

Short communication

## Redox behavior and surface characterization of LiFePO<sub>4</sub> in lithium hydroxide electrolyte

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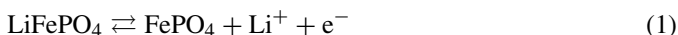
### Abstract

The redox behavior and surface characterization of LiFePO<sub>4</sub> in aqueous lithium hydroxide (LiOH) electrolyte have been investigated. The objective of this work is to investigate the electrochemical behavior of LiFePO<sub>4</sub> in an aqueous lithium hydroxide electrolyte and its comparison with that in non-aqueous lithium ion electrolytes. Cyclic voltammetry results show that LiFePO<sub>4</sub> undergoes partially reversible oxidation/reduction. The products formed on electrooxidation and subsequent reduction of LiFePO<sub>4</sub> were characterized by X-ray diffraction (XRD), X-ray photoelectron spectroscopy (XPS) and secondary ion mass spectrometry (SIMS). It is found that lithium extraction from LiFePO<sub>4</sub> occurs during oxidation. The products formed on subsequent reduction consist of LiFePO<sub>4</sub> and Fe<sub>3</sub>O<sub>4</sub>.  
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### 1. Introduction

Lithium iron phosphate (LiFePO<sub>4</sub>) with an ordered olivine structure has been proposed to be a potential candidate for use as a cathode in non-aqueous electrolyte lithium batteries [1–5]. It is not only cheaper but also less toxic and has higher energy density compared to other phosphate based olivine compounds e.g. LiCoPO<sub>4</sub>, LiNiPO<sub>4</sub> or LiMnPO<sub>4</sub>. The electrochemical behavior of LiFePO<sub>4</sub> in lithium non-aqueous lithium electrolytes is widely reported in the literature [1–5]. In this media, the electrochemical reaction of LiFePO<sub>4</sub> is generally represented as



Reversible Li<sup>+</sup> ion extraction/insertion (intercalation) occurs on oxidation/reduction of LiFePO<sub>4</sub>. We have carried out a study of the electrochemistry and its surface characterization of LiFePO<sub>4</sub> in aqueous lithium hydroxide electrolyte with metallic zinc as the counter electrode. In this paper, we report our investigation of the reduction/oxidation (redox) behavior of LiFePO<sub>4</sub> in an aqueous lithium hydroxide electrolyte and its comparison with

that in non-aqueous lithium ion electrolytes. This work follows on to our recent study of MnO<sub>2</sub> [6,7] where we reported that MnO<sub>2</sub> in aqueous lithium electrolytes behaved quite similar to MnO<sub>2</sub> in non-aqueous electrolytes. To the best of our knowledge there is no reported literature on investigations of LiFePO<sub>4</sub> in aqueous systems.

### 2. Experimental

The material LiFePO<sub>4</sub> (5 wt.% carbon included) was received from University of Wollongong (UW). Analytical grade Zn foil (99.9%) from BDH Chemicals, reagent grade ZnSO<sub>4</sub>·7H<sub>2</sub>O from Ajax Chemicals and reagent grade LiOH·H<sub>2</sub>O from Sigma Chemicals Company were used as received.

For the cyclic voltammetric studies a standard three-electrode system [6,7] was used. The LiFePO<sub>4</sub> working electrode was made by pressing LiFePO<sub>4</sub> powder onto a disc of Pt gauze. On the other side of the disc, a layer of carbon was also pressed. The disc was inserted into a Teflon barrel. Another Pt disc was inserted into the barrel on top of the carbon side and electrical contact was made by means of a stainless steel plunger. The LiFePO<sub>4</sub> was exposed to the electrolyte through a hole in the Teflon barrel as reported in our previous publications [6,7]. The counter electrode was a zinc foil, which was separated from the

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main electrolyte by means of a porous frit. A saturated calomel electrode (SCE) served as the reference electrode. The recorded values are reported as such. The electrolyte was a saturated aqueous solution of lithium hydroxide. The working electrode was cycled between  $-0.65$  and  $0.1$  V, each time starting at  $-0.65$  V, going initially in the anodic direction.

An EG&G PAR Potentiostat/Galvanostat model 273A, operated by model 270 software (EG&G) was used to scan the potential at  $25 \mu\text{V s}^{-1}$  in all experiments. All electrochemical measurements were carried out at ambient room atmosphere ( $25 \pm 1^\circ\text{C}$ ). The products formed during the oxidation/reduction were characterized by a Siemens X-ray diffractometer using Philips Co  $K\alpha$  radiation. X-ray photoelectron spectroscopy (Kratos Ultra Axis Spectrometer) using monochromatic Al  $K\alpha$  ( $1486.6 \text{ eV}$ ) radiation was used to analyze the chemical binding energy of the samples. The XPS analysis was started when the pressure in the analysis chamber fell below  $1 \times 10^{-9}$  hPa. Carbon, C (1s), was used as a reference for all the samples. Secondary ion mass spectrometry (SIMS) spectra were collected on a Cameca ims 5f instrument at the Australian Nuclear Science and Technology Organization (ANSTO), Lucas Heights, Sydney. An  $\text{O}_2^+$  primary ion source ( $12.5 \text{ kV}$ ) was used to generate secondary ions. A primary beam of  $50 \text{ nA}$  was rastered over an area of  $250 \mu\text{m} \times 250 \mu\text{m}$  in all experiments. The SIMS negative ion signals corresponding to  $^7\text{Li}$  and  $^{56}\text{Fe}$  were recorded. An energy offset of  $-350 \text{ V}$  was used to suppress molecular interferences on the peaks of interest.

### 3. Results and discussion

The X-ray diffraction spectra of the  $\text{LiFePO}_4$  material is shown in Fig. 1. The spectra is similar to that reported by Bewlay et al. [8]. This confirms that the material was crystalline of orthorhombic structure.

Fig. 2 shows a typical cyclic voltammogram (CV) of  $\text{LiFePO}_4$ . The scan was initiated at  $-630 \text{ mV}$  going in the anodic direction to  $+100 \text{ mV}$  and then reversing the scan back

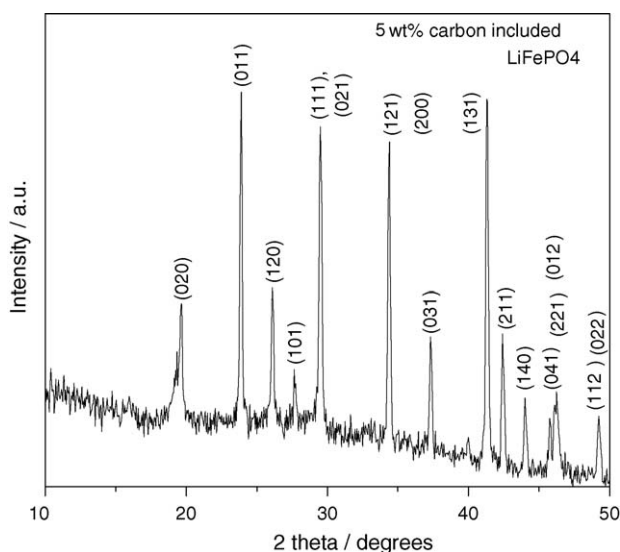


Fig. 1. X-ray diffraction spectra of the  $\text{LiFePO}_4$ .

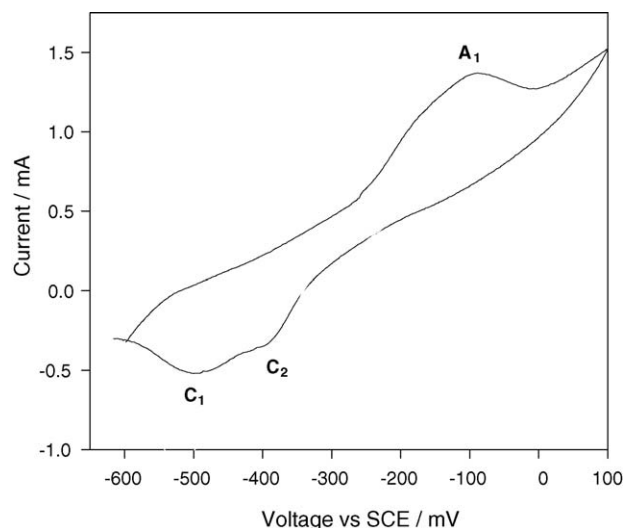


Fig. 2. Cyclic voltammogram of  $\text{LiFePO}_4$  in lithium hydroxide aqueous solution.

to the starting potential. As can be seen, an oxidation peak  $A_1$  at  $-42 \text{ mV}$  occurs during the anodic going portion of the CV. Two cathodic peaks  $C_1$  ( $-490 \text{ mV}$ ) and  $C_2$  ( $-370 \text{ mV}$ ) are observed during the reverse scan. Two observations can be made from Fig. 2:

- The material undergoes oxidation at  $-42 \text{ mV}$ .
- Two separate reduction processes occurs during the reverse cathodic scan.

In another experiment (not shown here) the scan was initiated in the same way as before but was held constant for 30 and 60 min at the anodic limit ( $-42 \text{ mV}$ ) before reversing the scan. It was found that the peak heights of both  $C_1$  and  $C_2$  increased with the length of time for which the electrode was held at  $-42 \text{ mV}$ . This confirms the cathodic peak ( $C_1$  and  $C_2$ ) corresponded to the oxidation reaction occurring at  $-42 \text{ mV}$ . The cathode material utilization of  $\text{LiFePO}_4$  in aqueous solutions with zinc metal as the anode was found to be 41% ( $70 \text{ mA h g}^{-1}$ ) for the first cycle with a voltage profile of  $0.8 \text{ V}$  [9]. The utilization dropped to 30% ( $50 \text{ mA h g}^{-1}$ ) and 20% ( $40 \text{ mA h g}^{-1}$ ) for the second and fifth cycles, respectively.

X-ray diffraction spectra of the starting material  $\text{LiFePO}_4$  before oxidation and those of the product formed on its electrooxidation together with that of the material formed on subsequent electroreduction are shown in Fig. 3. The X-ray diffraction pattern of  $\text{LiFePO}_4$  before oxidation (Fig. 3a) consists of peaks at  $2\theta = 35.3^\circ, 38.19^\circ, 42.16^\circ, 43.25^\circ, 44.87^\circ$  and  $47.05^\circ$ . This data matches that reported in the literature for  $\text{LiFePO}_4$  [1,8]. The spectra of the material formed on its electrooxidation (Fig. 3b) consists of peaks at  $2\theta = 35.52^\circ, 38.47^\circ, 42.45^\circ, 43.57^\circ, 45.16^\circ$  and  $47.41^\circ$ . This data matches that of  $\text{FePO}_4$  reported in the literature [1]. These results indicate that  $\text{FePO}_4$  is formed on oxidation of  $\text{LiFePO}_4$ . Thus the oxidation of  $\text{LiFePO}_4$  in aqueous  $\text{LiOH}$  involves de-intercalation of  $\text{Li}^+$  and hence the mechanism resembles that in non-aqueous solvents reported by Padhi et al. [1].

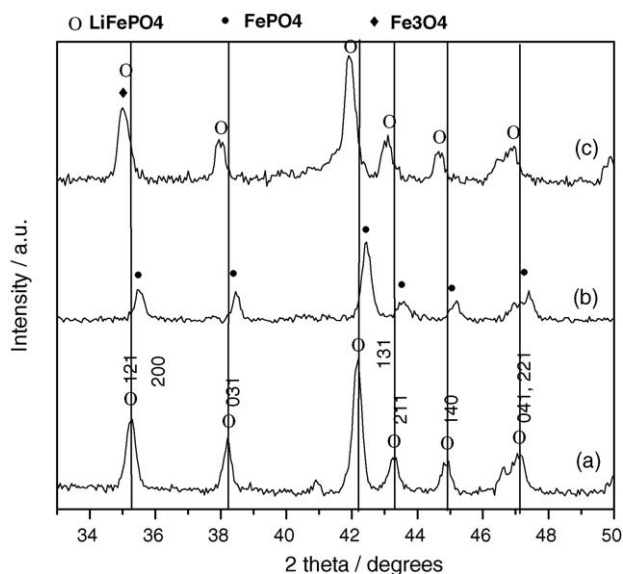


Fig. 3. XRD patterns showing the changes occurring during the redox process in aqueous solutions (a) before electrochemical treatment, (b) after oxidation and (c) reduction.

The spectra of the material formed on subsequent reduction of the oxidized product (Fig. 3c) consists of peaks at  $2\theta = 35.02^\circ$ ,  $37.95^\circ$ ,  $41.93^\circ$ ,  $43.10^\circ$ ,  $44.65^\circ$  and  $46.95^\circ$ . This data is again similar to that reported by Padhi et al. in non-aqueous media, who related this to the reversibility of lithium extraction and insertion process. Thus, LiFePO<sub>4</sub> in aqueous LiOH media behaves almost identical to that in non-aqueous media. A careful examination of Fig. 3c indicates that there is evidence of the presence of peaks e.g.  $2\theta = 35.02^\circ$ , which could be assigned to Fe<sub>3</sub>O<sub>4</sub>. Thus, the oxidation of LiFePO<sub>4</sub> to FePO<sub>4</sub> is not fully reversible. Subsequent reduction of the oxidation product of LiFePO<sub>4</sub> produces a mixture of LiFePO<sub>4</sub> and Fe<sub>3</sub>O<sub>4</sub>.

Fig. 4 shows the X-ray photoelectron spectra of the Li (1s) region of LiFePO<sub>4</sub> before and after oxidation. For the sample before the oxidation (Fig. 4a) a peak at 55.3 eV corresponding to Li (1s) with a high intensity is seen. The peak at 55.3 eV

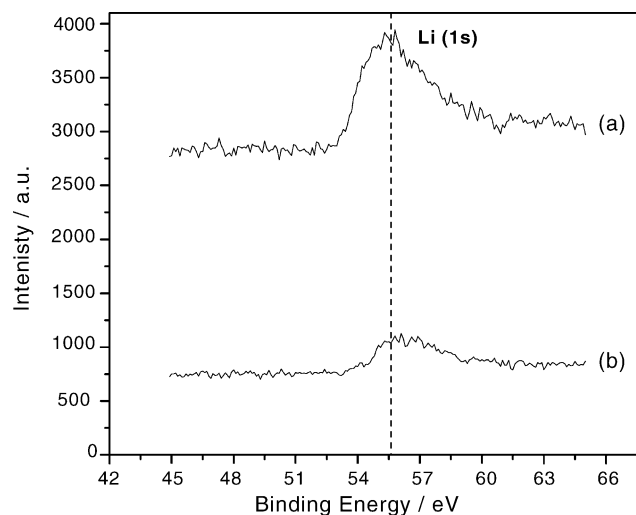


Fig. 4. XPS spectra of Li (1s) of LiFePO<sub>4</sub> (a) before and (b) after oxidation.

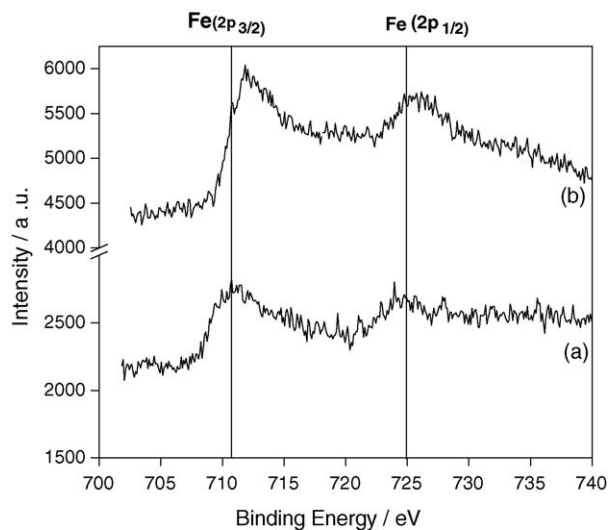


Fig. 5. XPS spectra of Fe (2p) of LiFePO<sub>4</sub> (a) before and (b) after oxidation.

for the oxidized sample (Fig. 4b) appears as a shoulder with much reduced intensity. This confirms that Li<sup>+</sup> is extracted from LiFePO<sub>4</sub> during oxidation. Fig. 5 shows the XPS spectra of the Fe (2p) region of LiFePO<sub>4</sub> before and after oxidation. The Fe 2p with spin-orbit splitting component of 2p<sub>1/2</sub> at 710.6 eV and 2p<sub>3/2</sub> at 724 eV can be seen in the figure. After oxidation a chemical shift of 1.2 eV for Fe 2p<sub>1/2</sub> is observed even though the 2p<sub>3/2</sub> does not show any shift. The chemical shift towards higher binding energy can be attributed to the oxidation of Fe(II) to Fe(III) [10].

Further confirmation of extraction/insertion processes of Li<sup>+</sup> during oxidation/reduction of LiFePO<sub>4</sub> comes from the data shown in Fig. 6. This figure shows changes in the Li/Fe ratio as obtained by secondary ion mass spectroscopic analysis of the products formed on oxidation/reduction of LiFePO<sub>4</sub>. The data clearly shows that Li/Fe ratio decreases during oxidation and then increases slightly during the reverse process. Based upon the results discussed it can be concluded that LiFePO<sub>4</sub> undergoes partially reversible oxidation/reduction via lithium extraction/insertion (intercalation) mechanism in a manner similar to that reported for LiFePO<sub>4</sub> in non-aqueous media.

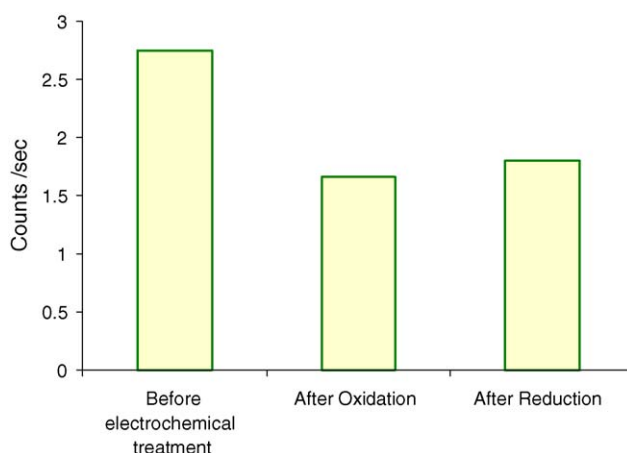


Fig. 6. SIMS isotopic mass ratio of LiFePO<sub>4</sub>.

#### 4. Conclusions

The electrochemical oxidation of  $\text{LiFePO}_4$  in a saturated aqueous lithium hydroxide ( $\text{LiOH}$ ) electrolyte occurs via lithium extraction mechanism forming  $\text{FePO}_4$  similar to that known for non-aqueous media. The reverse reduction of  $\text{FePO}_4$  however is not fully reversible as it forms a mixture of  $\text{LiFePO}_4$  and  $\text{Fe}_3\text{O}_4$ . In this regard,  $\text{LiFePO}_4$  behaved slightly different from  $\text{MnO}_2$  and  $\text{TiO}_2$  for which we previously reported to undergo reversible lithium intercalation during reduction/oxidation in aqueous  $\text{LiOH}$  electrolyte. However, if the characterization of the material and the cycling efficiency could be improved then  $\text{LiFePO}_4$  can be used as a cathode in a 1 V battery using lithium hydroxide as the electrolyte. The conclusions are confirmed by X-ray diffraction (XRD), X-ray photoelectron spectroscopy (XPS) and secondary ion mass spectrometry (SIMS).

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