

Application of Polyanion Compounds for Magnesium Battery Cathode

Yuki Oriksa¹, Kentaro Yamamoto¹, Titus Masese¹,
Takuya Mori¹, Zhen-Dong Huang¹, Taketoshi Minato²,
Yoshiharu Uchimoto¹

¹Graduate School of Human and Environmental Studies,
Kyoto University, Sakyo-ku, Kyoto 606-8501, Japan
²Office of Society-Academia Collaboration for Innovation,
Kyoto University, Gokasho, Uji, Kyoto 611-0011, Japan

Magnesium battery is one of candidates for next generation battery system.¹ The advantage of Magnesium battery is the theoretical high energy density, low cost and stability.^{2,3} The magnesium battery suffers from low cell voltage, low capacity and low diffusivity of magnesium. One of the problems for the practical application is cathode material. Compared to lithium ions, magnesium ions insertion reaction into the host compounds has more difficulty due to stronger ionic interaction and harder redistribution of the charge of the inserted multivalent cations in host materials⁴. Therefore, the compounds which can serve as magnesium hosts are limited. In order to design the host materials for magnesium battery, it's very important to understand the difference between the insertion/extraction reaction mechanism of magnesium and that of lithium. Polyanion compounds, e.g. LiFePO₄, show high stability and relatively high power density.^{5,6} Therefore polyanion compounds are one of candidate materials for magnesium ion battery cathode. In this study, we investigate electrochemical magnesium insertion and extraction of polyanion compounds such as FePO₄. And then the mechanism of magnesium insertion and extraction with polyanion compounds is analyzed.

LiFePO₄/C was prepared with solid state reaction. The stoichiometric amount of Li₂CO₃, FeC₂O₄ · 2H₂O and (NH₄)₂HPO₄ were mixed by wet ball milling with ethanol for 12 hours at 400 rpm. The mixture was mixed with acetylene black 10 wt% to LiFePO₄ by dry ball milling for 24 hours at 400 rpm. The precursor was pelletized and calcined at 600 °C for 6 hours under 3% H₂ + 97% Ar atmosphere. FePO₄ was prepared by chemical oxidation of the obtained LiFePO₄/C using nitronium tetrafluoroborate (NO₂BF₄) as an oxidizing agent. NO₂BF₄ was dissolved in acetonitrile, and then LiFePO₄/C powder was stirred in the solution for 48 hours. The particle size of the prepared FePO₄/C was about 100 nm determined by SEM observation. As the cathode materials, several kinds of polyanion compounds were applied. Electrochemical measurements were carried out using a three-electrode cell. The electrolyte was magnesium trifluoromethanesulfonyl-imide (Mg(TFSI)₂) in organic solvent and/or ionic liquid. The electronic and structural change of these cathode materials were characterized with X-ray absorption spectroscopy (XAS) and X-ray diffraction (XRD) without air exposing.

Figure 1 shows discharge/charge profile of FePO₄ under 0.5 M Mg(TFSI)₂ in acetonitrile. The obtained discharge capacity (162 mAh/g) was comparable to the capacity for 1 lithium insertion to FePO₄, demonstrating that 0.5 magnesium was inserted to FePO₄. A flat plateau observed around -0.4 V (Ag⁺/Ag) indicates two-phase reaction like the case of lithium insertion. Fe K-edge

XANES spectrum for the sample after discharge indicated reduction of Fe in FePO₄ with magnesium insertion.

In charge process, the obtained capacity was 111 mAh/g which corresponds to 0.3 magnesium extraction. This result indicates that magnesium insertion/extraction reaction in FePO₄ is irreversible and that magnesium extraction is more difficult than insertion. In addition, the flat plateau like in discharge process was not observed, meaning that the mechanism of magnesium extraction is different from that of magnesium insertion.

We will show electrochemical properties of other polyanion compounds, and discuss the performance of magnesium batteries using polyanion compounds.

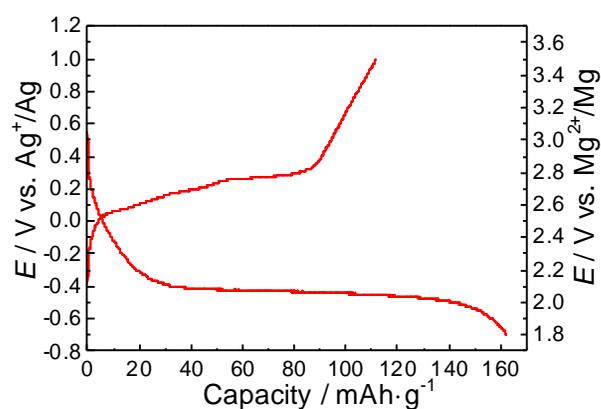


Fig. 1. Discharge/charge curves of FePO₄ at 1/50 C in 55 °C

Acknowledgments

This work was supported in part by Core Research for Evolutional Science and Technology (CREST) program of Japan Science and Technology Agency (JST) in Japan.

References

1. D. Aurbach, Z. Lu, A. Schechter, Y. Gofer, H. Gizbar, R. Turgeman, Y. Cohen, M. Moshkovich and E. Levi, *Nature*, **407**, 724 (2000).
2. P. Novak, R. Imhof and O. Haas, *Electrochim Acta*, **45**, 351 (1999).
3. J. O. Besenhard and M. Winter, *Chemphyschem*, **3**, 155 (2002).
4. E. Levi, M. D. Levi, O. Chasid and D. Aurbach, *J. Electroceram.*, **22**, 13 (2009).
5. B. Kang and G. Ceder, *Nature*, **458**, 190 (2009).
6. N. Meethong, Y. H. Kao, W. C. Carter and Y. M. Chiang, *Chem. Mater.*, **22**, 1088 (2010).