Electrochemical Properties of Heterosite FePO_4 in Aqueous Mg^{2+} Electrolytes

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ABSTRACT

There is currently much interest in advanced energy storage systems because of their potential relevance to power grid storage media. Both earth abundance and high energy density of divalent Mg^{2+} ion make Mg batteries attractive as alternatives to Li-ion batteries, but the number of host materials for reversible intercalation is very limited due to the strong coulombic interaction induced in solid matrix. In this work, we report the electrochemical properties of FePO_4 in aqueous Mg^{2+} electrolyte. The charge/discharge experiments showed that FePO_4 delivers the first discharge capacity of 90 mAh g^{-1} with subsequent partial reversibility. The ex-situ Mössbauer spectroscopy confirmed reversible redox of $\text{Fe}^{3+}/\text{Fe}^{2+}$ during the discharge and charge processes, while little change was observed in the ex-situ X-ray diffraction patterns. Activation energy for Mg^{2+} diffusion in FePO_4 lattice was calculated to over three times larger than that of Li^+ . It is postulated that the electrochemical reaction of FePO_4 in aqueous Mg^{2+} electrolyte proceeds in part by non-topochemical Mg^{2+} (de)intercalation accompanied by the irreversible transformation from the crystalline state to the amorphous state in the vicinity of particle surface.

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1. Introduction

Development of advanced energy storage is one of the most urgent challenges to realize sustainable society. Li-ion batteries are the state-of-the-art power sources for most portable electronic devices; however, large scale application for power grid requires inexpensive and safe batteries, which has spurred research activities for new battery systems.

One possible way to achieve inexpensive and safe batteries is to utilize magnesium systems.¹ In contrast to less abundant and mal-distributed Li in the earth, Mg is earth abundant and evenly distributed, allowing to reduce the cost of the batteries. Another possible positive outcome is efficient charge storage by divalent cation (Mg^{2+}), which may lead to large energy density. Thus, exploring reversible Mg^{2+} (de)intercalation compounds are critical toward suitable electrode materials of rechargeable Mg batteries.

An intrinsic obstacle for reversible Mg^{2+} (de)intercalation is large deformation of the local structure by accommodation of two-electron associated with Mg^{2+} .^{2–4} For example, the Chevrel phase Mo_6T_8 ($T = \text{S}$ and Se) shows fast and reversible Mg^{2+} intercalation, because multiple electrons can be accommodated with delocalized orbital of a Mo_6T_8 cluster to relieve the local structure deformation.² Recent works on Mg^{2+} intercalation have focused on nanosized compounds such as V_6O_{13} ,⁵ MoS_2 ,⁶ MgMSiO_4 ($M = \text{Mn}$, Fe , and Co),^{7–9} RuO_2 ,¹⁰ Co_3O_4 ,¹¹ TiS_2 ,¹² and MnO_2 , but with unimpressive battery performance,^{13,14} where the detailed reaction mechanism has not been clarified.

In this work, we investigate the electrochemical reaction of heterosite FePO_4 in aqueous Mg^{2+} electrolyte. Heterosite FePO_4 is a metastable phase obtained by delithiation from triphillite LiFePO_4 and an important host electrode material because of the intercalation capability with various monovalent cations as guest species.^{15,16} Herein, we clarify the electrochemical reaction mechanism of FePO_4

with Mg^{2+} in aqueous electrolyte by ex-situ Mössbauer spectroscopy, X-ray diffraction experiments, and ab-initio calculation.

2. Experimental

LiFePO_4/C composites including 10 wt% additive carbons (8 wt% carbon black, and 2 wt% vapor-grown carbon nano fiber) were synthesized according to the procedure reported previously.¹⁷ FePO_4/C composites were prepared by chemical oxidation of LiFePO_4/C composites with nitronium tetrafluoroborate (NO_2BF_4 ; Alfa Aesar, 96%) in acetonitrile.¹⁷ The products were filtered several times by acetonitrile to remove impurities before they were dried under vacuum at 60°C .

The X-ray diffraction measurement was conducted at room temperature by using Bruker AXS D8 ADVANCE powder diffractometer equipped with $\text{Co K}\alpha$ radiation source in the 2θ range from 15° to 80° . Structural refinement was performed by using a Topas ver. 3.0 program.

The paste for the working electrode was prepared by mixing 85 wt% FePO_4/C composite, 5 wt% carbon black, and 10 wt% polytetrafluoro-ethylene (PTFE), which was pressed onto Ti meshes. The total carbon content in the electrode is 13.5 wt%. All the electrochemical measurements were performed with three-electrode beaker-type cells at 298 K. A platinum mesh and Ag/AgCl electrode were used for the counter and reference electrodes, while 0.5 mol dm^{-3} MgSO_4 aqueous solution (pH 7.82) was used as the electrolyte. Note that oxygen dissolved in the electrolyte was degassed by Ar gas bubbling for 2 h. For cyclic voltammetry (CV), linear potential sweep was repeated with a scan rate of 0.03 mVs^{-1} in the voltage range between -0.5 and 0.5 V (vs. Ag/AgCl). For charge/discharge measurements, a constant current at a rate of C/20 was applied in the voltage range between -0.6 and 0.6 V (vs. Ag/AgCl).

Figure 1. X-ray diffraction pattern and the Rietveld refinement result for chemically oxidized FePO₄. The inset shows a typical SEM image of FePO₄ particles.

⁵⁷Fe Mössbauer spectra were collected with a transmission optics spectrometer (Toplogic System, Inc.). A ⁵⁷Co dispersed Rh matrix was used as the radiation source and the proportional counter. α -Fe was used as a standard to calibrate velocity and isomer shift at room temperature with MossWinn Ver. 3.0 software. The chemical composition of the electrode material during the discharge-charge processes was determined by the inductively coupled plasma atomic emission spectrometry (ICP-AES, iCAP DUO-6300). The electrodes after soaked to the electrolyte, after first discharge, and after first charge were dissolved in 0.1 mol dm⁻³ HCl solution for the ICP measurements, respectively. The amount of Fe and Mg was calibrated by Fe(NO₃)₃ and Mg(NO₃)₂ solution (0–4 ppm).

All the DFT calculations were performed by the Vienna Ab-Initio Simulation Package (VASP).¹⁸ The PBE exchange-correlation functional¹⁸ was employed and the wavefunctions are treated with the PAW method.¹⁹ The energy cutoff for the plane-wave basis was 520 eV and a $2 \times 2 \times 2$ k-point mesh was used. The calculations were spin-polarized with the ordering of spins on the Fe ion assumed to be ferromagnetic. A supercell with a size of $1 \times 2 \times 2$ that of the unit cell of FePO₄ was used. The calculations were done by firstly optimizing the unit cell after inserting one Li/Mg ion into the supercell, then the unit cell dimensions were kept at the optimized values and the Li/Mg diffusion path was computed with the climbing-image nudged elastic band method.²⁰ The criterion for force convergence was 0.010 eV/Å.

3. Results and Discussion

Figure 1 shows the X-ray diffraction (XRD) pattern and the Rietveld refinement result of the FePO₄/C composite, which was synthesized by the chemical oxidation of the LiFePO₄/C composite. The refined parameters are summarized in Table 1. The fitting is satisfactory ($R_{wp} = 1.28\%$, $R_p = 0.98\%$, $R_{Bragg} = 0.559$, and $GOF = 1.45$), and all the Bragg reflections are indexed in orthorhombic lattice parameters of $a = 9.8246$ (4) Å, $b = 5.7981$ (2) Å, $c = 4.7846$ (2) Å, and $V = 272.55$ (2) Å³ with $Pnma$ symmetry. These values are consistent with the previous result ($a = 9.819$ Å, $b = 5.792$ Å, $c = 4.782$ Å, and $V = 272.0$ Å³),²¹ suggesting successful fabrication of a single FePO₄ phase without impurity.

The mean size of the crystallites is estimated as 48.0(4) nm by the Rietveld refinement. SEM images of FePO₄ particles (inset in Fig. 1) show that the average particle size is 46 ± 11 nm, which is consistent with the Rietveld refinement result.

Figure 2 shows the cyclic voltammograms of the FePO₄ electrode in 0.5 mol dm⁻³ MgSO₄ aqueous solution at 298 K with a scan rate of 0.03 mVs⁻¹. While a sharp cathodic wave is observed

Table 1. Refined structural parameters of chemically oxidized FePO₄.

Site	<i>x</i>	<i>y</i>	<i>z</i>	<i>g</i>	<i>B_{eq}</i>
Fe	0.2750 (4)	0.25	0.9516 (3)	1	0.6
P	0.0935 (2)	0.25	0.3930 (6)	1	0.6
O1	0.1198 (4)	0.25	0.7141 (9)	1	1
O2	0.4373 (6)	0.25	0.1597 (7)	1	1
O3	0.1683 (4)	0.0399 (4)	0.2450 (5)	1	1

$a = 9.8246$ (4) Å, $b = 5.7981$ (2) Å, and $c = 4.7846$ (2) Å

$R_{wp} = 1.28\%$, $R_{exp} = 0.88\%$, $R_p = 0.98\%$, and $GOF = 1.45$

Figure 2. Cyclic voltammogram of FePO₄ electrode in 1 mol dm⁻³ MgSO₄ aqueous solution at a scan rate of 0.03 mV s⁻¹.

Figure 3. Discharge/charge curves of FePO₄ in 1 mol dm⁻³ MgSO₄ aqueous solution at a rate of C/20 (conducting at 298 K).

at -0.42 V (vs. Ag/AgCl), a broad anodic wave is observed at -0.10 V. The separation between the cathodic and anodic peaks is very large (~ 320 mV) even with the very slow scan rate of 0.03 mV s⁻¹, suggesting the slow kinetics and/or irreversibility of the electrode reaction. Furthermore, the significant difference between the cathodic and anodic wave shapes strongly implies irreversible electrode reaction. Since the peak current of the cathodic wave decreases with repeating the CV cycle, the FePO₄ electrode has poor cycle stability against the electrochemical reaction with aqueous Mg²⁺ electrolyte.

Figure 3 shows the discharge/charge curves at C/20 rate during the initial three cycles. The potential profile on the first discharge exhibits a sloping plateau centered at ca. -0.4 V (vs. Ag/AgCl), delivering the specific capacity of 90.5 mAh g⁻¹. Under the

Figure 4. (Color online) Ex-situ Mössbauer spectra of the pristine, discharged, and charged FePO_4 electrodes.

assumption that the electric current is derived entirely from the Mg^{2+} intercalation ($\text{FePO}_4 + x\text{Mg}^{2+} + 2x\text{e}^- \rightarrow \text{Mg}_x(\text{FePO}_4)$); theoretical capacity: 177 mAh g^{-1} for $0 < x < 0.5$), the first discharge capacity corresponds to 0.25 Mg^{2+} intercalation.

The first charge curve exhibits a sloping potential profile over a wide voltage range from -0.4 to 0.5 V , which agrees with the broad anodic wave in the CV curve. The first charge capacity is 56.6 mAh g^{-1} with coulombic efficiency of 63%. As suggested by the CV cycles, the discharge/charge capacity decreases with repeating the cycle. Thus, the FePO_4 electrode has suffered from poor cycle stability in aqueous Mg^{2+} electrolyte.

To reveal the reaction mechanism, ex-situ Mössbauer spectroscopy was carried out for the pristine, discharged and charged samples (Fig. 4). The results for the curve fitting are summarized in Table 2. The pristine FePO_4 compound shows a doublet peak, which is fitted mainly by a doublet with the isomer shift (IS) of 0.427 mm s^{-1} and the quadrupole splitting (QS) of 1.531 mm s^{-1} . These values are consistent with those reported for high spin Fe^{3+} in FePO_4 (IS = 0.42 mm s^{-1} and QS = 1.5 mm s^{-1}).²² However, note that the best fit needs 8.1% of another doublet (IS = 0.42 mm s^{-1} and QS = 0.661 mm s^{-1}), suggesting existence of defects or surface sites.

The Mössbauer spectrum for the discharged compound is best fitted by four doublets. The fraction of the Fe^{3+} doublet observed for

Figure 5. Ex-situ X-ray diffraction patterns of the pristine, discharged, and charged FePO_4 electrodes.

the pristine compound decreases from 92% to 40%, whereas two new doublets with IS of $1.22\text{--}1.27 \text{ mm s}^{-1}$ and QS of $2.5\text{--}3.0 \text{ mm s}^{-1}$ emerge. These IS and QS values are close to those reported for high spin Fe^{2+} in LiFePO_4 (IS = 1.2 and QS = 3.0 mm s^{-1}).²² Thus, 50% of Fe^{3+} in the pristine FePO_4 is reduced to Fe^{2+} by discharging, which is in good agreement with the initial discharge capacity of 90.5 mAh g^{-1} . It should be emphasized that QS of one Fe^{2+} doublet ($\text{Fe}^{2+}(4)$; 2.46 mm s^{-1}) is smaller than that of LiFePO_4 (3.0 mm s^{-1}). This result suggests that the local coordination change of Fe by the electrochemical reaction in aqueous Mg^{2+} electrolyte differs from that by Li^+ intercalation. After charge, the Fe^{2+} doublets almost disappear while the fraction of the Fe^{3+} doublet is recovered to 85%. Thus, reversible redox of $\text{Fe}^{3+}/\text{Fe}^{2+}$ occurs on discharge–charge with Mg^{2+} aqueous electrolyte.

To further clarify the reaction mechanism, we conducted the ex-situ XRD measurements for the pristine, discharged, and charged compounds. The XRD patterns in Fig. 5 show neither peak shift of the original phase nor emergence of new peaks for a Mg^{2+} intercalated phase on discharge/charge. Whole profile fitting analyses on the diffraction patterns suggest only ca. 1.0% of reversible volume expansion/contraction. Furthermore, significant peak broadening in all indices suggests strong lattice distortion and inhomogeneity at the discharged state. The solid solution state, Mg_xFePO_4 may exist as in Li_xFePO_4 .¹⁷ However, the 1.0% volume change is much smaller than that (ca. 7%) predicted for $\text{FePO}_4/\text{Mg}_{0.5}\text{FePO}_4$ by density functional theory (DFT) calculation.²³ Thus, reversible redox of $\text{Fe}^{3+}/\text{Fe}^{2+}$ in the FePO_4 electrode cannot be explained solely by topochemical Mg^{2+} (de)intercalation.

Table 2. Refined parameters for Mössbauer spectrum of the pristine, discharged and charged FePO_4 .

		Isomer shift/ mm s^{-1}	Quadrupole splitting/ mm s^{-1}	Fraction/%	Line width/ mm s^{-1}
Pristine	Fe^{3+} (1)	0.4268 (2)	1.5309 (8)	91.9 (2)	0.313 (9)
	Fe^{3+} (2)	0.424 (4)	0.661 (9)	8.1 (1)	0.256 (8)
Discharged	Fe^{3+} (1)	0.417 (3)	1.549 (8)	40.1 (1)	0.256 (8)
	Fe^{3+} (2)	0.428 (16)	1.11 (5)	10.5 (1)	0.256 (8)
	Fe^{2+} (3)	1.224 (5)	2.97 (2)	28.8 (1)	0.256 (8)
	Fe^{2+} (4)	1.270 (11)	2.46 (5)	20.6 (1)	0.43 (3)
Charged	Fe^{3+} (1)	0.4259 (6)	1.530 (1)	85.4 (2)	0.3051 (2)
	Fe^{3+} (2)	0.406 (6)	0.72 (1)	11.8 (2)	0.3051 (2)
	Fe^{2+} (3)	1.255 (2)	2.84 (4)	2.8 (2)	0.3051 (2)

Normalized χ^2 for each fitting were 2.07, 1.0007, and 1.28 for pristine, first discharged, and first charged FePO_4 electrodes, respectively.

Figure 6. (a) Minimum energy path for Li^+ and Mg^{2+} -ions migration in FePO_4 . (b) Migration path along b direction in FePO_4 .

The DFT calculation also supports that facile topochemical Mg^{2+} intercalation is improbable in FePO_4 . Figure 6(a) shows the energies of Li^+ and Mg^{2+} along the minimum energy paths in FePO_4 calculated by the nudged elastic band method. The energy barriers for Li^+ diffusion are calculated to be about 0.20 eV. This agrees well with previously reported values.^{24,25} The minimum energy profile has a characteristic dip in the mid of the path where the Li^+ occupies a tetrahedral site [Fig. 6(b)]. For Mg^{2+} , the activation energy is found to be more than three times that of Li^+ , about 0.67 eV. The dip at the intermediate tetrahedral site is also found for Mg^{2+} but it is much more pronounced. These show that the smaller and higher-valent Mg^{2+} interacts much stronger with the framework when compare to the Li^+ . The large activation energy for Mg^{2+} suggests that the topochemical intercalation into FePO_4 is difficult.

The ICP measurement determines that the electrode after the first discharge contains 0.38 Mg per the formula unit of FePO_4 , while those before the first discharge and after the first discharge/charge cycle contain ca. 0.02 Mg. Thus, the FePO_4 electrode should react with Mg^{2+} . It is most likely that, on discharge, the crystalline FePO_4 phase is partially transformed to an amorphous phase by non-topochemical Mg^{2+} intercalation. On charge, the Mg^{2+} intercalated amorphous phase may be oxidized to another amorphous phase by Mg^{2+} deintercalation. In fact, very broad hump was observed at $2\theta = 15\text{--}20^\circ$ in the ex-situ XRD pattern after the discharge and charge processes, supporting formation of the partial amorphous phase. The irreversible partial phase transformation from the crystalline state to the amorphous state may explain both the asymmetric wave shapes in the CV curves and little change in the ex-situ XRD patterns.

4. Conclusion

The FePO_4 electrode shows partially reversible capacity with aqueous Mg^{2+} electrolyte on charge/discharge experiments. Reversible redox of $\text{Fe}^{3+}/\text{Fe}^{2+}$ is evidenced by ex-situ Mössbauer spectroscopy, whereas little structural change occurs in the ex-situ XRD patterns. DFT calculation revealed activation energy for Mg^{2+} diffusion is over three times larger than that of Li^+ , suggesting the topochemical intercalation into FePO_4 is not facile. All of these results might suggest that partial fraction of the FePO_4 phase becomes an amorphous phase by non-topochemical Mg^{2+} intercalation. This work suggests that an apparent capacity obtained in the charge/discharge experiments does not necessarily correspond to topochemical intercalation reaction, and therefore it is indispensable to analyze the structural and chemical states of the material as a function of incremental Mg^{2+} intercalation.

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