Low-strain TiP$_2$O$_7$ with three-dimensional ion channels as long-life and high-rate anode material for Mg-ion batteries

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Abstract
Rechargeable magnesium batteries are identified as a promising next-generation energy storage system, but their development is hindered by the anode–electrolyte–cathode incompatibilities and passivation of magnesium metal anode. To avoid or alleviate these problems, the exploitation of alternative anode materials is a promising choice. Herein, we present titanium pyrophosphate (TiP$_2$O$_7$) as anode materials for magnesium-ion batteries (MIBs) and investigate the effect of the crystal phase on its magnesium storage performance. Compared with the metastable layered TiP$_2$O$_7$, the thermodynamically stable cubic TiP$_2$O$_7$ displays a better rate capability of 72 mAh g$^{-1}$ at 5000 mA g$^{-1}$. Moreover, cubic TiP$_2$O$_7$ exhibits excellent cycling stability with the capacity of 60 mAh g$^{-1}$ after 5000 cycles at 1000 mA g$^{-1}$, which are better than previously reported Ti-based anode materials for MIBs. In situ X-ray diffraction technology confirms the single-phase magnesium-ion intercalation/deintercalation reaction mechanism of cubic TiP$_2$O$_7$ with a low volume change of 3.2%. In addition, the density functional theory calculation results demonstrate that three-dimensional magnesium-ion diffusion can be allowed in cubic TiP$_2$O$_7$ with a low migration energy barrier of 0.62 eV. Our work demonstrates the promise of TiP$_2$O$_7$ as high-rate and long-life anode materials for MIBs and may pave the way for further development of MIBs.

KEYWORDS
anode material, intercalation, low-strain, Mg-ion battery, TiP$_2$O$_7$
1 | INTRODUCTION

Energy storage technology plays an essential role in modern society and attaining an energy storage system with low cost, high safety, long life, and higher energy density is one of the urgent research targets.\(^{[1-3]}\) Benefiting from the advantages of magnesium metal anode, that is, abundant reserves, high volumetric capacity and low redox potential, rechargeable magnesium battery (RMB) was identified as a promising candidate for the next-generation energy storage system with the desired cost, safety, life, and energy density.\(^{[4-8]}\) However, the development of high-performance RMBs is hindered by the lack of satisfactory electrolytes. The conventional electrolytes of RMBs such as Mg(PF_6)_2, Mg(CIO_4)_2, and Mg[N(CF_3SO_2)_2]_2 (Mg(TFSI)_2)-based electrolytes, display high voltage stability (>4.0 V vs. Mg^{2+}/Mg) and well compatibility with most cathode materials, but low Mg plating/stripping efficiency due to their passivating effect on Mg metal anode.\(^{[9-11]}\) Although some Grignard reagent-based electrolytes with high Mg plating/stripping efficiency have been developed, the practical application is restrained by the low voltage stability and the corrosive due to the existence of halogen ion.\(^{[12-14]}\) Recently, some halogen-free organic magnesium borate-based electrolytes with high Mg plating/stripping efficiency, high voltage stability, and noncorrosive nature have been reported, but the practical application of these electrolytes suffers from complex synthesis and high cost.\(^{[15-17]}\)

To solve these issues, researchers take efforts in exploiting other anode materials that possess well compatibility with conventional electrolytes to replace Mg metal anode, that is, developing magnesium-ion batteries (MBs).\(^{[18-20]}\) Among various anode materials for MBs, Ti-based anode materials, such as TiO_2,\(^{[21-24]}\) Li_xTi_2O_12,\(^{[25]}\) Na_2Ti_3O_7,\(^{[26]}\) and Na_2Ti_5O_13\(^{[27]}\) have attracted much attention due to the good structural stability and suitable work voltage. For example, the cation-deficient anatase TiO_2 reported by Koketsu et al.\(^{[24]}\) displayed a reversible capacity of about 150 mAh g\(^{-1}\) at 20 mA g\(^{-1}\) and well-cycling stability for 500 cycles at 300 mA g\(^{-1}\). However, these Ti-based anode materials exhibit unsatisfying rate performance owing to the slow Mg-ion diffusion kinetics. Moreover, the compatibility of Ti-based anode materials with conventional electrolytes has not been well studied.

In this study, two titanium pyrophosphate (TiP_2O_7) paramorphs were synthesized and proposed as anode materials for MBs. Compared with metastable layered TiP_2O_7, the thermodynamically stable cubic TiP_2O_7 displays superior magnesium storage performance. The cubic TiP_2O_7 displays outstanding rate performance (72 mAh g\(^{-1}\) at 5000 mA g\(^{-1}\)) and cycling stability (60 mAh g\(^{-1}\) after 5000 cycles at 1000 mA g\(^{-1}\)), which are better than previously reported Ti-based anode materials for MBs. In addition, the magnesium storage mechanism of cubic TiP_2O_7 was investigated by in situ X-ray diffraction (XRD) and ex situ X-ray photoelectron spectroscopy (XPS) techniques. Moreover, density functional theory (DFT) calculation was employed to investigate the magnesium-ion storage sites and magnesium ion diffusion behavior in cubic TiP_2O_7.

2 | RESULTS AND DISCUSSION

First, XRD was performed to determine the crystal structure of as-synthesized samples. The XRD pattern of precursor (Figure 1A) corresponded well with Ti(HPO_4)_2⋅H_2O (JCPDS 44-0382). The XRD patterns of samples obtained from Ti(HPO_4)_2⋅H_2O precursor by annealing at 600°C and 800°C (i.e., TPO-600 and TPO-800) were well-indexed to the layered TiP_2O_7 (JCPDS 45-0037) and cubic TiP_2O_7 (JCPDS 52-1469), respectively. Those results demonstrate that layered and cubic TiP_2O_7 were successfully obtained from Ti(HPO_4)_2⋅H_2O precursor by annealing at different temperatures. Raman spectra of TPO-600 and TPO-800 were shown in Figure S1. The two bands at about 378 and 1043 cm\(^{-1}\) belong to vibrations of P–O–P and PO_3 units, respectively, corresponding well with the molecule structure of TiP_2O_7.\(^{[28]}\) These two bands are weaker in the Raman spectrum of TPO-600 compared with that of TPO-800, which is ascribed to the poor crystallinity of TPO-600. Besides, the characteristic bands of carbon materials, D and G bands, were also observed in the Raman spectra of both TPO-600 and TPO-800, implying the existence of carbon in as-synthesized samples (Figure S1).\(^{[29]}\) To determine the carbon contents of two samples, the TGA tests under air atmosphere were performed. The mass loss observed at 500–600°C was assigned to the combustion of carbon (Figure S2), indicating that the carbon contents of TPO-600 and TPO-800 are about 3.21% and 2.82%, respectively.

The thermogravimetry (TG) curve (Figure 1B) of precursor displays two weight loss steps at about 200°C and 500°C, respectively, corresponding to two dehydration reactions of Ti(HPO_4)_2⋅H_2O.\(^{[30,31]}\) After two dehydration processes, the metastable layered TiP_2O_7 were obtained. Moreover, the exothermal peak at about 700°C in the differential scanning calorimetry (DSC) curve is attributed to the transformation from metastable layered TiP_2O_7 to thermodynamically stable cubic TiP_2O_7. According to the XRD and TG/DSC results, the evolution of the crystal structure of Ti(HPO_4)_2⋅H_2O with the increase of temperature was summarized in Figure 1C. First, the
Ti(HPO₄)₂·H₂O was transformed to Ti(HPO₄)₂ with the removal of crystal water, which corresponds to the first weight loss step in the TG curve of Ti(HPO₄)₂·H₂O. With the increase of temperature, the condensation reaction of two P–OH groups occurred with the loss of one water molecule, which corresponded to the second weight loss step. This process results in the transformation from Ti(HPO₄)₂ to layered TiP₂O₇, which is mainly accompanied by the shrinkage of crystal lattice along c-axe.³⁰,³¹ By further increasing the temperature, the layered TiP₂O₇ was evolved to a cubic phase which is more stable thermodynamically.

The scanning electron microscope (SEM) image of TPO-600 was displayed in Figure S3A. The nanoflake morphology of TPO-600 was observed, which is similar to that of Ti(HPO₄)₂·H₂O precursor (Figure S4), demonstrating that the morphology was maintained after annealing. The TPO-800 sample is also composed of nanoflakes (Figure S3B). The transmission electron microscope (TEM) image of TPO-600 (Figure 1D) shows that some pore structures existed in the nanoflakes, which may be originated from the removal of water molecules during the annealing process. However, the pore structure was almost disappeared in TPO-800 (Figure 1F), indicating that the higher annealing temperature promoted the mass transfer and crystal growth. The lattice fringes with the spacing of 0.395 nm were observed in the high-resolution TEM (HRTEM) image of TPO-600 (inset of Figure 1D), which matches well with the diffraction peak at about 22.8° in the XRD pattern. Meanwhile, the lattice fringes corresponding to the (210) plane of cubic TiP₂O₇ were observed in the HRTEM image of TPO-800 (inset of Figure 1F). To confirm the chemical composition of two samples, energy dispersive spectroscopy (EDS) was employed. The uniform distribution of Ti, P, and O elements in both TPO-600 and
TPO-800 are displayed in the EDS elemental mappings (Figures 1E and 1G).

To evaluate the magnesium storage properties of as-synthesized two TiP$_2$O$_7$ polymorphs, the coin cells with 0.3 M Mg[N(CF$_3$SO$_2$)$_2$]$_2$ (Mg(TFSI)$_2$) in acetonitrile as the electrolyte and activated carbon (AC) as counter electrode were assembled. The potential of AC electrode is about 2.4 V versus Mg$^{2+}$/Mg.$^{[32]}$ The cyclic voltammetry (CV) curves of two samples were tested at first (Figure 2A). The reduction peaks located at 1.0 and 0.9 V (vs. Mg$^{2+}$/Mg) were observed in the CV curves of TPO-600 and TPO-800, respectively, associating with the intercalation of Mg-ions. At 200 mA g$^{-1}$, TPO-600 and TPO-800 deliver the discharge capacities of 114 and 122 mAh g$^{-1}$ at 20th cycle, respectively (Figure 2B). Compared with TPO-600, TPO-800 displays a lower discharge potential plateau at about 1.0 V (vs. Mg$^{2+}$/Mg) and smaller overpotential, which is favorable for realizing higher energy density and energy efficiency. The differences in charge/discharge curves of TPO-600 and TPO-800 are ascribed to the different crystal phases of these two samples. At first several cycles, two samples display abnormal capacities, which is attributed to the irreversible reaction, such as the decomposition of electrolyte (Figure S5). After 200 cycles at 200 mA g$^{-1}$, TPO-800 still exhibits a discharge capacity of 108 mAh g$^{-1}$, which is slightly higher than that of TPO-600 (Figure 2C).

**FIGURE 2** (A) Cyclic voltammetry (CV) curves in the potential range of 0.6–3.3 V (vs. Mg$^{2+}$/Mg) at 0.1 mV s$^{-1}$ of TPO-600 and TPO-800 after cycling at 200 mA g$^{-1}$ for 10 cycles, (B) charge/discharge curves at 20th cycle, and (C) cycling performance TPO-600 and TPO-800 at 200 mA g$^{-1}$; (D) rate performance of TPO-600 and TPO-800 (the discharge cut-off potential was extended to 0.5 V (vs. Mg$^{2+}$/Mg)) at 5000 mA g$^{-1}$; (E) the charge/discharge curves of TPO-800 at different current densities; (F) the comparison for rate performance of TPO-800 (TiP$_2$O$_7$ nanoflakes) and previously reported Ti-based electrode materials for MIBs; $^{[21–27,33,34]}$ (G) long-term cycling performance of TPO-800 at 1000 mA g$^{-1}$, and (H) the comparison for cycling stability of TPO-800 (TiP$_2$O$_7$ nanoflakes) and previously reported Ti-based electrode materials for magnesium-ion batteries (MIBs).$^{[21–27,33]}$
Meanwhile, the Coulombic efficiencies of TPO-600 and TPO-800 are increased to above 95% during the cycling (Figure S6).

In addition, the rate performance of TPO-600 and TPO-800 were evaluated (Figure 2D,E). Even at the high current density of 5000 mA g$^{-1}$, TPO-800 still achieves a reversible capacity of 72 mAh g$^{-1}$, which is much higher than that of TPO-600 (33 mAh g$^{-1}$). Moreover, the rate performance of TPO-800 (TiP$_2$O$_7$ nanoflakes) is much better than that of previously reported Ti-based electrode materials for MIBs including Li$_4$Ti$_5$O$_12$ nanoparticles,[25] Na$_2$Ti$_3$O$_7$ nanoribbons,[26] TiO$_2$(B) nanowires,[27] TiO$_2$ nanoflakes,[28] Li$_2$TiO$_3$ nanocrystals,[29] cation-deficient TiO$_2$(B) nanowires,[30] cation-deficient anatase TiO$_2$,[31] and TiO$_2$ ultrathin nanocrystals[32] (Figure 2F). Compared with TPO-600, TPO-800 is a more promising anode material for MIBs due to the lower work potential, smaller overpotential and better rate performance. Therefore, we further investigated the long-term cycling performance of TPO-800 (Figure 2G). After 5000 cycles at 1000 mA g$^{-1}$, the capacity of TPO-800 still remains at about 60 mAh g$^{-1}$, demonstrating the excellent cycling stability of TPO-800. This cycling performance is superior compared to that of previously reported Ti-based electrode materials for MIBs (Figure 2H). These results demonstrate that TPO-800 is a promising anode material for MIBs.

To investigate the magnesium storage mechanism of cubic TiP$_2$O$_7$, in situ XRD test was performed. In the discharge process, the (200), (210), and (211) diffraction peaks at 22.4°, 25.2°, and 27.7° shifted to a lower angle, which is associated with the expansion of crystal lattice of TPO-800 caused by the intercalation of Mg$^{2+}$ ions (Figure 3A). In the charge process, these diffraction peaks shifted back to a higher angle and recovered back to the original position, confirming that the intercalation of Mg$^{2+}$ ions into TPO-800 is reversible. Besides, no new peak was detected in the in situ XRD patterns, indicating that the magnesium storage mechanism of TPO-800 is a single-phase intercalation reaction. Based on the in-situ XRD patterns, the evolution of cell parameters of cubic TiP$_2$O$_7$ during the magnesium-ion intercalation/deintercalation process was calculated (Figure 3B). The cell volume change of cubic TiP$_2$O$_7$ during the charge/discharge process is only 3.2%. This means that cubic TiP$_2$O$_7$ is a low-strain anode material for MIBs, which is responsible for the excellent cycling performance of TPO-800.

**FIGURE 3** (A) In situ XRD patterns and (B) corresponding evolution of cell parameters of TPO-800 during charge/discharge process. (C) Ti 2p and (D) Mg 1s XPS spectra of fresh, discharged, and charged TPO-800. (E) EDS elemental mappings of discharged TPO-800. EDS, energy dispersive spectroscopy; XPS, X-ray photoelectron spectroscopy; XRD, X-ray diffraction
To reveal the valence state change of Ti in TPO-800 during the magnesium storage process, XPS spectra of TPO-800 at different states were detected (Figure 3C). For fresh TPO-800, the peak of Ti 2p$_{1/2}$ and Ti 2p$_{3/2}$ are located at 466.4 and 460.6 eV, respectively, which corresponds to Ti$^{4+}$. At discharged state, the binding energies of Ti 2p$_{1/2}$ and Ti 2p$_{3/2}$ peak reduced to 465.2 and 459.4 eV, respectively, indicating the reduction of Ti$^{4+}$ to Ti$^{3+}$ during the intercalation of Mg$^{2+}$ ions. After subsequent charging, the Ti 2p$_{1/2}$ and Ti 2p$_{3/2}$ peak shift back to higher energy position, implying the oxidation of Ti$^{3+}$ to Ti$^{4+}$ during the deintercalation of Mg$^{2+}$ ions. Besides, the Mg 1 s XPS spectra of TPO-800 at different states were also detected (Figure 3D). For fresh TPO-800, no Mg signal was detected. In the Mg 1 s XPS spectrum of discharged TPO-800, strong Mg 1 s peak can be observed, indicating the intercalation of magnesium ions. At the charged state, the intensity of the Mg 1 s peak was weakened, implying an important deintercalation of magnesium ions. Moreover, the EDS elemental mappings of discharged TPO-800 (Figure 3E) also demonstrate the intercalation of magnesium ions into TPO-800. From the above analysis, the theoretical electrode reaction of TiP$_2$O$_7$ in RMBs can be described as the following equation:

$$ Ti(IV)P_2O_7 + 0.5Mg^{2+} + e^- \leftrightarrow Mg_{0.5}Ti(III)P_2O_7 $$

To further understand the magnesium storage behavior of cubic TiP$_2$O$_7$, DFT calculation was employed to investigate the magnesium storage sites and magnesium-ion diffusion paths of cubic TiP$_2$O$_7$. First, the intercalation of one Mg-ion into TiP$_2$O$_7$ unit cell (Ti$_4$P$_8$O$_{28}$) was assumed, and two intercalation sites were selected (Figure S7A). The calculated intercalation energies for Mg$_{0.25}$TiP$_2$O$_7$ and Mg$_{0.25}$TiP$_2$O$_7$−2 are −3.01 eV and −3.26 eV (Table S1), respectively, demonstrating that the intercalation of Mg-ion into TiP$_2$O$_7$ lattice is a thermodynamically favorable process. In Mg$_{0.25}$TiP$_2$O$_7$−2, the Mg site is close to the five-membered ring composed of two [TiO$_6$] octahedrons and three [PO$_4$] tetrahedrons. The lower intercalation energy for Mg$_{0.25}$TiP$_2$O$_7$−2 indicates that the intercalation of Mg ion in this site is more stable in thermodynamics. Therefore, the

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**FIGURE 4** The schematic illustration for simulated Mg-ion migration paths in cubic TiP$_2$O$_7$: (A) Path 1, (C) Path 2 and (E) Path 3, and corresponding migration energy barriers of (B) Path 1, (D) Path 2, and (F) Path 3.
intercalation of the second Mg-ion into the unit cell of Mg_{0.25}TiP_2O_7−2 was further investigated (Figure S7B). The calculated intercalation energies for Mg_{0.5}TiP_2O_7−1 and Mg_{0.5}TiP_2O_7−2 are −5.35 eV and −5.61 eV, respectively (Table S1). In the structure of Mg_{0.5}TiP_2O_7−2 after relaxation, some [TiO_6] octahedrons were transformed to [TiO_5] pyramids due to the extreme elongation of one Ti–O bond, indicating that the Mg sites in this structural model are unreasonable. Therefore, the Mg sites in Mg_{0.5}TiP_2O_7−1 are more possible. In Mg_{0.5}TiP_2O_7−1, both the two Mg sites are close to the five-membered ring. With the intercalation of 2 Mg-ion in per unit cell, that is, 0.5 Mg-ion in per formula, the theoretical specific capacity of TiP_2O_7 is about 121 mAh g\(^{-1}\), which corresponds well with the results of the electrochemical performance test.

To investigate magnesium-ion diffusion behavior of cubic TiP_2O_7, the Mg site in Mg_{0.25}TiP_2O_7−2 was chosen as the initial site and three possible pathways were considered (Figure 4). The migration directions of Path 1 (Figure 4A) and Path 2 (Figure 4C) are approximate parallel with b-axis and c-axis, respectively. For Path 3, the migration direction is first along with c-axis and then turn to along with a-axis (Figure 4B). Notably, the migration energy barriers of magnesium-ion in these three paths are similar, which are about 0.62 eV. This Mg\(^{2+}\) migration energy barrier is lower than that of many other electrode materials for MIBs, such as α-V_2O_5 (1.30 eV)\(^{[35]}\), MoS_2 (0.97 eV)\(^{[36]}\), Mg_{0.5}FePO_4 (1.025 eV)\(^{[37]}\), Mg_{0.5}MoO_3O_5 (1.15 eV)\(^{[38]}\), and VOPO_4 (1.56 eV)\(^{[39]}\). The highest energy corresponds to the process of migrating through the five-membered ring. To confirm that, the energy of magnesium-ion migrating along b-axis to through five-membered ring (Path 4) was also calculated (Figure S8). The migration energy barrier of magnesium-ion in Path 4 is also about 0.62 eV. The above results demonstrate that cubic TiP_2O_7 possess three-dimensional diffusion pathways of magnesium-ion with the highest migration energy barrier of 0.62 eV, which is responsible for the outstanding rate performance of TPO-800. Moreover, this emphasizes the fact that cubic TiP_2O_7 is a promising anode material for high-performance MIBs.

3 | CONCLUSION

Layered and cubic TiP_2O_7 polymorphs are synthesized successfully and investigated as anode materials for RMBs. The electrochemical tests confirm that cubic TiP_2O_7 (TPO-800) displays better magnesium storage performance than the layered phase (TPO-600). The TPO-800 exhibits excellent rate performance of 72 mAh g\(^{-1}\) at 5000 mA g\(^{-1}\) and outstanding cycling stability with the capacity of 60 mAh g\(^{-1}\) after 5000 cycles at 1000 mA g\(^{-1}\). Besides, the magnesium storage mechanism of cubic TiP_2O_7 is demonstrated as a single-phase intercalation/deintercalation reaction with a low volume change of 3.2% by in-situ XRD technology. Based on the DFT calculation, the three-dimensional magnesium-ion migration pathways of cubic TiP_2O_7 are identified. Our work presents a new low-strain, high-rate, and long-life anode material for MIBs, which is significant for the development of MIBs.

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CONFLICT OF INTERESTS

The authors declare that there are no conflict of interests.

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