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PROGRESS REPORT FOR AINGRA07134P

PROJECT TITLE	Investigating the electrochemical behaviour of lithium manganese phosphate (LiMnPO₄) as a cathode material in aqueous solutions	
INVESTIGATOR(S)	Institution and Department	
Chief Investigator	Dr Pritam Singh	Chemistry, Murdoch University
Other Investigators	Dr John Hanna (ANSTO) Will contact John to get his agreement for collaboration. Dr. Touma Issa (Murdoch University)	
Students	Manickam Minakshi (Murdoch University)	
ANSTO Investigators	Kathryn Prince	
Specialist Committee	M	

SCIENTIFIC OBJECTIVES

The main objective of this project was to investigate any presence of lithium ions in the solid matrix of olivine-type lithium manganese phosphate (LiMnPO₄) cathode material and changes in its crystal structure while electro oxidizing / reducing 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 the key issues of study of this project. To achieve this, we have used X-ray diffraction (XRD) and Secondary ion mass spectrometry (SIMS) at ANSTO. The current work also suggests that LiMnPO₄ could be a potential candidate for a rechargeable aqueous electrolyte battery.

PROGRESS REPORT and RESEARCH OUTCOMES

We have collected some useful data from SIMS analysis at ANSTO. The confirmation of delithiation/lithiation of Li⁺ during oxidation/reduction of LiMnPO₄ cathode was obtained from the secondary ion mass spectrometry (SIMS) analysis. The figure 1 shows changes in the Li⁺ ion counts within ± 2 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 reveals the delithiation/lithiation mechanism is possible for oxidation/reduction of LiMnPO₄.

In order to study any changes in the LiMnPO₄ crystal structure and to confirm the lithium intercalation, x-ray analysis was performed on the oxidised/reduced samples. The diffraction spectra of the starting material LiMnPO₄ before oxidation and that after its electro oxidation are shown in Fig. 2 a and b. As can be seen in figure 2 b, the XRD spectrum of the oxidized material differs significantly from that of the starting material. New reflections at $2\theta = 25.1^\circ, 30.6^\circ, 35.3^\circ$ and 42.2° are seen. These peaks are in good agreement with those reported for the mineral (ICDD card No: 70-0180) of formula MnPO₄. 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 indicates that the phase observed at the end of electrochemical oxidation of LiMnPO₄ is MnPO₄, suggesting lithium is extracted in the process. Fig. 2 c shows the XRD pattern 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. The XRD results support the conclusion of the SIMS analysis (Fig. 1) performed on the same samples. This suggests that the electro oxidation of LiMnPO₄ is reversible via a lithium intercalation i.e. oxidation of LiMnPO₄ forms MnPO₄ which on subsequent reduction reverts back to LiMnPO₄.

Thus the electro oxidation/reduction of LiMnPO₄ in aqueous LiOH involves delithiation/lithiation and its mechanism is similar to that in non-aqueous solvents as reported by Delacourt et al [1] and Li et al [2].

The cathode material utilization versus the cycle number of this material is shown in Fig. 3. This suggests that this cathode material is rechargeable. However, the percentage of the material utilization during discharge process dropped from 44 to 32 % for the first cycle after which it stabilized. Thus this material has potential for being used as a cathode material in aqueous battery systems containing LiOH electrolyte.

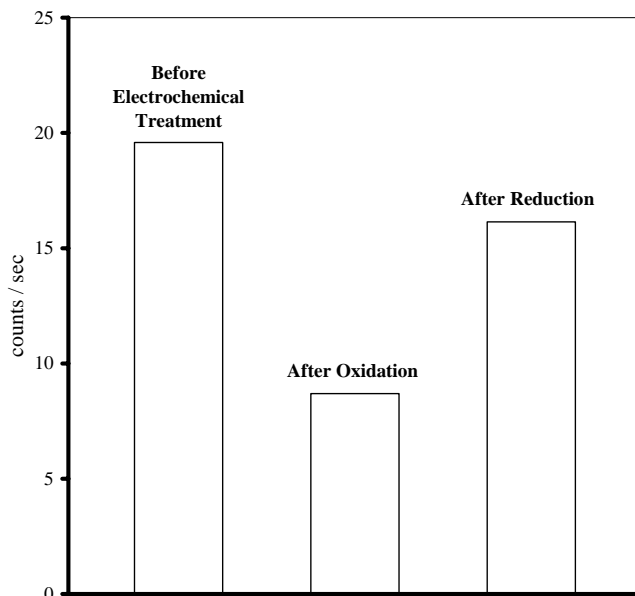


Fig. 1 SIMS Li ion counts of LiMnPO₄. Error bars represent the standard error

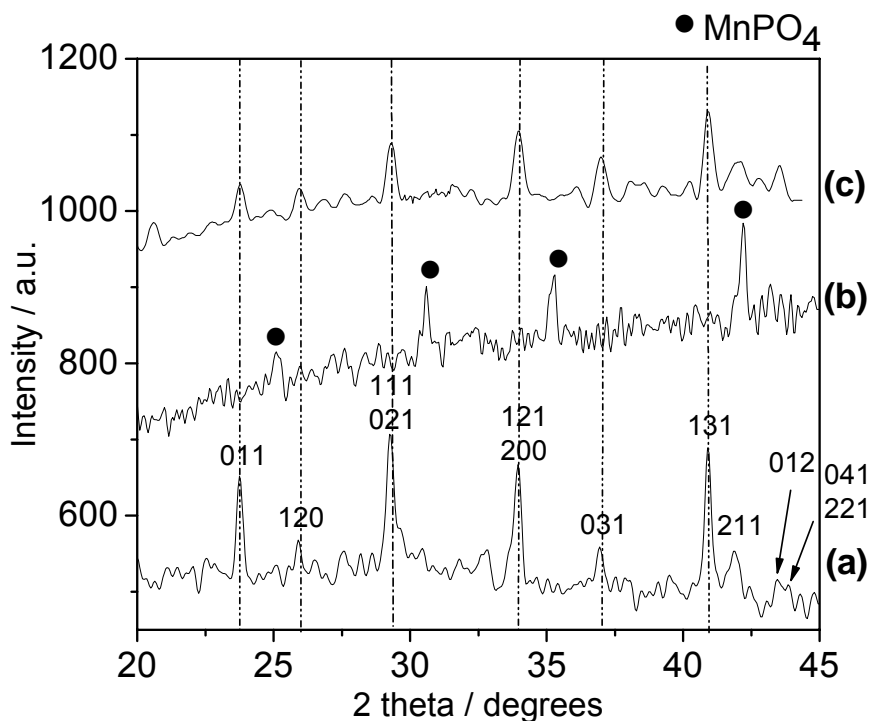


Fig. 2 X-ray diffraction spectra of LiMnPO₄ (a) before electro oxidation (b) after electro oxidation and (c) after reverse electro reduction.

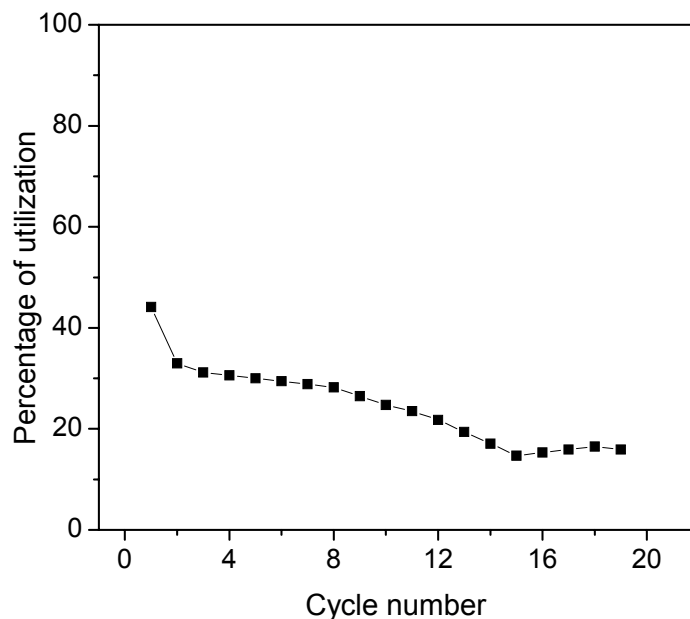


Fig. 3 The cathode material (LiMnPO_4) utilization in $\text{Zn}|\text{LiMnPO}_4|$ aqueous LiOH , ZnSO_4 battery versus cycle number.

References

[1] C. Delacourt, P. Poizot, M. Morcrette, J. M. Tarascon and C. Masquelier, *Chem. Mater.*, **16** (2004) 93.
 [2] G. Li, H. Azuma and M. Tohda, *Electrochem. Solid-State Lett.*, **5**, 135 (2002).

DATA

We have collected data from the SIMS, TEM and XRD techniques. The SIMS and XRD data are included in this report. TEM data had been used in one of our publication [2] quoted here.

Signature of Investigator preparing the report for After signing this report please fax this page with your signature for our files	Proj: AINGRA07134P Date:

PUBLICATIONS / REPORTS arising as a result of your work.

1. Manickam Minakshi, Pritam Singh, Stephen Thurgate and Kathryn Prince, "Electrochemical behavior of Phospho-olivine LiMnPO_4 in aqueous battery system" *Electrochem. Solid State Lett.*, **9 (10)** (2006) A 471.
 2. Manickam Minakshi, Pritam Singh, David R.G. Mitchell, Touma B. Issa and Kathryn Prince "A study of lithium insertion into MnO_2 containing TiS_2 additive a battery material in aqueous LiOH solution", *Electrochim. Acta*, **52 (24)** (2007) 7007.

PhD STUDENTS

Manickam Minakshi has finished his PhD