likun Zhu ^b, Youngsik Kim ^{a,*}

^a School of Energy & Chemical Engineering, Ulsan National Institute of Science and Technology (UNIST), Ulsan 689-798, Republic of Korea

^b Department of Mechanical Engineering, Indiana University-Purdue University Indianapolis, Indianapolis, IN 46202, USA

H I G H L I G H T S

- Porous $\text{LiMn}_{0.6}\text{Fe}_{0.4}\text{PO}_4$ (LMFP) was synthesized by a modified sol–gel process.
- The discharge capacity and energy density are 152 mAh g^{-1} and 570 Wh kg^{-1} , respectively.
- To prevent Mn dissolution, TMSP was added into the electrolyte as additive.
- TMSP additive in the electrolyte improved cycle stability and rate-capability of LMFP.

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Porous $\text{LiMn}_{0.6}\text{Fe}_{0.4}\text{PO}_4$ (LMFP) is synthesized by a modified sol–gel process. Highly conductive LMFP due to uniform dispersion of carbon throughout LMFP particles are achieved by the addition of sucrose as an additional carbon source. The LMFP obtained has a high specific surface area with a uniform, porous, and web-like nano-sized carbon layer on the surface. The initial discharge capacity and energy density of the LMFP cathode is 152 mAh g^{-1} and 570 Wh kg^{-1} , respectively, at 0.1C current rate. The combined effect of high porosity and high electrical conductivity lead to fast lithium ion diffusion and enhance initial capacity compared to materials prepared by the general sol–gel method. However, with conventional electrolyte (1M LiPF_6 in EC/DMC) poor cycle performance is observed due to HF attack. To improve the cycle stability we add tris (trimethylsilyl) phosphite (TMSP) as an additive in the electrolyte which dramatically improves cycle stability and rate-capability.

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1. Introduction

Lithium iron phosphate has become a promising cathode material for rechargeable lithium ion batteries, due to its low cost, environmental friendliness (non-toxic), appreciable theoretical capacities ($\sim 170 \text{ mAh/g}$), and high thermal and electrochemical stabilities [1,2]. The success of lithium iron phosphate inspired many research groups to further develop attractive phosphate alternatives. Compared to the cobalt-based cathode materials such as LiCoO_2 and the layered $\text{LiNi}_{1/3}\text{Mn}_{1/3}\text{Co}_{1/3}\text{O}_2$ [3,4], phosphate-based materials are more suitable for large scale applications, such as hybrid electric vehicles (HEVs) and backup power systems.

Recently, partial substitution of Mn and Co for Fe in LiFePO_4 was employed to achieve high energy density and high stability lithium

ion batteries. Indeed, LiMnPO_4 and LiCoPO_4 have potentials of 4.1 and 4.9 V vs. Li, respectively [5–7]. However, these materials have drawbacks that limit their use – the dissolution of substituted metal and decomposition of electrolyte above 4.5 V vs. Li. Moreover, LiMnPO_4 and LiCoPO_4 show poor discharge capacities and cycle stabilities [8]. Several groups have proposed solutions to mitigate these drawbacks. For instance, a coexistence of metal cations in LiFePO_4 is a promising strategy for high energy density lithium ion batteries [9–11]. Yamada et al. studied the dependence of Mn content on the structure and electrochemical properties of $\text{LiMn}_y\text{Fe}_{1-y}\text{PO}_4$ and we have achieved good electrochemical properties with a $\text{LiMn}_{0.4}\text{Fe}_{0.6}\text{PO}_4$ composite [12,13]. However, sufficient enhancement has not been made. The objective of this paper is to introduce a new method to improve the cycle ability and rate-capability of $\text{LiMn}_{0.6}\text{Fe}_{0.4}\text{PO}_4$ cathode material.

In this work, we have designed a porous $\text{LiMn}_{0.6}\text{Fe}_{0.4}\text{PO}_4$ cathode prepared by modified sol–gel method to improve lithium-ion battery capacity. In the modified sol–gel method sucrose is used

* Corresponding authors.

E-mail addresses: jaekwang@unist.ac.kr (J.-K. Kim), ykim@unist.ac.kr (Y. Kim).

as additional carbon source with citric acid because the carbon prepared by sucrose show high electrical conductivity [14,15]. Although the capacity and energy density have been significantly improved by high surface area and high electrical conductivity in the $\text{LiMn}_{0.6}\text{Fe}_{0.4}\text{PO}_4$, poor cycle performance was shown with high Mn dissolution. To enhance the cycle ability tris (trimethylsilyl) phosphite (TMSP) was added as additive into electrolyte. The TMSP additive can form SEI layer on the surface of cathode and prevent Mn dissolution caused by the destruction of SEI with HF attack, resulting in enhancement of cycle ability and rate-capability.

2. Experimental

$\text{LiMn}_{0.6}\text{Fe}_{0.4}\text{PO}_4$ was synthesized by the modified sol–gel method, described in a previous study for LiFePO_4 [14]. Li_2CO_3 , $\text{FeC}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$, $\text{Mn}(\text{COOCH}_3)_2 \cdot 4\text{H}_2\text{O}$ and $\text{NH}_4\text{H}_2\text{PO}_4$ (All 99%, Aldrich) and citric acid (Shinyo Pure Chemicals, 99%) were used as starting materials to synthesize $\text{LiMn}_{0.6}\text{Fe}_{0.4}\text{PO}_4$. Sucrose was added as an additional carbon source. All the components were dissolved in deionized water at room temperature and added to a citric acid solution. After homogenous mixing, the sol was dried by keeping it at 80 °C for 12 h under magnetic stirring. The gel obtained was placed in a vacuum oven, heated at 70 °C for 12 h, and finally heated under nitrogen atmosphere at 700 °C for 10 h. The crystallographic structural characterization was performed by X-ray powder diffraction (XRD) and Rietveld refinement. XRD was done by a SIMENS D5005 X-ray diffractometer using $\text{CuK}\alpha$ radiation (35 mA/40 kV) and a graphite monochromator. Data for Rietveld structure refinement were collected in the 2θ range 15–120° with 0.02° step interval and 10 s step time. The sample was rotated at 30 rpm during data collection to minimize any preferred orientation and statistical errors in calculation. The crystal structure was refined in the space group $Pnma$ using the program FullProf. Scanning

electron microscopy (SEM) imaging was carried out with FE-SEM (Philips XL30 S FEG). The specific surface area was computed from N_2 sorption data (ASAP 2020 Analyzer) using the Brunauer–Emmett–Teller (BET) method. The chemical composition of active materials and Mn dissolution in the electrolyte were determined using inductively coupled plasma (ICP) analysis (Atomscan 25, Optima 4300DV) and carbon contents were obtained from elemental analysis (CHNS-932, LECO). To prepare the cathode, $\text{LiMn}_{0.6}\text{Fe}_{0.4}\text{PO}_4$ powder, super-P carbon black (Alfa) and poly(vinylidene fluoride) (PVdF) binder were mixed in 80:10:10 weight ratio in N-methylpyrrolidone (NMP) to form a viscous slurry that was cast on aluminum foil and dried at 95 °C under vacuum for 12 h. The film was cut into circular discs with an area of 0.95 cm^2 and mass ~3.0 mg, for use as cathodes. Two-electrode coin-type Li/ $\text{LiMn}_{0.6}\text{Fe}_{0.4}\text{PO}_4$ cells were fabricated by sandwiching a Celgard®-2200 separator containing 1M LiPF_6 in EC/DMC (1:1 vol.%, Samsung Co.) electrolyte between the lithium metal anode and the $\text{LiMn}_{0.6}\text{Fe}_{0.4}\text{PO}_4$ cathode. Tris (trimethylsilyl) phosphite was incorporated in 1 wt.% as additive. Cell assembly was performed under argon atmosphere in a glove box ($\text{H}_2\text{O} < 10$ ppm).

3. Results and discussion

The chemical composition of $\text{LiMn}_{0.6}\text{Fe}_{0.4}\text{PO}_4$ obtained from ICP analysis matched the theoretical molar ratio of Li: Mn: Fe: P as 1.01:0.61:0.39:0.99 (± 0.02) and contained ~10 wt.% carbon. The XRD pattern of $\text{LiMn}_{0.6}\text{Fe}_{0.4}\text{PO}_4$ (LMFP) is shown in Fig. 1. The crystal structure of the LMFP is consistent with a standard ordered orthorhombic olivine structure of PDF card No. 40–1499, and no impurities were detected, which indicates that the high purity LMFP could be synthesized by a typical sol–gel process. In the standard XRD pattern of LiFePO_4 , the peak intensity ratios of the (111)/(131) and (121)/(131) are 0.89 and 0.90, respectively. However, the peak intensity ratios of the LMFP are 1.01 and 0.97 (Fig. S1). These changes are mainly due to a distortion of the crystal lattice of LiFePO_4 caused by Mn atoms. The calculated LMFP lattice parameters are $a = 10.41$ Å, $b = 6.07$ Å, and $c = 4.73$ Å, which indicate that the introduced Mn causes an increase of the lattice parameters compared to pure LiFePO_4 [12,13]. On the LMFP structure, the LiO_6 octahedra form edge-sharing chains with the b -axis and the lithium ion transport carry out along the b -axis in a zig-zag pattern between adjacent Li sites [16]. The triangular LiO_6 octahedral faces ($\text{O}_2\text{—O}_3\text{—O}_1$) provide space for the transport of lithium ions and effective cross sectional area plays an important role in the Li ions diffusion (Fig. 1b). Table 1 gives the selected interatomic distance (Å) and angle (°) of LiO_6 obtained from the Rietveld analysis of LMFP structure. The cross-sectional area of $\text{O}_2\text{—O}_3\text{—O}_1$ triangle for LMFP is 4.535 Å² which is higher than LiFePO_4 (4.153 Å²) as a result of substituted Mn into iron sites of FeO_6 octahedron [17].

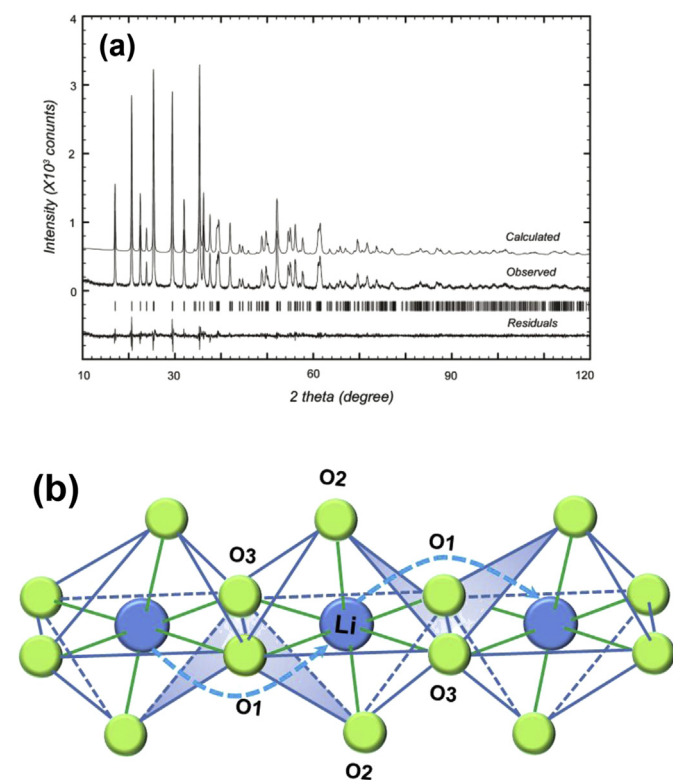


Fig. 1. (a) X-ray diffraction pattern and Rietveld refined result, and (b) schematic configuration on the LiO_6 octahedra of $\text{LiMn}_{0.6}\text{Fe}_{0.4}\text{PO}_4$.

Table 1
Selected interatomic distance (Å) and angle (°) of LiO_6 in $\text{LiMn}_{0.6}\text{Fe}_{0.4}\text{PO}_4$.

Bond		LMFP	
Li	Distances	(Li)—(O1) × 2	2.192(5)
		(Li)—(O2) × 2	2.092(3)
		(Li)—(O3) × 2	2.157(4)
Angles	(O1)—(Li)—(O2) × 2	88.1(3)	
	(O1)—(Li)—(O3) × 2	91.92(2)	
	(O2)—(Li)—(O3) × 2	84.3(3)	
	(O1)—(Li)—(O3) × 2	95.7(3)	
	(O2)—(Li)—(O3) × 2	70.9(3)	
(O2)—(Li)—(O3) × 2	109.1(3)		

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