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Electrochemical delithiation of LiMnPO₄ in aqueous battery system

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Abstract
The electrochemical behavior of lithium manganese phosphate (LiMnPO₄) as a cathode material has been investigated in a saturated aqueous lithium hydroxide electrolyte. The crystal structure and surface characterization of the olivine type LiMnPO₄ and the products which are formed on its oxidation and subsequent reduction were studied. X-ray diffraction (XRD), X-ray photoelectron spectroscopy (XPS), Scanning electron microscopy (SEM) and Secondary ion mass spectrometry (SIMS) were used for these investigations. LiMnPO₄ is found to be reversibly delithiated on electro oxidation.

Keywords: Aqueous battery, Delithiation, Olivine, Phosphate, Lithium manganese phosphate.

Introduction
Among the known Li extraction/insertion (delithiation/lithiation) compounds, the layered oxides LiCoO₂, LiNiO₂ and the spinel LiMn₂O₄ are now commercially used as cathode materials in rechargeable lithium batteries [1-3]. However, these materials suffer from poor electrochemical stability in their highly oxidized state [4]. In the case of LiMn₂O₄, the reduction of manganese below Mn⁴⁺ leads to a Jahn-Teller distortion. The major problem hindering the development of LiMnPO₄ as a cathode material is the loss of capacity with extensive cycling [5]. Phosphate-based electrode materials, especially the phospho-olivines LiMPO₄ (where M = Fe, Mn, Co and Ni) are now recognized as attractive alternatives to oxide materials [6-9]. The presence of PO₄³⁻ polyanion with a strong P-O covalent bond in the olivine type structure provides a stable system when the electrode is charged. Since the pioneering study on LiFePO₄ by Padhi et al [7], significant work has been reported on the substitution of Fe with Mn, Co and Ni and their suitability as cathode materials in lithium batteries. LiMnPO₄ is an attractive cathode material owing to its high potential for use in batteries. Its electrochemical behavior in non-aqueous solvents has been reported in the literature [10-12].

In one of our previous paper [13], we reported a systematic study of the electrochemistry of LiFePO₄ in aqueous lithium hydroxide electrolyte. The objective was to establish how this material behaved as a cathode material in aqueous media in comparison to that in non-aqueous electrolytes. In this paper, we explore the electrochemical behavior of LiMnPO₄ for use in aqueous batteries.

Experimental
The material LiMnPO₄ (10 wt% carbon included) was received from Tokyo Institute of Technology and its cathode properties are reported elsewhere [14]. Analytical grade Zn foil (99.9%) from BDH chemicals, reagent grade LiOH·H₂O from Sigma Chemicals Company was used as received.

The experimental procedures for the cyclic voltammetric studies were similar to those reported earlier [13]. A standard calomel electrode (SCE) was used as reference electrode and values are reported as such.

An EG&G PAR Potentiostat/Galvanostat model 273A, operated by model 270 software (EG&G) was used to scan the potential at 25 μV/s in all experiments. For X-ray analysis a Siemens X-ray diffractometer using Philips Co-Kα radiation was used. Kratos Ultra Axis Spectrometer using monochromatic Al Kα (1486.6 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 x 10⁻⁹ hPa. The surface analysis of the materials was conducted by using a scanning electron microscope (Philips Analytical XL series 20). 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 O₂⁺ primary ion source (12.5 KV) was used to generate secondary ions. A primary beam of 50 nA rastered over an area of 250 x 250μm was used in all experiments. The SIMS positive ion signals corresponding to ³³Li was recorded.

Results and Discussion
Figure 1 shows the XRD profile of LiMnPO₄. The data matched with single-phase orthorhombic (olivine structure) as reported in the literature [7-8]. Its redox behavior can be seen from the cyclic voltammogram in the potential region - 0.65 to 0 V in Fig. 2. The scan was initiated at -630 mV going first in the anodic direction to +100 mV and then reversing it back to the starting potential. An oxidation peak A₁ occurs at 65 mV in the anodic going portion of the CV. A cathodic peak C₁ is observed during the reverse scan at -480 mV. Thus the material undergoes electro oxidation/reduction presumably involving change of the oxidation state of the Mn atom in LiMnPO₄. The large gap
between the oxidation and reduction potentials seems to suggest that the process is not totally reversible in aqueous solutions.

![Figure 1](image1.png)

**Fig. 1** X-ray diffraction spectrum of the starting material LiMnPO$_4$

![Figure 2](image2.png)

**Fig. 2** A typical cyclic voltammogram of LiMnPO$_4$

With the objective of identifying the products formed on electro oxidation and reverse reduction, the following experiment was done. The material was subjected to electro oxidation in a three cell configuration under galvanostatic conditions (0.25 mA/cm$^2$). The products formed were examined by XRD, SEM, XPS and SIMS. The electro oxidized material was then subjected to reverse reduction galvanostatically at the same current density. The resulting material was also analysed by using the same techniques as noted above.

X-ray diffraction spectra of the starting material LiMnPO$_4$ before oxidation and that after its electro oxidation are shown in Fig. 3. As can be seen from the figure 3, the XRD spectrum of the oxidized material differs significantly from that of the starting material. New reflections at 2\(\theta = 22.5^\circ, 35.0^\circ\) and 42.0\(^\circ\) are seen. These peaks are assigned to

![Figure 3](image3.png)

**Fig. 3** X-ray diffraction spectra of LiMnPO$_4$ (a) before and (b) after electro oxidation.

![Figure 4](image4.png)

**Fig. 4** SEM micrographs of LiMnPO$_4$ (a) before and (b) after electro oxidation.

22.5\(^\circ\), 35.0\(^\circ\) and 42.0\(^\circ\) are seen. These peaks are assigned to
MnPO₄ in accordance with the values quoted in the ICDD card No: 70-0180. The XRD pattern of the product formed on electro oxidation of LiMnPO₄ is indicative of the lower crystallinity of the product which in this case is delithiated MnPO₄. This is also reflected in the Scanning electron micrograph (SEM) of this material as shown in Fig. 4. The product has very different morphology compared to the material before the oxidation (Fig. 4). Fig. 5 shows the XRD patterns of the material formed on reverse reduction of the MnPO₄ formed previously by electro oxidation of LiMnPO₄. The XRD pattern of this material now matches that of the original raw material which had not been subjected to any electrochemical treatment. This suggests that the electro oxidation of LiMnPO₄ is reversible i.e. oxidation of LiMnPO₄ forms MnPO₄ which on subsequent reduction reverts back to LiMnPO₄. Thus the oxidation of LiMnPO₄ in aqueous LiOH involves delithiation which is similar to that in non-aqueous solvents reported by Masquelier et al [10] and Li et al [12].

Figure 6 shows the XPS spectra of the Li (1s) and Mn (3s) region for the LiMnPO₄ material (a) before electrochemical treatment, (b) after electro oxidation and (c) after electrochemical reduction of the material following to the electro oxidation. The peaks at 48.7 eV and 56.4 eV correspond to the Mn 3s and Li 1s [15]. As can be seen from the figure 6, the peak at 48.7 eV corresponding to Mn (3s) is present in all the three samples. Whereas, the peak at 56.4 eV corresponding to Li (1s) is present in sample (a) and (c) but not for sample (b). This confirms that on electro oxidation, Li⁺ is removed from LiMnPO₄ and is re-inserted into MnPO₄ after the material has been reduced back. This result provides further evidence to reversible delithiation of LiMnPO₄ on oxidation.

Further confirmation of delithiation/lithiation of Li⁺ during oxidation/reduction of LiMnPO₄ is obtained from the secondary ion mass spectrometry (SIMS) analysis. The figure 7 shows changes in the Li⁺ ion count as obtained by SIMS analysis of the products formed on oxidation of LiMnPO₄ and its reverse reduction. The data shows that during oxidation the Li⁺ count is decreased and then increases on reverse reduction. This supports the delithiation mechanism for oxidation/reduction of LiMnPO₄.

Based upon, the results discussed above it can be concluded that the electrochemical oxidation of LiMnPO₄
leads to the phase MnPO₄ and on subsequent reduction reverts back to LiMnPO₄.

Conclusion

The preliminary electrochemical investigation of LiMnPO₄ in aqueous LiOH shows that delithiated MnPO₄ is formed when LiMnPO₄ is electro oxidized. This process is reversible. This is confirmed by the analysis of the products formed on electro oxidation / reduction of LiMnPO₄ by using XRD, SEM, XPS and SIMS.

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References
