Inorganic Chemistry

Olivine FePO₄ Cathode Material for Rechargeable Mg-Ion Batteries

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S Supporting Information

ABSTRACT: In this work, Mg_xFePO₄ is exploited as a cathode material for rechargeable Mg-ion batteries. FePO₄/C prepared via electrochemical delithiation of LiFePO₄/C is directly used as the cathode in aqueous Mg^{2+} electrolyte, and reversible capacity is achieved for the first time. Notably, the capacity (82 mA h/g) is half of the theoretical value (164 mA h/g) and "asymmetric" discharge/charge behavior can be observed. In addition, firstprinciples calculations show it is the strong Mg-ion interactions between adjacent channels that not only limit the capacity of the cathode but also lead to the difference in rates for Mg-ion intercalation and deintercalation. This work provides experimental and theoretical evidence that reveal the mechanism of Mg-ion intercalation and deintercalation in a FePO₄ host, which gives guidance in designing cathode materials for rechargeable batteries based on multivalent metal ions.



1. INTRODUCTION

There is increasing demand for electronic devices and equipment, making advanced energy storage devices highly desirable. Li-ion batteries have been widely used as energy storage devices. However, the development of Li-ion batteries is limited by their high prices, low energy densities, and safety issues.^{1–4}

One possible approach to achieve inexpensive and safe batteries is to explore rechargeable batteries based on multivalent cation charge carriers. Magnesium-ion batteries have received much attention recently because of the potential to provide a greater amount of energy density, the lower cost, and the safer operation with Mg-metal anodes. However, due to sluggish Mg insertion and diffusion in cathode materials, finding cathode materials for reversible Mg²⁺ (de)intercalation has been challenging until now.^{5–10}

In contrast, Li-ion batteries are experiencing rapid development and widespread application. The so-called "diagonal relationship" in the periodic table suggests the chemical similarity between lithium and magnesium, which shows Mg²⁺ has an ionic size similar to that of Li^{+,11} Therefore, hosts that have been currently used in Li-ion batteries are of referential significance for Mg-ion batteries. There have been attempts to use compounds analogous to classical Li-ion battery cathodes as Mg-intercalation hosts, including spinels,^{12–15} layered oxides,^{16,17} disulfides,^{18,19} polyanions,²⁰ and openchannel compounds.²¹ Though some hosts that exhibit excellent electrochemical performance in Li-ion batteries that may also accommodate the intercalation of Mg²⁺, the unclear mechanism of Mg²⁺ intercalation leads to the possibility that Li and Mg ions may behave very differently in the same host. In addition to experimental studies, there are also extensive theoretical studies of Mg-ion batteries,²²⁻²⁶ where the

mechanisms of Mg-ion intercalation and deintercalation in various types of hosts have been discussed.

Olivine LiFePO₄ (LFP) is the most commercialized Li-ion battery cathode with good energy density, stable cycling, and high rate capability.²⁷ Hence, it would be interesting to examine the performance of olivine compounds as Mg-ion battery cathodes in comparison with Li cathodes. Unlike oxide hosts, the crystal structure of LiFePO4 remains stable after being oxidized to $FePO_4^{28,29}$ making $FePO_4$ a potential cathode material candidate for Mg-ion rechargeable batteries. Chemically oxidized FePO₄ has been previously investigated as a Mgion host; however, it has been reported that the electrochemical performances are not satisfactory and issues such as low specific capacity and poor capacity retention have yet to be addressed.^{30,31}

Herein, nanosized LiFePO4 is synthesized and then electrochemically delithiated into FePO₄, which is used as the cathode material for Mg-ion batteries. For the first time, reversible capacity is obtained from electrochemically delithiated FePO₄ in aqueous Mg²⁺ electrolyte. The galvanostatic cycling results reveal that only half of the theoretical capacity can be realized. It is also found that the intercalation/deintercalation processes of Mg²⁺ are "asymmetrical" and the charging process is the ratelimiting step for the performances of the cells. First-principles calculations of this system have also been performed. The calculated results are in good agreement with the experimental results, where half of the theoretical capacity of Mg_rFePO₄ can be achieved due to the significant differences in energy barriers for Mg-ion diffusion in different Fe interlayers. This work demonstrates not only experimental evidence but also

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Figure 1. (a) X-ray powder diffraction (XRD) and (b) scanning electron micrograph (SEM) of the morphology of the prepared LFP/C nanoparticles.



Figure 2. (a) Charge and discharge curves at 1 C current density (1 C = 170 mA g^{-1}) between -0.2 and 0.75 V (vs Ag/AgCl) in 1 M LiNO₃ aqueous electrolyte (active material LFP on smooth Au slice). (b) Cyclic voltammogram (CV) for the prepared 45 nm LFP nanoparticles in 1 M LiNO₃ aqueous electrolyte.

theoretical explanation about the magnesiation mechanism of a classical cathode material for Li-ion batteries.

2. EXPERIMENTAL SECTION

2.1. Materials Characterization. The crystal structure of LiFePO₄/C samples was analyzed by X-ray diffraction (XRD) using a Bruker D8-Advantage powder diffractometer (Cu K radiation) with 2θ from 10 to 90° at 1 s per step. The morphology of the samples was investigated by scanning electron microscopy (SEM; Zeiss SURPA 55) operated at 5 kV. Inductively coupled plasma (ICP) was carried out by an ICP-AES instrument (JY2000-2).

2.2. Preparation of LiFePO4. LiFePO4 particles with a mean size of 45 nm (calculated from the Scherrer equation) were synthesized by the reflux route in ethylene glycol solution under atmospheric pressure. In a typical route, FeSO4.7H2O, H3PO4, and LiOH·H2O were used as starting materials in a molar ratio of 1:1.5:2.7 and ethylene glycol (EG) was applied as solvent. H₃PO₄ was slowly introduced to the LiOH solution with stirring, and then FeSO4 solution was added to the mixture. After homogenization, the reaction mixture was heated under reflux conditions for 10 h under an Ar atmosphere. The resulting suspension was washed several times with water and ethanol. To achieve carbon coating, LiFePO4 nanoparticles were mixed with 20 wt % of glucose and then carbonized at 650 °C for 6 h under an Ar atmosphere. For the synthesis of LiFePO₄ nanoparticles with a mean size of 101 nm (calculated from the Scherrer equation), the feeding sequence was changed. In this case, H₃PO₄ was slowly introduced to the FeSO₄ solution with stirring.

Then LiOH solution was added to the mixture. Other steps are the same as those described in ref 32.

The electrode materials were prepared by mixing the LFP/C nanocrystals (9 mg), carbon nanotubes (6 mg), and Nafion (0.15 g) as binder into N-methyl-2-pyrrolidone (NMP) solution, ultrasonicating for 60 min, and then casting a drop of slurry on quartz monitor crystals (about 0.9 mg cm⁻² electrode materials on working electrode).

2.3. Electrochemical Measurements. A three-electrode system was used to measure the electrochemical properties, An Au electrode, platinum electrode, and Ag/AgCl electrode were used as working electrode, counter electrode, and reference electrode, respectively. Cyclic volmammetry measurements were carried out with a CHI electrochemistry workstation (CHI 660E, Shanghai Chenhua). Galvanostatic charge–discharge tests were performed using a battery test system (Maccor, MC-16). The delithiation process of LiFePO₄ was performed in 1 M LiNO₃ aqueous solution. After delithiation, the electrodes were thoroughly washed with 1 M MgSO₄ aqueous solution. Then the Mg-ion intercalation/deintercalation experiments were performed using the as-prepared electrode in 1 M MgSO₄ aqueous electrolyte.

The apparent diffusion coefficients (D) were calculated by the equation

$$I_{\rm p} = (2.69 \times 10^5) n^{3/2} A D^{1/2} \nu^{1/2} C$$

where I_p is the peak current, *n* is the number of electrons, *A* is the area of the electrode, ν is the scanning rate, and *C* is the ion concentration in the electrolyte.

2.4. Theoretical Study. The theoretical study was based on density functional theory (DFT) calculations. DFT calculations were performed with the Vienna ab initio Simulation Package (VASP) using projector-augmented wave (PAW) pseudopotentials and the exchange-correlation functionals parametrized by Perdew, Burke, and Ernzerhof for the generalized gradient approximation (GGA-PBE). The cutoff energy was set as 450.0 eV. To obtain reliable optimized structures and the total energy, all atomic positions and cell parameters were fully relaxed until the force on each atom was smaller than 0.03 eV/Å and energies were converged to within 1×10^{-5} eV per atom. The PBE+U approach was employed to take account of the strong onsite Coulomb interaction (U) presented in the localized 3d electrons of Fe, with the U values set to 5.3 eV.

The diffusion barrier of the diffusion of Mg^{2+}/Li^+ was calculated with the climbing-image nudged elastic band (cNEB) method. Five intermediate images were constructed to interpolate the initial and final states along the Mg^{2+}/Li^+ diffusion path. Lattice parameters of every image were fixed. In this case, the smallest supercells were used to calculate the diffusion barrier of ions, the specific values are in the later content.

3. RESULTS AND DISCUSSION

The crystallite LiFePO₄ was prepared by a reflux route in ethylene glycol solution under atmospheric pressure. The prepared LiFePO₄ sample was mixed with 20 wt % of glucose and then carbonized at 650 °C for 6 h under an Ar atmosphere.³² Figure 1a shows that the crystallite of LiFePO₄/C was a single LiFePO₄ phase and all peaks can be well attributed to PDF #40-1499. The SEM image of the prepared LiFePO₄/C is shown in Figure 1b, and the average diameter of the particles is approximately 45 nm.

An electrochemical delithiation method was chosen to prepare FePO₄. A solution-casting method was taken to prepare the cathode, and the resultant loading of active material was approximately 0.9 mg cm⁻². The delithiation experiment was performed in a three-electrode system using 1 M LiNO₃ aqueous electrolyte. Figure 2a shows the charge/ discharge profiles of LiFePO₄/C at a rate of 1 C in 1 M LiNO₃; the charge capacity is 162 mA h g^{-1} , indicating an almost complete delithiation. This is supported by the results from ICP measurements, where the active material after charging at 1 C contains only 0.10 Li per formula unit of FePO₄. Figure 2b shows a cyclic voltammogramm of the cell at a scan rate of 1 mV s⁻¹ between -0.25 and 0.65 V (vs Ag/AgCl), where two sharp peaks can be found at 0.23 and 0.16 V, corresponding to the oxidation and reduction processes, respectively. From Figure 2a, it can also be found that the overpotential is only 0.02 V. Therefore, under this experimental condition, the polarization effect that comes from the system is negligible.

Figure 3 shows the CV curves of the FePO₄ electrode in 1 M MgSO₄ aqueous solution measured at scan rates from 0.1 to 1 $mV s^{-1}$. It is shown that the oxidation peaks are always sharper in comparison to reduction peaks, which implies that the kinetics of Mg²⁺ intercalation is slower than that of deintercalation. Furthermore, the normalized CV curves (inset) showed that, as the scan rate increased, the shape of the oxidation peaks barely changed while the shape of the reduction peaks became increasingly broader, which also implies that the Mg-ion intercalation process is kinetically unfavorable in comparison to the deintercalation process. Furthermore, the apparent Mg²⁺ diffusion coefficients are estimated from the \overline{CV} curves: for Mg ion intercalation, D = $8.88 \times 10^{-13} \text{ cm}^2 \text{ S}^{-1}$, while for Mg ion deintercalation, D = $4.79~\times~10^{-12}~{\rm cm}^2~{\rm S}^{-1}$, defining a much slower diffusion intercalation process in comparison to deintercalation. The



Figure 3. CV of an FePO_4 electrode at different scan rates in 1 M MgSO₄ solution. The inset gives the normalized CV at different scan rates.

desolvation step plays an important role in Mg-ion intercalation.^{33–35} Therefore, it is speculated that the slow kinetics for Mg-ion deintercalation may be due to the high desolvation energy of Mg^{2+} in aqueous solution.

The rate performances of FePO₄ in 1 M MgSO₄ solution are shown in Figure 4. In Figure 4a, it is shown that two cycling protocols have been employed (C rates are calculated on the basis of the theoretical capacity of Mg_{0.5}FePO₄, which is 164 mA h g^{-1}). In protocol 1 (P1), the charge rates changed along with the discharge rates (black squares); in protocol 2 (P2), only the charge rates were changed while the discharge rates were kept constant at 0.1 C (red/white dots). At 0.1 C, the discharge capacity obtained from P1 (80 mA h g⁻¹) is very close to that from P2 (82 mA h g^{-1}). When the rate was increased to 0.2 C, P2 started to exhibit much better electrochemical performance (74 mA h g⁻¹) in comparison with P1 (58 mA h g^{-1}). This gap continued to grow as the rate increased to 0.5 C (72 vs 37 mA h g^{-1}) and 1 C (67 vs 21 mA h g^{-1}). After 20 cycles, the capacity retentions for P1 and P2 were 89% and 94%, respectively. It is very clear that by application of P2, where the discharge rate was kept relatively low, better rate capability was achieved. This is another piece of evidence showing that the processes of Mg²⁺ deintercalation/intercalation into FePO4 are "asymmetrical". In other word, the cycling capabilities of the cell at higher rates are limited by the slow Mg²⁺ intercalation into FePO₄ to a great extent. From the potential profiles (Figure 4b,c), it can be seen that, for both protocols, smooth and flat discharge/charge plateaus were obtained and the overpotentials of Mg-ion cells remained relatively low at lower rates. However, the cell using P1 exhibited much higher overpotentials as higher discharging rates were applied. In addition, it is also observed that the redox voltage (Figure 4c) is 0.03 V (vs Ag/AgCl, i.e. 3.29 vs Li/Li⁺), which is 0.16 V lower than that of LiFePO₄ in Figure S1b in the Supporting Information (0.19 V vs Ag/AgCl, i.e. 3.45 V vs Li/ Li⁺). Therefore, it can be assumed that the electric current is derived from the Mg²⁺ intercalation. In order to prove this assumption, a post-mortem experiment was carried out to determine the elemental composition of the ion host after Mg²⁺ intercalation. After one discharge/charge cycle at 0.1 C, the cell was dissembled and ICP measurement was performed on the cathode. It was found that the electrode contains 0.26 Mg per



Figure 4. (a) Rate performances of $FePO_4$ in 1 M MgSO₄ solution using P1 (black squares) and P2 (red/white dots). (b) Potential profiles of the cell using P1. (c) Potential profiles of the cell using P2.

formula unit of FePO₄, which is in good agreement with the number calculated on the basis of the discharge capacity (0.24). By further examination of the discharged cathode material, it can be seen from the TEM image (Figure 5a) and the EDS images (Figure 5b-f) that Mg ions have successfully inserted into the FePO₄ host, indicating the formation of Mg_xFePO₄.

To further study the mechanism of Mg distribution in FePO₄, first-principles calculations have also been carried out. Since Mg^{2+} carries two positive charges, when they replace Li⁺, Mg^{2+} ions will occupy half of the Li⁺ positions. The structures of LiFePO₄ and $Mg_{0.5}FePO_4$ are shown in Figure S1 in the Supporting Information. The diffusion pathways of Mg^{2+} have been described in previous work.³⁰ In order to have a

straightforward concept of the difficulty of Li or Mg ions to diffuse into the host, the calculated diffusion barriers for vacancies are shown in Table S1 in the Supporting Information (a supercell with a size of $2 \times 1 \times 1$ and a $3 \times 4 \times 2$ *k*-point mesh was used). Table S1 shows that the diffusion barriers of Mg²⁺ and Li⁺ in FePO₄ have similar values (0.52 and 0.32 eV, respectively). However, diffusion barriers of Mg²⁺ in Mg_{0.5}FePO₄ (>1.3 eV) are much higher than that of Li⁺ in LiFePO₄ (0.53 eV). This huge difference could be due to the strong Coulomb interaction between divalent magnesium ions. Hence, it is very likely that Mg ions have a different intercalation mechanism in comparison to Li ions.

In the structure of FePO₄, ions will travel along the [010] direction;³⁶ these pathways can be thought of as many parallel diffusion channels for ions. As shown in Figure 6, there are six adjacent channels near each channel. It is assumed that the diffusion barrier of Mg^{2+} in the selected channel (channel 0, shown in Figure 6) is more likely to be influenced by its six adjacent channels. Depending on whether there is a Fe–O layer interposed between a Fe–O layer interposed between two adjacent channels, these six channels can be classified into types 1 and 2, as shown in Figure 6a.

As shown in Table. 1, when the channel 0 is occupied by Mg^{2+} , by calculation of the diffusion barriers of Mg^{2+} in a type 1 or type 2 channel, it is found that the diffusion barrier of Mg²⁺ in a type 1 channel is about 1.26 eV (0.43 eV for Li⁺), but the diffusion barrier of Mg²⁺ in a type 2 channel is only about 0.82 eV (0.39 eV for Li⁺), which is similar to the diffusion barrier of $\text{Li}^{\scriptscriptstyle +}$ in $\text{Li}_2\text{FeSiO}_4.^{37}$ In $\text{Li}_2\text{FeSiO}_4,$ the diffusion barrier of about 0.8 eV makes Li⁺ diffuse slowly, but the process is still feasible. According to the result, when a channel is occupied by Mg^{2+} , its adjacent type 1 channels will no longer be available for other Mg ions, while its adjacent type 2 channels could still accept additional Mg ions. This difference may be explained by the fact that the inserted Mg ions could polarize Fe ions, which in turn affect the insertion energy barrier of the adjacent Fe interlayer.³⁸ On this basis, it is believed that Mg²⁺ will tend to gradually intercalate in the same Fe–O interlayer and it has difficulty in intercalating into the adjacent Fe-O interlayers. Consequently, as the ideal half-full state is reached, the energy barrier for further ion intercalation will become very high, indicating the end of the intercalation. This conclusion well explains the experimental results. Note that the Li-ion interaction between adjacent channels in Li, FePO4 also exist but is too small to make much of a difference in the diffusion barrier.

Although ideally the Mg²⁺ ions tend to fill every alternate Fe-O interlayer, the situation where two Mg²⁺ ions intercalate into two nonadjacent channels but in adjacent Fe-O interlayers may also occur when many Mg²⁺ ions are intercalating at the same time. This type of situation results in a fewer number of channels in which Mg²⁺ can diffuse. For example, if the 2-I channel and 1-II channel have Mg²⁺ inside at the same time, then the surrounding 0, 1-I, 1-III, and 2-II channels will not be available for other Mg ions. Therefore, it is speculated that, at higher discharging rates, instead of an orderly arrangement of occupied channels, random distributions of occupied channels may result, leading to lower capacities. In contrast, at the charging step, all inserted Mg ions can freely deintercalate from the host without a high energy barrier; therefore, higher charging C rates can be applied. Although Mg²⁺ and Li⁺ have similar sizes, the different insertion behaviors of Mg and Li ions into FePO₄ might be due to the



Figure 5. TEM image (a) and EDS images (b-f) of discharged cathode material.



Figure 6. (a) Crystal structure of $Mg_{0.5}FePO_4$ and (b) the channels classification diagram.

Table 1. Calculated Diffusion Barriers (eV) for Mg^{2+} and Li^+ Insertion into Different Types of Channels

	channel type	
	1	2
Mg ²⁺	1.26	0.82
Li ⁺	0.43	0.39

extra positive charge that the Mg ion carries, which causes much stronger Coulomb repulsions between ions within a finite range to generate "local stress" to influence the ionic diffusion barrier.

4. CONCLUSIONS

In summary, electrochemically delithiated nanosized FePO₄ was prepared as the cathode material for Mg-ion batteries. Using this as-prepared cathode, for the first time, a reversible capacity of 82 mA h g^{-1} was obtained in aqueous Mg^{2+} electrolyte at 0.1 C, which was about half of the theoretical capacity of Mg_{0.5}FePO₄. In addition, it is also found that the

sluggish intercalation process of the Mg^{2+} into FePO₄ limits the rate performance of the cell at the discharging step, while the charging step can be carried out at higher C rates. To fully understand the different electrochemical behaviors of Mg^{2+} and Li^+ in this system, first-principles calculations have been carried out and it is found that cationic interactions between adjacent channels generally exist for the first time and Mg^{2+} exhibits a much higher insertion diffusion energy barrier in comparison to Li^+ , which is due to the strong interaction between two adjacent Mg ions in different Fe interlayers. This work not only reveals the behavior of Mg ion intercalation and deintercalation in the FePO₄ host but also gives guidance in designing cathode materials for rechargeable batteries based on multivalent metal ions.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.inorg-chem.7b02150.

Crystal structures of LiFePO₄ and Li⁺/Mg²⁺ distributions and the energy barriers of Li⁺ and Mg²⁺ in the host (PDF)

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Notes

The authors declare no competing financial interest.

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