



# Octahedral magnesium manganese oxide molecular sieves as the cathode material of aqueous rechargeable magnesium-ion battery



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## ABSTRACT

Aqueous magnesium-ion batteries have shown the desired properties of high safety characteristics, similar electrochemical properties to lithium and low cost for energy storage applications. The micro-sheet morphology of todorokite-type magnesium manganese oxide molecular sieve (Mg-OMS-1) material, which applies as a novel cathode material for magnesium-ion battery, is obtained by the simple hydrothermal method. The structure and morphology of the particles are confirmed by X-ray powder diffraction, X-ray photoelectron spectroscopy, inductively coupled plasma, scanning and transmission electron microscopy. The electrochemical performance of Mg-OMS-1 is researched by cyclic voltammetry (CV), electrochemical impedance spectroscopy (EIS) and constant current charge-discharge measurement. Mg-OMS-1 shows a good battery behavior for  $Mg^{2+}$  insertion and deinsertion in the aqueous electrolyte. When discharging at  $10\text{ mA g}^{-1}$  in  $0.2\text{ mol dm}^{-3}$   $MgCl_2$  aqueous electrolyte, the initial discharge capacity reaches  $300\text{ mAh g}^{-1}$ . The specific capacity retention rate is 83.7% after cycling 300 times at  $100\text{ mA g}^{-1}$  in  $0.5\text{ mol dm}^{-3}$   $MgCl_2$  electrolyte with a coulombic efficiency of nearly 100%.

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## 1. Introduction

Facing the increasingly serious global climate change and environmental issues, many researchers have focused on the study of energy storage technologies and their practical applications, which could take full advantage of using renewable power sources such as natural wind and solar [1–6]. The rechargeable battery with high power, long cycle life and high energy efficiency is an important field for electric energy storage in a large scale. In recent years, several aqueous rechargeable batteries have emerged and shown special safety, low cost and high rate capability [7–11], which overcome the disadvantage of traditional technologies.

Aqueous rechargeable Li-ion batteries (ARLBs), earning broad interests in recent years as a possible large scale energy storage device, were first proposed by Dahn [12–14] and his co-workers in 1994. They used  $LiMn_2O_4$  as the cathode material,  $VO_2$  as the anode material and  $5\text{ mol dm}^{-3}$   $LiNO_3$  aqueous solution as the electrolyte.

This battery system is more preponderant than other aqueous battery systems, such as lead-acid and Ni-Cd battery, due to their environmental friendliness [15,16]. Nevertheless, the low energy density and poor capacity retention are still the major problems for practical applications. One of the key approaches to solve these difficulties is the development of high-performance positive electrode materials. The lithium intercalation compounds such as  $LiCoO_2$  [17],  $LiMn_2O_4$  [18] and ternary doping or carbon coating  $LiMn_2O_4$  [19] as the positive electrode materials have been extensively studied. However, the lithium resource is limited [20]. Therefore, aqueous rechargeable sodium batteries (ARSBs) were garnered further concerns as alternative power sources owing to the abundant sodium reserves. Whereas, only a few ARSBs such as  $AC/Na_{0.44}MnO_2$  [21] and  $Na_2CuFe(CN)_6-NaTi_2(PO_4)_3$  [22] have been studied because of the shortage of applicable sodium compounds for  $Na^+$  ion intercalated. The radius of sodium ion is much larger than that of the lithium ion is the major issue, which makes it more difficult to insert into and extract from the lattices. So the aqueous rechargeable magnesium batteries (ARMBs) [23,24], deriving from the radius of the  $Mg^{2+}$  ion similar to that of the  $Li^+$  ion, with abundant resources and low cost, emerged at this time.

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The todorokite-type magnesium octahedral molecular sieves (Mg-OMS-1), owning one-dimensional (1D)  $3 \times 3$  tunnel ( $6.9 \text{ \AA} \times 6.9 \text{ \AA}$ ) structure through the *b*-axis [25], is one forms of manganese dioxide ( $\text{MnO}_2$ ) minerals. Due to this large tunnel size, magnesium ions might be able to diffuse into the tunnel of Mg-OMS-1. Before, this material with poor electrochemical performance, using as the cathode for lithium-ion battery, have been reported by Nazar's group [26]. In this work, the micro-sheet structure of Mg-OMS-1 was prepared by a hydrothermal method, which shows the better rate capability and cycle performance as the cathode material of aqueous rechargeable magnesium-ion battery.

## 2. Experimental

### 2.1. Preparation and characterization of Mg-OMS-1

The typical synthesis for micro-sheet Mg-OMS-1 was as follows [27,28]. The precursor of sodium-birnessite was first prepared by slowly mixing 0.9 mol NaOH and 12 mmol  $\text{KMnO}_4$  in 100 mL water, and then, adding a mixture solution (100 mL) of 6 mmol  $\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  and 32 mmol  $\text{MnCl}_2 \cdot 6\text{H}_2\text{O}$ . After stirring for 1 h, the obtained suspension was kept at  $25^\circ\text{C}$  for 24 h, and then filtered and washed with deionized water until the pH reaches  $\sim 7$  to obtain the sodium-birnessite precursor. The precursor was ion-exchanged with a 200 mL  $0.1 \text{ mol dm}^{-3}$   $\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  solution at  $25^\circ\text{C}$  for 24 h to replace the sodium ions with magnesium ions. After ion-exchange reaction, the solid sample was collected by filtration and washing several times with deionized water (denoted as Mg-buserite), and finally treated under hydrothermal condition (in a Teflon autoclave at  $150^\circ\text{C}$  for 48 h). The obtained solid was washed with DDW and dried at room temperature to gain Mg-OMS-1.

Phase identification was performed by X-ray diffractometer (XRD, Rigaku TTR III) with Cu  $K\alpha$  radiation ( $\lambda = 0.1514178 \text{ nm}$ ). The morphology and size of Mg-OMS-1 particles were investigated by the scanning electron microscope (SEM, JEOL JSM-6480), transmission electron microscope (TEM) and high-resolution TEM (HRTEM) (FEI Teccai G2 S-Twin), respectively. The inductively coupled plasma atomic emission spectrometer (ICP, Xseries II, Thermo Scientific) and thermogravimetry-differential thermal analysis (TG-DSC, Netzsch STA 449C) were used to define the molecular formula of the samples. Oxidation and reduction states of Mn were investigated by X-ray photoelectron spectroscopy with Al  $K\alpha$  radiation (XPS, ThermoESCALAB 250).

### 2.2. Electrochemical measurement of Mg-OMS-1 electrode

The Mg-OMS-1 cathode slurry was made by mixing the 80% Mg-OMS-1, 10% acetylene black and 10% polyvinylidene difluoride (PVDF) binder dispersed in 1-methyl-2-pyrrolidone (NMP). Electrodes were obtained by painting the slurry onto carbon fiber cloths (CFC,  $1.0 \text{ cm} \times 1.0 \text{ cm}$ ) with the mass loadings of Mg-OMS-1 about  $7 \text{ mg cm}^{-2}$ , and then the electrodes were dried in vacuum at  $80^\circ\text{C}$  for 24 h. The cyclic voltammetry (CV) and electrochemical impedance spectroscopy (EIS) were performed on a potentiostat (VMP3/Z Bio-Logic) controlled by the EC-lab software. The LAND Battery Testing system (model CT2001A, Land, China) was used for the galvanostatic charge and discharge measurements. All the electrochemical tests were performed using a conventional three-electrode electrochemical cell including a working electrode (Mg-OMS-1), a counter electrode (graphite rod) and a reference electrode (saturated calomel electrode, SCE). The electrolytes of  $\text{MgCl}_2$ ,  $\text{Mg}(\text{NO}_3)_2$  and  $\text{MgSO}_4$  with different concentrations were made up using analytical grade chemical reagents and Milli-Q water.

## 3. Results and discussion

### 3.1. Characterization of the Mg-OMS-1

To synthesize the todorokite Mg-OMS-1, the precursor of Na-birnessite with the layered structure was yielded primarily, in which each  $\text{Na}^+$  ion was harmonized with a water molecule in the interlayer distance of  $7.3 \text{ \AA}$ . Then the ion exchange process, signifying the increase of interlayer spacing to  $\sim 9.8 \text{ \AA}$ , is the forming process of Mg-buserite. After treating under hydrothermal process, the layered Mg-buserite transformed to the tunnel structure of todorokite Mg-OMS-1. The Mg-OMS-1 has  $3 \times 3$  tunnels ( $6.9 \text{ \AA} \times 6.9 \text{ \AA}$ ) along the *c*-axis, which is comprised of four edge-sharing  $\text{MnO}_6$  octahedral panel. The panel utilizes the corner-sharing octahedra to link with each other [26]. One magnesium ion and four water molecules, together used for holding the tunnel structure [29], are coordinated inside the tunnels. Therefore, the possible molecular formula of todorokite Mg-OMS-1 is defined by TG and ICP tests. In Fig. 1a, it is clearly found that the large weight loss of  $\sim 7.5\%$  (A point) is mainly due to the loss of adsorbed water, and after that, it begins to loss the hydrated water in the large tunnels. At B point, no water exists as reported in the article [30]. Then, the gradual weight loss at  $350 \sim 600^\circ\text{C}$  is probably due to the process of phase changed. The reduction of manganese stops at C point, which leads to the formation of  $\text{Mn}_3\text{O}_4$  [30]. Combining with the ICP ( $\text{Mg} = 0.0025 \text{ g}$  and  $\text{Mn} = 0.0218 \text{ g}$ ) analyses, the molecular formula of todorokite Mg-OMS-1 can be speculated to be  $\text{Mg}_{1.6}\text{Mn}_6\text{O}_{12} \cdot 5.7\text{H}_2\text{O}$ . Fig. 1b shows the XRD pattern of Mg-OMS-1, which is well consistent with the standard crystallographic tables JCPDS card 13-164. The todorokite Mg-OMS-1 belongs to the monoclinic  $P2_1/m$  space group. The XRD diffraction peak at  $2\theta = 8^\circ$  has a *d* spacing of  $\sim 9.5 \text{ \AA}$  for the (100) planes, which illustrated the existence of the large size aperture of tunnel (the aperture size of tunnel is the above  $6.9 \text{ \AA} \times 6.9 \text{ \AA}$  or even larger that based on the doped metal). The second diffraction peak in line with the (200) planes, of which intensity is bigger than that of the (100) plane, has a *d* spacing of  $\sim 4.7 \text{ \AA}$ , which reveals that a part of  $\text{Mg}^{2+}$  ions replaced the tunnel panel of some  $\text{Mn}^{2+}$  ions in the synthesis process and also influence the electrochemical performance [31] of Mg-OMS-1. These above two main peaks are the characteristic peaks for todorokite Mg-OMS-1 [32].

The morphological features of the materials are shown in Fig. 1c. The Mg-OMS-1 micro-sheet is uniformly distributed, whose length is  $\sim 2 \text{ \mu m}$ . The thickness of Mg-OMS-1 micro-sheet obtained by the hydrothermal method is  $\sim 100 \text{ nm}$  and their shapes are irregular. Fig. 1d and e shows the TEM images of the Mg-OMS-1 samples. From Fig. 1d, several sporadic nanofibers (showed in the dashed rectangle) were observed by the reason that the falling nanofibers derived from the Mg-OMS-1 micro-sheet during the ultrasonic preparing process of the TEM samples. Therefore, it is clearly observed that many nanofibers constitute the micro-sheet in Fig. 1e. The tunnels is original from the observed nanofiber [33], which mainly include a triple-chain width along the *a* and *b* axes. The HRTEM image of Mg-OMS-1 is shown in Fig. 1f. As seen, the *d* spacing of lattice fringes is  $0.94 \text{ nm}$ , which corresponds to the width of  $3 \times 3$  tunnels. This result is in good accordance with the (100) plane of Mg-OMS-1 from the peak at  $2\theta = 9.2^\circ$  in XRD pattern, which also strongly proves the existence of  $3 \times 3$  tunnels. It is effortless to indentify the todorokite Mg-OMS-1 owns the  $3 \times 3$  tunnels structure along the *c*-axis, of which direction parallels to the plane of micro-sheet. Consequently, the length of micro-sheet is just the pathway of magnesium ion insert/extract into/from the Mg-OMS-1. The todorokite Mg-OMS-1, due to its unique tunnel structure such as large tunnel size and short tunnel length for magnesium ion insertion/extraction, could be utilized as the cathode material of aqueous rechargeable magnesium-ion battery.

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