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MOF derived TiO₂ with reversible magnesium pseudocapacitance for ultralong-life Mg metal batteries

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ABSTRACT

Magnesium metal batteries have attracted much attention due to the good safety, low cost of magnesium and high theoretical volumetric capacity. However, developing magnesium metal batteries is restricted by large polarization and sluggish kinetics during Mg insertion/deinsertion process. Herein, TiO₂ ultrafine nanocrystals derived from Ti-metal–organic-framework (Ti-MOF) are applied as the cathodes in magnesium metal batteries. Remarkably, an ultralong life of the Mg(s) || TiO₂ battery can be obtained during cycling (capacity retention of 75% after 1000 cycles). On the basis of *in-situ* XRD characterization and cyclic voltammetry analysis, a high pseudocapacitive performance is found, which results in the high kinetics. Moreover, according to Arrhenius behavior, carbon skeleton in TiO₂ cathode can facilitate ion migration and Faraday reaction, thus improving the magnesium storage performance.

1. Introduction

The energy storage systems with high energy density, low cost and improved safety have been urged in recent years for the serious energy crisis and people's growing demands [1–4]. As a potential energy storage system, magnesium metal batteries have attracted significant attention due to the advantages of Mg metal anodes. Besides the high abundance of Mg resources, magnesium delivers a high volume specific capacity of 3833 mAh cm⁻³, much higher than that of lithium (2622 mAh cm^{-3}) [5–7]. Thus the Mg metal batteries are one of the most promising alternatives to lithium ion batteries (LIBs) [8,9]. However, there are still some problems to the development of Mg metal batteries. The divalent Mg^{2+} ions induce strong interaction with the host lattice, resulting in sluggish kinetics during Mg insertion [10]. On the other hand, it is difficult to develop appropriate electrolytes for Mg dissolution/deposition with wide electrochemical window, good compatibility with cathodes and high coulombic efficiency [11,12]. Therefore, the development of cathodes with excellent Mg²⁺ reaction kinetics in appropriate electrolytes is crucial for Mg metal batteries [13].

Since Aurbach *et al* reported Chevrel phase Mo_6S_8 as the cathode of Mg metal batteries in 2000 [14], some magnesium battery cathodes with

reasonable electrochemical performance have been developed, for example, the transition metal oxides (V₂O₅, Mn₃O₄, et al) [15,16] and, 2D-layered materials (VOPO₄, MoS₂, TiS₂, et al) [17-19]. Benefiting from the effective contact between the electrolytes and active materials, the nanosizing of the electrode materials has been widely investigated in rechargeable ion batteries [20]. The specific surface area will be larger after the materials are nanosized, giving rise to increasing the active sites and the faster kinetics [21]. Some reactions in Mg metal batteries are impossible for the long ion migration path, but the materials nanosizing can overcome this obstacle [22]. Thus it is an effective method to improve the sluggish Mg kinetics in the electrochemical reaction [20,23,24]. Titanium dioxide (TiO₂), which has been investigated by Xiong *et al* as one of the materials with ultrafast ions storage [25–27], one of the good candidates for its high capacity, has been confirmed to be possible as the cathode in Mg metal batteries [28-30]. Meng et al prepared TiO₂-(B) nanowires by a hydrothermal method and used it as the magnesium battery cathode in all phenyl complex (APC) electrolyte [31], showing only 35 mAh g^{-1} discharge capacity at the low current density of 200 mA g⁻¹. To improve the magnesium storage of anatase TiO₂, Strasser et al tried to introduce the titanium vacancies acting as intercalation sites and the reversible capacity increased from 25 mAh

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Received 28 October 2020; Received in revised form 22 December 2020; Accepted 8 January 2021 Available online 14 January 2021 1385-8947/© 2021 Published by Elsevier B.V. g^{-1} to 140 mAh g^{-1} at very low density of 20 mA g^{-1} [29]. These vacancies can effectively improve the capacity of pure TiO₂, but it is very difficult to control the chemical reaction of manufacturing defects. Thus, it is necessary to find other methods to promote the magnesium storage of TiO₂.

Herein, we have prepared TiO_2 nanocrystals with carbon skeleton and investigated the charge-storage mechanism of anatase TiO_2 in Mg metal batteries by DFT calculations, *in-situ/ex-situ* characterizations and cyclic voltammetry analysis, demonstrating a high pseudocapacitive performance. The pseudocapacitive behavior ensures the fast kinetics, resulting in cathodes with ultralong-life (capacity retention of 75% after 1000 cycles). The targeted introduction of carbon skeleton derived from MOFs can be a viable method to design other magnesium storage cathodes.

2. Results and discussion

2.1. Surface redox reaction in anatase TiO_2

The magnesium insertion mode into an atase $\rm TiO_2$ was analyzed by utilizing density function theory (DFT) calculations. A series of calculations were performed to compare insertion energies and crystal volumes for $\rm Mg^{2+}, MgCl^+, Mg^{2+}MgCl^+$ insertion modes shown in Fig. 1. The $\rm Mg^{2+}MgCl^+$ co-insertion mode shows the lowest insertion energy, indicating the most thermodynamically stable state. Therefore, the $\rm Mg^{2+}MgCl^+$ co-insertion mode can be regarded as the most possible insertion mode based on DFT.

To test the DFT calculation results and investigate the insertion mechanism in anatase TiO₂, *in-situ* X-ray diffraction (*in-situ* XRD) characterizations were performed in the *in-situ* Mg metal battery whose cathode was anatase TiO₂. The peak located at 25° represents the characteristic (101) lattice plane in anatase TiO₂ (Fig. 2a). In the whole charge and discharge process, there is no obvious offset of the (101) peak, indicating that there is no obvious lattice change in the charge/ discharge process. The *ex-situ* X-ray photoelectron spectroscopy (XPS)

analysis is used to further investigate the transformation of the chemical compositions and states of the anatase TiO₂ during the magnesiation/ demagnesiation process. For Mg and Cl, there is no obvious peak at pristine state (Fig. S1), demonstrating the nonexistence of the two elements chemical compositions. As for Ti at pristine state (Fig. 2d), two peaks at ~459.5 eV and ~465.5 eV correspond to Ti (IV) according to the previous report [32]. At discharged state, the peak shifts to the lower binding energy ~458.8 eV, which is the mixture of Ti (IV, 459.5 eV) and Ti (III, 458.2 eV) [32], indicating the lower valance state of Ti after magnesiation. When the cathode is charged, the Ti peak shifts back to the higher binding energy ~459.5 eV, corresponding the oxidation of Ti (III) to Ti (IV). Moreover, as for Mg (Fig. 2b) and Cl (Fig. 2c), there can be observed the peaks at ${\sim}1034$ eV and ${\sim}198$ eV at charged state, respectively. This demonstrates that Mg and Cl exist in the depth of ${\sim}5$ nm under the material surface. And at charged state, there can hardly capture the signals of Mg and Cl, indicating the deinsertion of the Mg and Cl from the cathode. On the other hand, the two elements mapping by HAADF-STEM (Fig. 2e-l) can also reflect the variations of Mg and Cl at discharged/charged state, which is consistent with the ex-situ XPS characterizations. According to the *in-situ* and *ex-situ* characterizations, it is reasonable that the redox reaction in anatase TiO₂ can only exist on the material surface of several nanometers depth. Furthermore, the redox reaction can be expressed as:

Anode:
$$3 \text{ Mg} + \text{MgCl}_2 \leftrightarrow 2 \text{ MgCl}^+ + 2 \text{ Mg}^{2+} + 6e^-$$
 (2.1)

Cathode: 4 TiO₂ + 3e⁻ + MgCl⁺ + Mg²⁺
$$\leftrightarrow$$
 Mg²⁺[Ti₃(III)Ti(IV) O₈]³⁻MgCl⁺ (2.2)

Full:
$$3 \text{ Mg} + \text{MgCl}_2 + 8 \text{ TiO}_2 \leftrightarrow 2 \text{ Mg}^{2+}[\text{Ti}_3(\text{III})\text{Ti}(\text{IV})\text{O}_8]^{3-}\text{MgCl}^+$$
 (2.3)



Fig. 1. DFT calculations results of the three possible insertion modes.

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Fig. 2. (a) In-situ XRD characterization during initial discharge and charge processes; XPS spectra of (b) Mg 1 s, (c) Cl 2p and (d) Ti 2p at pristine, discharged and charged states; (e-h) EDX mapping at discharged state; (i-l) EDX mapping at charged state.



Fig. 3. (a) The schematic diagram of synthesis process of prepared two samples. (b) XRD patterns of the prepared two samples. TEM images of (c) TiO₂-UN and (d) TiO₂-UN@C. (e-h) EDX mapping of TiO₂-UN@C.

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2.2. Electrochemical properties improvement and pseudocapacitive analysis

In this case, it is of great significance to improve the surface of the raw anatase TiO₂, whose capacity is only about 25 mAh g^{-1} at 20 mA g^{-1} [29], inferior to other oxides cathodes in the Mg metal batteries. Inspired by the reports of Liu et al who introduced the in-situ carbon into nanomaterials derived from metal-organic-frameworks [30,33,34], we utilized the Titanium (IV) oxide bis(2,4-pentanedionate) as the Lewis base and terephthalic acid as the Lewis acid to react, obtaining the Timetal-organic-framework (Fig. 3a). After 500 °C sintering in argon and air, TiO2 ultrafine nanocrystals with carbon skeleton (written as TiO2-UN@C) and TiO_2 ultrafine nanocrystals without carbon (written as TiO₂-UN) can be obtained, respectively. The phases of the two samples can be identified as tetragonal TiO₂ (JCPDS No. 78-2486) by the X-ray diffraction (XRD) characterization (Fig. 3b). The crystal structure belongs to the I41/amd space group or anatase structure. The morphology of the two samples, obtained from the transmission electron microscope (TEM), shows that the diameter of TiO₂-UN is $10 \sim 15$ nm (Fig. 3c) and TiO₂-UN@C is 7 nm. Small size of TiO₂ nanocrystals ensure the large specific surface area, facilitating the cathodes contacting with the all phenyl complex (APC) electrolyte and the surface redox reaction. The Raman spectra (Fig. S2a) show the only difference between the two prepared samples is carbon. According to energy dispersive X-ray spectrometry (EDX) mapping, the carbon, titanium, oxygen in TiO₂-UN@C distribute uniformly in the nanocrystals (Fig. 3e-h) and the carbon content calculated from the thermogravimetric analysis (TGA, Fig. S2b) was 14 wt%. The carbon skeleton in the sample can not only enhance the electrical conductivity but also stabilize the TiO₂-APC interface.

To evaluate the electrochemical performance improvement of TiO₂-UN@C, comparing with TiO₂-UN, we utilized the Mg metal as anode to assemble the coin batteries. TiO₂-UN@C showed relatively less polarization, much higher discharge capacity and better rate performance than TiO₂-UN (Fig. S6). Remarkably, at the large current density of 500 mA g⁻¹ (Fig. 4a), TiO₂-UN@C is still able to deliver the capacity of 61 mAh g⁻¹ after 1000 cycles and shows the high capacity retention of 75% (0.025% capacity decrease per cycle). The high discharge capacity and ultralong cycling life can result from the carbon skeleton. As compared with other Mg-storage materials (Fig. 4b) [29,35–39], TiO₂-UN@C can exhibit superior performance than most of the cathodes at various current density, especially at large current density.

Cyclic voltammetry tests at various scan rates (Fig. 4c and Fig. S7a) were performed to investigate the diffusion kinetics process and the capacitive contribution. The obvious oxidation peaks at various scan rates can be observed, which corresponds to the Faradaic reaction from Ti^{3+} to Ti^{4+} [40]. With the scan rate increasing, there is no obvious shift of the location of the oxidation peak, indicating the fast kinetics and



Fig. 4. (a) Long-term cycling performance at 500 mA g⁻¹ of the two samples. (b) Comparison with other Mg-storage materials in magnesium metal batteries. (c) CV curves of TiO₂-UN@C at scan rates ranging from 0.2 to 1.0 mV/s. (d) Capacitive contributions to the charge storage of TiO₂-UN@C and TiO₂-UN. (e) Capacitive contribution (shaded area) to charge storage of TiO₂-UN@C at 1.0 mV/s. (f) Normalized capacity versus scan rate^{-1/2} of TiO₂-UN@C and TiO₂-UN. (g) Arrhenius plots of TiO₂-UN@C and TiO₂-UN in Mg metal batteries.

small polarization. The peak current (*i*) and the scan rate (ν) follow the relationship as below [41]:

$$i(v) = av^b \tag{2.4}$$

The parament *b* is determined by plotting log(i) versus log(v). For a diffusion-controlled process, the peak current is proportional to the square root of scan rate, thus the *b* value is 0.5. The process is a faradaic charge-storage process. Whereas, b = 1 indicates a capacitive or a non-faradaic charge-storage process. The *b*-values of TiO₂-UN@C and TiO₂-UN are 0.7873 and 0.7877 (Fig. S7c), suggesting the mixture of capacitive and diffusion-controlled process. The capacitive and diffusion-controlled process.

$$i(v) = k_1 v + k_2 v^{1/2} \tag{2.5}$$

where $k_1 v$ and $k_2 v^{1/2}$ represent the surface-controlled and diffusioncontrolled processes, respectively. Comparing the capacitive contributions of the two samples (Fig. 4d), TiO2-UN@C shows the lower capacitive proportion than TiO₂-UN, indicating the more proportion of the faradaic charge-storage process. In other words, a more complete redox and higher specific capacity can be obtained in TiO₂-UN@C. At the scan rate of 1.0 mV/s (Fig. 4e), the capacitive contribution of TiO₂-UN@C is 65.08% and the capacitive charge-storage process is the dominant process. The high pseudocapacitance contribution means that the Faraday reactions take place on the shadow sites rather than deep adsorption sites [43]. The shadow sites reside near the surface of nanomaterials, which are easily assessed by cations in electrolyte. However, deep adsorption sites locate in the interior of materials whose activation barriers is higher [44]. Therefore, there is no obvious phase change of TiO₂ in the discharge/charge process. This can also explain the seemingly contradictory results that the lattice change in DFT calculations is not consistent with the unobvious offset of the peak position in in-situ XRD. To investigate the response of the capacity to scan rate, normalized capacities under different scan rates were calculated in Fig. 4f. From 0.2 mV/s to 1.0 mV/s, it can be obviously observed that the normalized capacities of TiO₂-UN vary quite violently whereas the TiO₂-UN@C varies more slightly. This indicates that the capacity of TiO₂-UN@C is more independent on the current and a large proportion of capacity is intrinsic of the nanomaterial. This can also indicate the more proportion of the faradaic charge-storage process, because the faradaic

process is independent of the variation of scan rate. To explore the reason for the capacity improvement with the carbon skeleton, we tested the response of the impedance to temperature to compare with the Arrhenius behaviors of the two samples (Fig. 4g and Fig. S10). The activation energy of TiO2-UN@C is 14.93 kJ/mol, obviously lower than TiO₂-UN (26.44 kJ/mol). The lower activation energy indicates the enhanced ability of ion migration on the TiO₂-APC interface. Moreover, in the GITT tests (Fig.S12), the calculated diffusivity magnitude of TiO₂-UN@C $(10^{-10} \sim 10^{-11})$ is much higher than magnitude of TiO₂-UN $(10^{-12} \sim 10^{-13})$. These two aspects demonstrate the system with carbon skeleton exhibits the faster kinetics. In other words, the ion can easily go through the TiO₂-APC interface, thus faradaic process can be facilitated. This can account for the more faradaic process in TiO2-UN@C and higher discharge capacity than TiO2-UN. For the discharge process, $MgCl^+$ and Mg^{2+} are inserted into the TiO₂-UN@C in the depth of several nanometers under the material surface (Fig. 5). Ti(IV) in TiO₂ nanocrystals obtains the electron and transforms into Ti(III). The surface-controlled process and faradaic process both contribute to the high capacity and ultralong cycling life.

3. Conclusion

In summary, we prepared the anatase TiO₂ ultrafine nanocrystals with carbon skeleton as an ultralong-life cathode material for Mg metal batteries. The Mg storage mechanism is demonstrated to be the pseudocapacitive charge storage by the DFT calculations with *in-situ/ex-situ* characterizations. The carbon skeleton derived from Ti-MOF can lower the activation energy of ion migration and facilitate Faraday reaction, resulting in the higher discharge capacity and ultralong cycling life. The capacity retention of 1000 cycles can achieve as high as 75% at 500 mA g⁻¹ for Mg storage. The investigations of cathodes in Mg metal batteries are still facing challenges, thus this work may open the way for the development of high-performance cathodes in Mg metal batteries.

4. Experimental section

4.1. Synthesis of TiO₂@C ultrafine nanocrystals (TiO₂-UN@C)

Firstly, 0.5242 g titanium (IV) oxide bis(2,4-pentanedionate) (99%, Alfa Aesar) was dissolved into 40 mL N,N-dimethylformamide (DMF)



Fig. 5. The schematic diagram of the charge storage mechanism of TiO₂-UN@C in Mg metal batteries.

followed by 10 min stirring. Then, 1.0 g p-phthalic acid (99%, Aladdin) was added into the solution under intense stirring. The yellow transparent solution was heating at 180 °C in a 50 mL Teflon-lined stainlesssteel autoclave. After 12 h, the autoclave cooled down to 25 °C. The product was washed with alcohol (95%) for several times and dried at 60 °C in a vacuum oven for 10 h. Finally, the precursor was sintered at 500 °C for 4 h at argon atmosphere to obtain TiO₂-UN@C.

4.2. Synthesis of TiO₂ ultrafine nanocrystals (TiO₂-UN)

TiO₂-UN was synthesized by sintering the dried precursor at 500 °C for 4 h in air.

4.3. Preparation of all phenyl complex (APC) electrolyte

The all phenyl complex electrolyte can be prepared in an argon-filled glove box (<1 ppm of oxygen and water) according to the previous report [45]. Specifically, 10 mL AlCl₃/tetrahydrofuran complex solution (0.5 M, Aldrich) was diluted with 5 mL tetrahydrofuran (99.9%, anhydrous). After 6 h stirring, the solution was slowly dropped into 5 mL phenyl magnesium chloride solution (2 M PhMgCl/THF, Macklin, 2.0 M). The APC electrolyte can be formed after another 12 h vigorous stirring.

4.4. Materials characterizations

X-ray diffraction (XRD) was conducted to investigate the sample structure by using a Burker D8 Discover X-ray diffractometer with Cu-Kα radiation. A microscope (JEOL-7100F) was utilized to obtain fieldemission scanning electron microscopic (FESEM) images. Transmission electron microscope (TEM) images and high angular annular dark field image-scanning transmitted electron (HAADF-STEM) images were gained by utilizing another microscope (JEM-2100F/Titan G2 60-300 transmission electron microscope). The VG Multi Lab 2000 instrument was used to collect X-ray photoelectron spectroscopic (XPS) spectra. Raman characterizations were measured with green laser (532 nm) using LABRAM HR Evolution Raman spectrometer. The Tristar II 3020 instrument was used to measure BET specific surface area by nitrogen adsorption at 77 K. DSC- TGA was performed on STA-449C.

4.5. Electrochemical characterizations

The electrochemical properties were tested by assembling of 2016 coin cells in an argon-filled glove box (<1 ppm of water and oxygen). Reference and counter electrode were both metallic magnesium. The separator was the Whatman glass fiber (GF/D). The two TiO₂ samples (TiO₂-UN@C, TiO₂-UN) and APC were used as the working electrode and electrolyte, respectively. The molybdenum foil was placed on electrode materials to avoid the corrosion of the battery shell by the electrolyte. The working TiO2-UN@C electrode was made by mixing prepared TiO2-UN@C samples (70 wt%), acetylene black (20 wt%) and poly(tetrafluoroethylene) (PTFE) (10 wt%). The working TiO2-UN electrode was made by mixing prepared TiO2-UN samples (60 wt%), acetylene black (30 wt%) and poly(tetrafluoroethylene) (PTFE) (10 wt %). The electrode was cut into slices with the mass loading of $1.2 \sim 1.6$ mg cm $^{-2}$. The as-prepared electrodes were dried under vacuum at 60 °C for 12 h. The galvanostatic charge/discharge measurements were tested on LAND CT2001A battery testing system in a voltage range of 0.1-2.6 V (vs. Mg²⁺/Mg). Cyclic voltammetry was tested on Autolab PGSTAT 302 N electrochemical workstation. Electrochemical impedance spectroscopy (EIS) was tested from 0.1 Hz to 1 MHz with an amplitude of 10 mV via Autolab PGSTAT302N.

Declaration of Competing Interest

interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi. org/10.1016/j.cej.2021.128491.

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