

Olivine-structured Mg_xFePO_4 : Cathode material for Mg-ion batteries

Rajeev Ranjan, Daniel Buttry Ph.D

Department of Chemistry and Biochemistry
Arizona State University

PO Box 871604, Tempe, AZ 85287-1604

rranjan3@asu.edu, Daniel.Buttry@asu.edu

Magnesium ion batteries:

Our work focus on evaluating olivine structured FePO_4 as a cathode material for magnesium ion batteries. Chevrel phases¹ and various oxides² have been studied before and suffer from low capacity. LiFePO_4 is considered as a potential candidate for cathode material³ due to its comparable intercalation voltage, high theoretical capacity (170 mAhg^{-1}), thermal stability, low cost, reduced toxicity and high abundance. In this work, we synthesized a new material, Mg_xFePO_4 , to be used as an intercalation material for rechargeable Mg-ion batteries. The synthesized particles were characterized using x-ray powder diffraction, energy dispersive x-ray spectroscopy and scanning electron microscopy.

Synthesis of LiFePO_4 , FePO_4 and Mg_xFePO_4 :

LiFePO_4 was synthesized following the procedure described by Gibot *et al.*⁴. Li was chemically de-intercalated from LiFePO_4 to obtain FePO_4 by the oxidation of LiFePO_4 using H_2O_2 . Magnesium was chemically intercalated into FePO_4 to obtain olivine structured Mg_xFePO_4 .

XRD pattern of LiFePO_4 and Mg_xFePO_4 :

All peaks in the XRD pattern of LiFePO_4 and Mg_xFePO_4 could be indexed on the basis of reported XRD pattern of lithium iron phosphate (LiFePO_4) reported in JCPDS # 98-000-0443 (Triphylite). In Fig. 1, we have compared the XRD pattern of LiFePO_4 and Mg_xFePO_4 . All the peaks match and confirm the formation of Mg_xFePO_4 in olivine structure. Peaks are slightly shifted which may be due to magnesium insertion. Rietveld refinement of the XRD data were done to confirm the changes in the lattice parameter of the olivine with the magnesium intercalation.

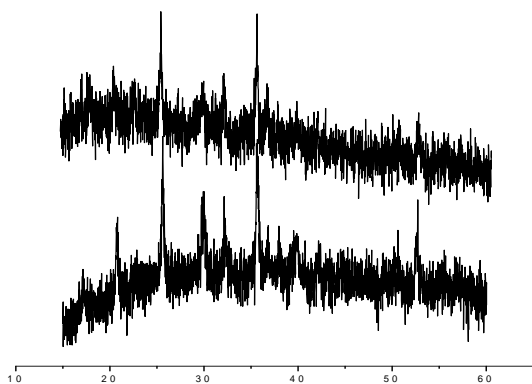


Figure. 1. XRD pattern of Mg_xFePO_4 (top) and LiFePO_4 (bottom)

SEM and EDX of Mg_xFePO_4 :

Mg_xFePO_4 particles of length $400 \pm 100 \text{ nm}$ and width of $200 \pm 50 \text{ nm}$ were found as seen by the SEM. Ratio of magnesium, iron and phosphorus atom in Mg_xFePO_4 is approximately 0.5:1:1 as confirmed by EDX.

Electrochemical study of Mg_xFePO_4 for magnesium ion intercalation/de-intercalation:

We studied the electrochemical behavior of Mg_xFePO_4 using cyclic voltammetry. Pellets having a composition of 70 % Mg_xFePO_4 , 20 % Carbon black and 10 % PVDF binder were pressed between the steel mesh and served as the working electrode. Pt and Ag/AgCl was used as a counter and reference electrode. We have preliminary results for the magnesium ion insertion as shown in Fig. 2. Reversible intercalation/de-intercalation has not been observed, may be due to slow kinetics and passivation of working electrode by the electrolyte. Further work on electrolyte composition and optimization of other variables are under progress.

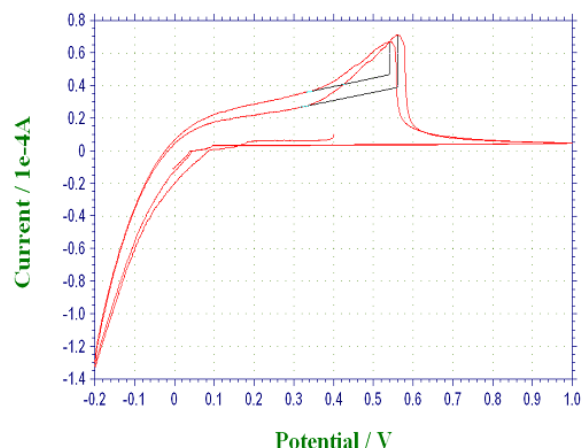


Figure 2: Cyclic voltammetry of Mg_xFePO_4

Acknowledgements: This work was supported by the Department of Energy ARPA – e program.

References:

1. Mitelman, A.; Levi, M. D.; Lancry, E.; Levi, E.; Aurbach, D. *Chem. Commun.*, 2007, 4212–4214
2. Novak, P.; Imhof, R.; Haas, O. *Electrochimica Acta.*, 1999, 45, 351–367
3. Tarascon, J. M.; Armand, M. *Nature* **2001**, 414, 359–367.
4. Gibot, P.; Casas-Cabanas, M.; Laffont, L.; Levasseur, S.; Carlach, P.; Hamelet, S.; Tarascon, J. M.; Masquelier, C. *Nature Materials* **2008**, 7, 741–747.