



# Preparation of $\text{LiCoPO}_4$ and $\text{LiFePO}_4$ coated $\text{LiCoPO}_4$ materials with improved battery performance

I.C. Jang<sup>a</sup>, H.H. Lim<sup>a</sup>, S.B. Lee<sup>a</sup>, K. Karthikeyan<sup>a</sup>, V. Aravindan<sup>a</sup>, K.S. Kang<sup>b</sup>, W.S. Yoon<sup>c</sup>, W.I. Cho<sup>d</sup>, Y.S. Lee<sup>a,\*</sup>

<sup>a</sup> Faculty of Applied Chemical Engineering, Chonnam National University, Gwang-ju 500-757, Republic of Korea

<sup>b</sup> Department of Materials Science and Engineering, KAIST, Daejeon 305-701, Republic of Korea

<sup>c</sup> School of Advanced Materials Engineering, Kookmin University, Seoul 136-702, Republic of Korea

<sup>d</sup> Energy and Environment Division, Korea Institute of Science and Technology, Seoul 136-791, Republic of Korea

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## ABSTRACT

Olivine  $\text{LiCoPO}_4$  material has been successfully synthesized by solid-state reaction method without any carbon coating. The X-ray diffraction pattern shows that  $\text{LiCoPO}_4$  has a well developed orthorhombic structure with  $Pnma$  space group. The SEM analysis shows the particulate nature of the prepared materials with <200 nm size. The TEM analysis confirms that a 2–3 nm thick  $\text{LiFePO}_4$  layer is coated onto  $\text{LiCoPO}_4$ . The  $\text{LiFePO}_4$  coated  $\text{LiCoPO}_4$  cell delivers a high initial discharge capacity of  $132 \text{ mAhg}^{-1}$ , which is  $19 \text{ mAhg}^{-1}$  higher than the parent  $\text{LiCoPO}_4$ . Furthermore, the  $\text{LiFePO}_4$  coated  $\text{LiCoPO}_4$  cell exhibits an improved capacity retention compared to the original  $\text{LiCoPO}_4$  during cycling.

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## 1. Introduction

Since Padhi et al. demonstrated the electrochemical Li insertion/extraction behavior in  $\text{LiFePO}_4$  [1], transition metal phosphates with olivine structured  $\text{LiMPO}_4$  ( $M = \text{Fe, Mn, Co}$ ) compounds have attracted attention as a prospective cathode materials for lithium secondary batteries [2]. Although  $\text{LiFePO}_4$  is a promising candidate that has been extensively studied, several kinetics problems remain unsolved [3]. Moreover, the operating voltage is restricted to  $\sim 3.4 \text{ V}$  in the charge–discharge process [3]. First, Amine et al. [4] demonstrated the electrochemical activity of  $\text{LiCoPO}_4$  with an average voltage of  $4.8 \text{ V}$ , and offered a theoretical capacity of  $167 \text{ mAhg}^{-1}$ . However, the practical use of  $\text{LiCoPO}_4$  is doubtful for the following two reasons, poor compatibility with in conventional electrolyte solutions, which is associated with its inherent electronic conductivity. The oxidation of the  $\text{Co}^{2+}/3^{+}$  couple normally occurred in the range of  $4.8\text{--}5.1 \text{ V}$ , which exceeds the electrochemical stability of the conventional  $\text{LiPF}_6$  based electrolytes. As a result, less attention has been paid towards the development of  $5 \text{ V}$   $\text{LiCoPO}_4$  cathodes. Poor electronic conductivity is a common problem for olivine structured materials. This intrinsic behavior is easily circumvented through surface modification,

especially through carbon coating with  $\text{LiFePO}_4$ . Surface modification not only improves the conductivity, but also leads to a high rate performance in the cell with a negligible amount of capacity fading. In contrast to  $\text{LiFePO}_4$ , it is very difficult to modify  $\text{LiCoPO}_4$  with carbon, and carbon coating results in a poor cycling performance in the cell [5]. The electrochemical performance of  $\text{LiFePO}_4$  was significantly improved by creating Li deficient/rich phases and doping the Fe sites with various transition metal ions. A similar procedure was employed by Ping et al. [6] to investigate the  $\text{LiCoPO}_4$  system through *ab initio* calculations and the results suggested that the doping of Li sites hindered the one dimensional motion of  $\text{Li}^+$  ions, which decreases the  $\text{Li}^+$  ion diffusivity. Further, the substitution of various metal ions (isovalent and aliovalent) into Co sites, which also suppresses the operating voltage of the  $\text{LiCoPO}_4$  system.

In this study, the surface of olivine  $\text{LiCoPO}_4$  was modified with electro-active olivine  $\text{LiFePO}_4$  for the first time in order to improve the cycle retention rate of the  $\text{Li/LiCoPO}_4$  cell. Previously, a  $\text{LiFePO}_4$  coating was successfully employed by this group for  $\text{LiNi}_{0.5}\text{Co}_{0.2}\text{Mn}_{0.3}\text{O}_2$  [7] and by Wang et al. for  $\text{LiCoO}_2$  [8]. The effect of the  $\text{LiFePO}_4$  coating on the electrochemical behavior of  $\text{LiCoPO}_4$  is studied and discussed in the present paper.

## 2. Experimental

$\text{LiCoPO}_4$  was synthesized using a conventional solid-state method without carbon coating. Stoichiometric amounts of  $\text{LiOH}\cdot\text{H}_2\text{O}$  (Junsei, Japan),  $\text{Co}_3\text{O}_4$  (Aldrich, USA) and  $(\text{NH}_4)_2\text{HPO}_4$  (Aldrich, USA) were ground and calcined at  $400^\circ\text{C}$  for 10 h in

\* Corresponding author. Tel.: +82 62 530 1904; fax: +82 62 530 1909.  
E-mail address: [leey@chonnam.ac.kr](mailto:leey@chonnam.ac.kr) (Y.S. Lee).

air. The product was ground again and recalcined at 800 °C for 10 h to obtain a single  $\text{LiCoPO}_4$  phase. The surface of the sample was modified with  $\text{LiFePO}_4$  using a sol–gel route. Briefly, an appropriate amount of  $\text{LiCoPO}_4$  was poured into  $\text{LiFePO}_4$  sol, which was mixed with the starting materials (materials used for preparing  $\text{LiFePO}_4$  sol) and dispersed in ethanol. The intermediate product was dried at 90 °C for 6 h to obtain the gel precursor. This gel precursor was precalcined at 400 °C for 3 h to decompose the acetate moieties. After decomposition, the product was ground again and fired at 670 °C for 5 h under an Ar atmosphere for the  $\text{LiFePO}_4$  coating process. A powder X-ray diffractometer (XRD, Rint 1000, Rigaku, Japan) that was equipped with a  $\text{CuK}\alpha$  radiation source was used for the structural analysis. The surface morphological features were recorded using a field emission scanning electron microscope (FE-SEM, S-4700, Hitachi, Japan). The microstructures of the coated particles were examined using a transmission electron microscope (TEM, TECNAI, Philips, Netherlands). The cyclic voltammetry (CV) experiments were performed using a Solartron (1287, Ametek, UK) with a three electrode cell configuration. In the CV measurements, Li metal served as the counter and reference electrodes and the measurements were carried out in a voltage range between 3.0–5.2 V at a scanning rate of 0.02  $\text{mVs}^{-1}$ . The cycling performances were determined using a CR2032 coin-type cell between 3.5 and 5.2 V at room temperature. The detailed description of the cell assembly was provided in a previous publication [9]. The electrolyte that was used in this work was 1 M  $\text{LiPF}_6$  in an ethylene carbonate (EC)/dimethyl carbonate (DMC) (1:1, v/v, Techno Semichem Co., Ltd., Korea) mixture.

### 3. Results and discussion

The XRD patterns of the parent  $\text{LiCoPO}_4$  and  $\text{LiFePO}_4$  coated  $\text{LiCoPO}_4$  materials are shown in Fig. 1. The reflections in the XRD patterns were indexed according to the orthorhombic structure with a  $Pnma$  space group [10]. No obvious differences between the XRD patterns of the parent  $\text{LiCoPO}_4$  and  $\text{LiFePO}_4$  coated  $\text{LiCoPO}_4$  were observed because the coating amount of 10 wt.% was too small to detect. No impurity reflection patterns were observed in either case. The structure of  $\text{LiCoPO}_4$  is described by the hexagonal close-packing of oxygen with the Li and Co ions that are located at half of the octahedral sites and by the P atom that lays in one of the eight tetrahedral positions [4,10,11].

Fig. 2(a) and (b) show the scanning electron microscopy images of the parent  $\text{LiCoPO}_4$  and  $\text{LiFePO}_4$  coated  $\text{LiCoPO}_4$  materials. The

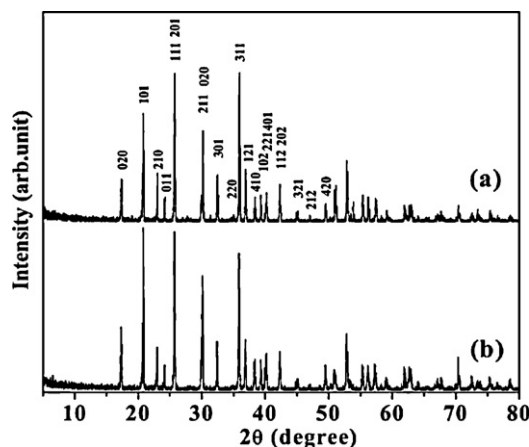


Fig. 1. X-ray diffraction patterns of (a)  $\text{LiCoPO}_4$  and (b)  $\text{LiFePO}_4$  coated  $\text{LiCoPO}_4$ .

particulate morphology of the parent  $\text{LiCoPO}_4$  had a small particle size of 100–150 nm and exhibited a uniform particle distribution (Fig. 2(a)). On the other hand, the  $\text{LiFePO}_4$  coated  $\text{LiCoPO}_4$  material contained agglomerated particulates, which occurred during the final calcination process of the  $\text{LiFePO}_4$  coating procedure in the sol–gel technique. During this calcination, the  $\text{LiFePO}_4$  layers were interconnected with each other and looked like aggregated particulates (Fig. 2(b)). Although the  $\text{LiFePO}_4$  coating was not clearly detected in the SEM image, the coating material was well distributed on all of the  $\text{LiCoPO}_4$  powder. The TEM studies were conducted in order to confirm the presence of the coating layer. The TEM images are provided in Fig. 2(c) and (d). In Fig. 2(d), a 2–3 nm thick  $\text{LiFePO}_4$  layer was observed on the single  $\text{LiCoPO}_4$  particle compared to parent  $\text{LiCoPO}_4$ . From these microscopic studies, the aggregations of small particles were probably caused by the weak interconnection between the  $\text{LiFePO}_4$  layers.

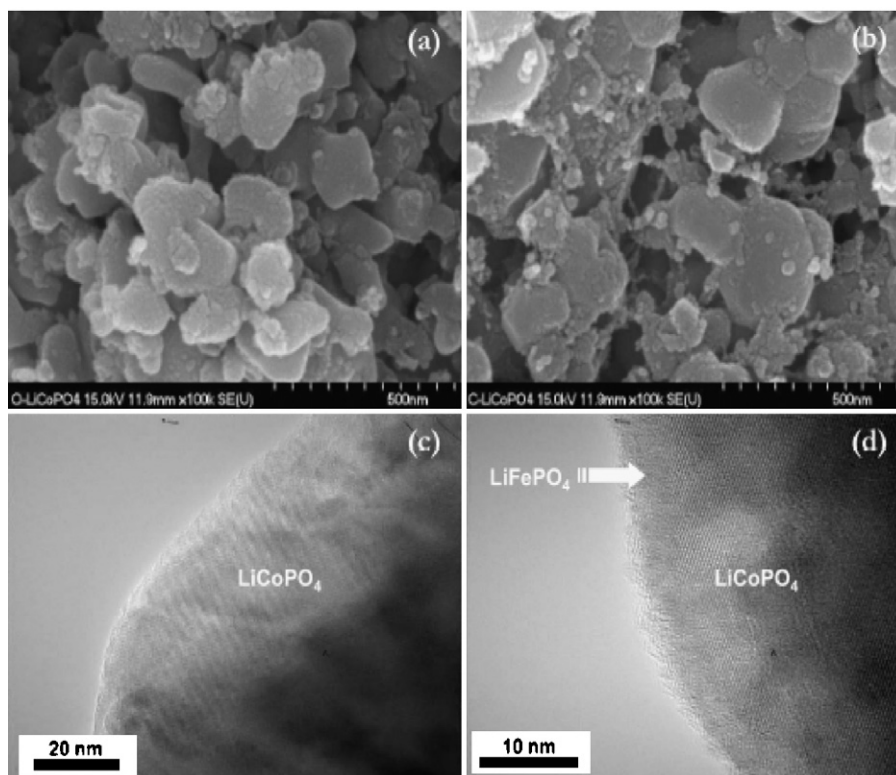
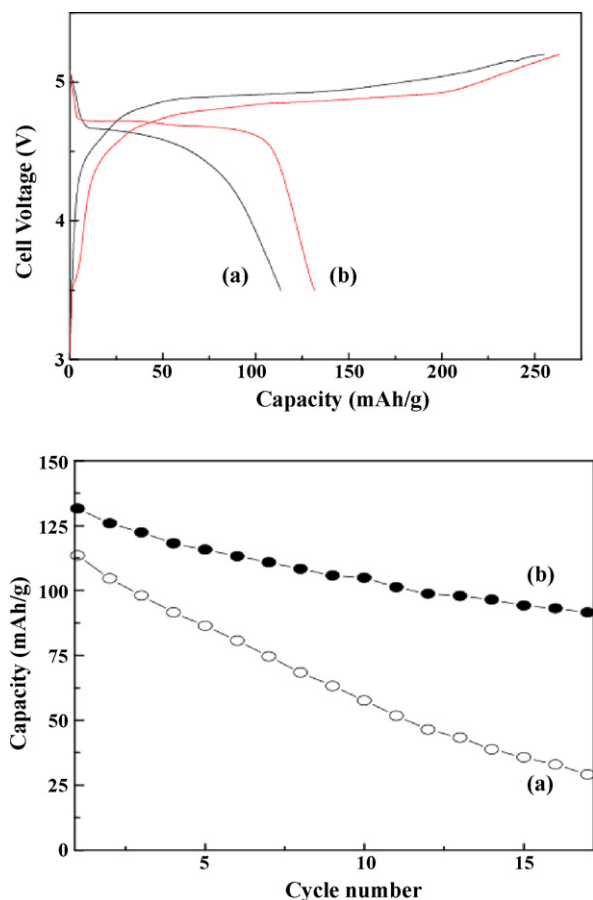
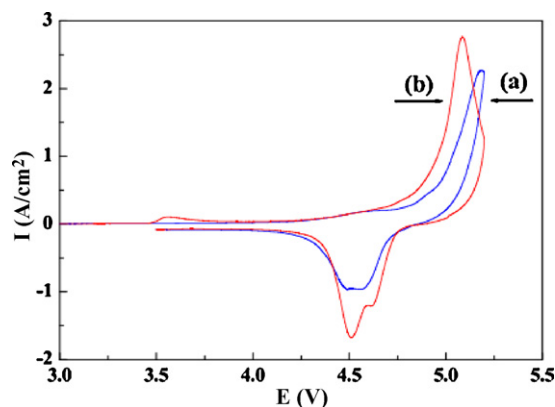


Fig. 2. SEM images of (a)  $\text{LiCoPO}_4$  and (b)  $\text{LiFePO}_4$  coated  $\text{LiCoPO}_4$ , and TEM pictures of (c)  $\text{LiCoPO}_4$  and (d)  $\text{LiFePO}_4$  coated  $\text{LiCoPO}_4$ .



**Fig. 3.** Initial charge–discharge curves and cycling profiles of (a) LiCoPO<sub>4</sub> and (b) LiFePO<sub>4</sub> coated LiCoPO<sub>4</sub>.

The charge–discharge studies were conducted between 3.5–5.2 V at room temperature for parent and LiFePO<sub>4</sub> coated LiCoPO<sub>4</sub> materials, and illustrated in Fig. 3. The Li/LiCoPO<sub>4</sub> and Li/LiFePO<sub>4</sub> coated LiCoPO<sub>4</sub> cells delivered initial discharge capacities of 113 and 132 mAhg<sup>−1</sup>, respectively. The Li/LiFePO<sub>4</sub> coated LiCoPO<sub>4</sub> cell not only offered a higher discharge capacity but also maintained a discharge plateau around 4.8 V, which was a typical electrochemical behavior of the Li/LiCoPO<sub>4</sub> cell with a long distinct voltage plateau in the first discharge process. Variations in the discharge plateau corresponded to the decomposition of the electrolyte used, which confirms the poor compatibility of LiCoPO<sub>4</sub> with electrolyte solution used in the present study [10]. A clear distinction was observed between the cycling profiles of the LiCoPO<sub>4</sub> and LiFePO<sub>4</sub> coated LiCoPO<sub>4</sub> materials. At the end of 17th cycle, discharge capacities of 29 and 92 mAhg<sup>−1</sup> were observed for the Li/LiCoPO<sub>4</sub> and Li/LiFePO<sub>4</sub> coated LiCoPO<sub>4</sub> cells, respectively. The improved capacity was attributed to the thin LiFePO<sub>4</sub> coating layer on the LiCoPO<sub>4</sub> surface. Until now, several inactive coating substances have been used to improve the electrochemical performance of cathode materials. These inactive particles often undergo an unwanted side reaction with the electrolyte counterparts, which leads to the formation of an inactive mass on the electrode surface [3,12]. Furthermore, the diffusion of Li<sup>+</sup> ions is hindered by this inactive mass during charge–discharge process, and as a result, capacity fading is observed [2,3,12]. On the other hand, the electro-active LiFePO<sub>4</sub> has an excellent compatibility with the conventional electrolyte system, and a strong P–O bond provides thermal safety at elevated operation temperatures for the cell [7,9]. The discharge capacity monotonously decreased with cycling in both cases. However, at the end of 17th cycle,



**Fig. 4.** Cyclic voltammograms of (a) LiCoPO<sub>4</sub> and (b) LiFePO<sub>4</sub> coated LiCoPO<sub>4</sub>, which were recorded with a scan rate of 0.05 mVs<sup>−1</sup>.

more than three times of the capacity was retained for LiFePO<sub>4</sub> coated LiCoPO<sub>4</sub> compared to the parent material. Therefore, the LiFePO<sub>4</sub> coating material played an important role in improving the cycle performance of the Li/LiFePO<sub>4</sub> coated LiCoPO<sub>4</sub> cell.

Fig. 4 shows the cyclic voltammograms (CV) in order to understand the kinetic properties of the LiFePO<sub>4</sub> coating material during the initial charge–discharge process. The voltammetric traces were recorded at a scan rate of 0.05 mVs<sup>−1</sup>, and lithium served as both the counter and reference electrodes. The parent and LiFePO<sub>4</sub> coated LiCoPO<sub>4</sub> materials exhibited typical voltammograms with different kinetic properties. Compared to LiFePO<sub>4</sub>, the asymmetry between the cathodic and anodic CV traces in the LiCoPO<sub>4</sub> material implied that the Li<sup>+</sup> ions diffused between the charge and discharge processes. Both materials exhibited a plateau at around 4.7–4.9 V corresponding to the Co<sup>3+</sup>/Co<sup>2+</sup> redox couple [13]. However, sluggish kinetic behavior was observed for the parent LiCoPO<sub>4</sub>, whereas LiFePO<sub>4</sub> coated LiCoPO<sub>4</sub> exhibited a well pronounced pattern that suggested enhanced kinetic properties. The presence of the shoulder like appearance at around 3.4 V during the cathodic sweep corresponded to one of the electrochemical characterizations of LiFePO<sub>4</sub> and confirmed the presence of the LiFePO<sub>4</sub> layer. Additionally, the appearance of the dual reduction peak corroborated the co-existence of the CoPO<sub>4</sub> phase during anodic sweep. However, the poor kinetic behavior of pure LiCoPO<sub>4</sub> hindered the separation of the CoPO<sub>4</sub> phase with a large interfacial resistance [14]. Upon cycling, the inactive CoPO<sub>4</sub> phase gradually grew and co-existed with the LiCoPO<sub>4</sub> phase, which led to a low cell performance [14]. From these results, the thin LiFePO<sub>4</sub> layer was strongly believed to hamper the formation of the inactive CoPO<sub>4</sub> phase along with the LiCoPO<sub>4</sub> phase during lithiation, improving the performance of the LiFePO<sub>4</sub> coated LiCoPO<sub>4</sub> cell over the parent LiCoPO<sub>4</sub>. Detailed structural investigations are currently underway in order to elucidate the exact mechanism of the initial cycles.

#### 4. Conclusion

LiCoPO<sub>4</sub> was successfully synthesized using a solid-state reaction method. LiFePO<sub>4</sub> was effectively coated onto the surface of LiCoPO<sub>4</sub> using a sol–gel process. The morphological study showed that the synthesized particles exhibited a particulate nature and the TEM pictures confirmed the existence of the thin LiFePO<sub>4</sub> layer. The Li/LiFePO<sub>4</sub> coated LiCoPO<sub>4</sub> cell delivered an initial discharge capacity of 132 mAhg<sup>−1</sup>, which was 19 mAhg<sup>−1</sup> higher than the parent LiCoPO<sub>4</sub>. The CV study provided information on the reversibility of the lithium ions during the initial charge–discharge cycles.

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