



Manganese dioxides as rechargeable magnesium battery cathode; synthetic approach to understand magnesiation process



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HIGHLIGHTS

- A variety of MnO₂ samples were synthesized and tested in Mg batteries.
- Initial capacity was proportional to the surface area of MnO₂ up to 70 m²/g.
- High capacity of 250 mA h/g was maintained above 70 m²/g regardless of polymorph.
- Physical properties of MnO₂ did not affect the cycling performance significantly.
- This study supported that MnO₂ followed conversion-type reaction in Mg batteries.

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ABSTRACT

A variety of manganese dioxides (MnO₂) are systematically characterized to summarize its magnesiation process in rechargeable Mg batteries, focusing on the influence of its physical parameters on the electrochemical performances. The type and quantity of stabilizing ions (species) in α -MnO₂ improve the initial performance, but these parameters are not significantly affected. Instead, high surface area of MnO₂ above 70 m²/g maintains high initial discharge capacity of about 250 mA h/g regardless of its polymorph, suggesting that the magnesiation process is strongly governed by the active surface area of MnO₂ and tends to be performed by conversion-type reaction rather than intercalation reaction. At present, 70 m²/g of surface area looks high enough to obtain high initial capacity and the capacity is not proportional to the surface area of MnO₂, which implies that the magnesiation process is limited not only by surface reaction but also by kinetically slow process. On the other hand, for all the samples, the discharge capacity fades quickly to less than 50 mA h/g within 10 cycles. The physical parameters of MnO₂ do not have great impacts on the cycling performance. Overall, this synthetic approach provides conclusive evidences for the reaction mechanism of MnO₂ as Mg battery cathode.

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1. Introduction

Back to 2000, a great success of rechargeable magnesium (Mg) battery was achieved by Aurbach et al. in the system comprising a Mg metal anode, a Chevrel phase cathode and an organo-haloaluminate based electrolyte [1]. The prototype Mg battery exhibited operation voltage of about 1.1 V vs. Mg and reversible capacity of approximately 110 mA h/g, and indeed worked very well over >2000 cycles with good capacity retention at a reasonable rate. This demonstration has proven that the Mg battery is capable of competing with Lead-acid batteries and Nickel–Cadmium

batteries. Nowadays, rechargeable Mg batteries reach a turning point to be considered as a post lithium-ion (Li-ion) battery. Li-ion batteries have been widely spreading in the market of portable devices, but there exist some concerns about cost, energy density, power density and durability in scaling up to automobile, aerospace and smart-grid applications. Since commercialized Li-ion batteries have difficulties to meet all the requirements perfectly, in a broad sense of coexisting with Li-ion batteries, the possibility of the Mg batteries as a post Li-ion battery is of practical and scientific interests.

Guided by the great discovery and review articles [1–3], intensive researches on anode, cathode and electrolyte materials have accelerated all over the world, to seek for outstanding features of the rechargeable Mg batteries. Since it was found in 1990 that Grignard-type solutions can be applicable to Mg battery electrolyte

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[4], much effort has been devoted to further improvement of the electrolyte [1–3,5–20]. One of the well-known electrolytes is the $\text{PhMgCl}-\text{AlCl}_3$ system, which is abbreviated as APC and was developed by Aurbach et al. [1–3]. This electrolyte has an advantage of high oxidation stability exceeding 3.0 V on Pt as a cathode current collector. However, the in-situ generated APC electrolyte has complicated equilibriums, generating lots of chloride complexes in the media [3]. Unfortunately, some complexes have been found to severely corrode aluminum and stainless steel as a practical current collector and battery case [5–10,21]. Very recently, non-corrosive electrolytes with higher oxidation stability have been reported [7,11–18]. The widespread researches of electrolytes have opened a new horizon to establish high energy-density type of rechargeable Mg batteries and to position them as a post Li-ion battery.

In targeting such Mg batteries, a major challenge is lack of practical cathode materials besides Chevrel phase molybdenum chalcogenides (Mo_6T_8 , T = S, Se) [1–3,22]. Although the Chevrel phase compounds work very well, the theoretical voltage and capacity are still low (1.2 V vs. Mg and 129 mA h/g), resulting in low energy density as an entire battery system. New cathode materials with high energy density, that is to say, high operation voltage and high capacity, are strongly desired. A variety of classic and unique approaches have been reported so far, but these are still in the exploratory phase [3,5,7,13,19,23–37]. One of the candidates is a well-known material, manganese dioxide (manganese (IV) oxide, MnO_2), which has been studied in various fields of battery [38], capacitor [39] and catalyst [40]. We have previously reported α phase MnO_2 (α - MnO_2) cathode for a rechargeable Mg battery [31] and have tried to understand its reaction mechanisms [41,42]. α - MnO_2 cathode showed higher average voltage of 1.5 V vs. Mg and higher initial capacity of 280 mA h/g than Chevrel phase cathodes [31]. The reversibility of Mn redox species was confirmed, but it faced the issue that the capacity faded quickly to 50 mA h/g within 20 cycles due to loss of the crystallinity of α - MnO_2 . Our previous study by high resolution transmission electron microscopy (HR-TEM) and soft X-ray absorption spectroscopy (sXAS) indicated that during magnesiation (discharge), a new amorphous layer consisting of Mn^{2+} species was formed on the surface of α - MnO_2 but the α - MnO_2 crystalline core remained unused [41]. The Mn^{2+} species was reasonably detected because it was a trace of the reduction reaction of α - MnO_2 during the discharge process. However, the morphology comprising both amorphous shell and unused core suggested that the shell apparently hindered further magnesiation, and then implied that the magnesiation process into α - MnO_2 was not diffusive well and was kinetically slow. Density functional theory (DFT) also supported that a conversion reaction (2α - $\text{MnO}_2 + \text{Mg} = \text{MgO} + \text{Mn}_2\text{O}_3$) was thermodynamically preferable rather than an intercalation reaction (2α - $\text{MnO}_2 + \text{Mg} = \alpha$ - MgMn_2O_4) [42], which was in good agreement with the aforementioned morphological change into amorphous layer. In further theoretical studies, severe structural Jahn–Teller distortion which is comparable to LiMn_2O_4 spinel was observed, if the intercalation reaction of Mg into α - MnO_2 was assumed. Additionally, a huge increase of migration barrier over 1 eV was observed after a certain amount of Mg was presumably intercalated, indicating that Mg^{2+} ion diffusion in the α - MnO_2 host structure was very sluggish [42].

Here in this paper, through a variety of synthetic approaches, we reinforce further mechanistic understanding of the magnesiation process into MnO_2 which has been led by both advanced analyses and theoretical considerations. To provide more strong evidences, we synthesized a series of MnO_2 materials as listed below, controlling some physical properties such as particle size, surface area, type and quantity of stabilizing species and polymorph. In terms of initial and cycling performances, the synthesized materials were systematically characterized as a cathode in the Mg battery system

with Mg metal anode and well-known Mg battery electrolyte. Influences of the physical parameters on the electrochemical performances are discussed, and then some crucial points are newly covered to conclude the reaction mechanism of MnO_2 as Mg battery cathode. Finally, based on a series of studies, we propose some idea to improve further the battery performances.

2. Experimental

2.1. Synthesis of manganese dioxide

Table 1 lists all of the MnO_2 materials used for this study. Sample A, potassium-ion (K^+) stabilized α - MnO_2 nanorod, which was previously demonstrated as a Mg battery cathode [31], was purchased from Erachem Comilog, Inc. Sample B was simply obtained by calcination of the sample A at 400 °C for 3 h under air condition. Compared with these materials, a variety of MnO_2 listed as samples C–O were synthesized in-house by the following methods. On the other hand, commercially available β - MnO_2 (sample P) and γ - MnO_2 (sample Q) were purchased from Erachem Comilog, Inc. for comparison in this study.

2.1.1. α - MnO_2 with different amounts and kinds of stabilizing species

The synthesis of α - MnO_2 has been reported in many papers [43,44]. The preparation methods described here are similar to those references but are modified according to the final products. The K^+ stabilized α - MnO_2 nanorod, which is listed as sample C, was prepared via three steps. First, manganese (III) oxide (Mn_2O_3) was prepared by heating electrolytic manganese dioxide (EMD) powder (Erachem Comilog, Inc) at 700 °C for 4 h under air condition. Then, the obtained Mn_2O_3 was mixed with potassium sulfate (K_2SO_4 , Aldrich, 99%) in the 4.5 M sulfuric acid (H_2SO_4 , Aldrich, 95–97 %) solution at 107 °C (boiling point of this solution), which resulted in the disproportionation of Mn_2O_3 into a soluble Mn^{2+} species and α - MnO_2 as a precipitate. The soluble Mn^{2+} species was removed by a centrifuge machine repeatedly with distilled water. Finally, to remove residual water completely, the solid α - MnO_2 powder was heated at 275 °C for 4 h under air condition.

Followed by this methodology, the amount of K^+ stabilizing ion was controlled by changing the concentration of K_2SO_4 in the solution. In this study, nominal values of 1: 16, 1: 4 and 1: 1 in molar ratio of K_2SO_4 and Mn_2O_3 as precursors were chosen for K^+ stabilized α - MnO_2 , which are listed as samples C, D and E, respectively.

In the similar way, different kinds of ions were stabilized in the α - MnO_2 host structure by replacing K_2SO_4 with M_2SO_4 (M = Rb, Ag and NH_4 , Aldrich, 99%). The nominal value of M to Mn was fixed to be 1: 1 in the solution. H_2O stabilized α - MnO_2 were prepared without adding K_2SO_4 . In order to maintain the H_2O stabilized structure, the heat treatment temperature was reduced from 275 °C to 120 °C. Herein, the H_2O , Ag^+ , Rb^+ and NH_4^+ stabilized α - MnO_2 are listed in Table 1 as samples F, G, H and I, respectively.

2.1.2. MnO_2 with different polymorphs

Different types of MnO_2 were prepared by a simple precipitation method [45]. Stoichiometric amount of 0.3 M manganese nitrate ($\text{Mn}(\text{NO}_3)_2$, Aldrich, 99%) aqueous solution was slowly added to acidic KMnO_4 aqueous solution under vigorous stirring at room temperature, where the concentrations of nitric acid (HNO_3 , Aldrich, 70%) and potassium permanganate (KMnO_4 , Aldrich, 99.5%) were 0.1 M and 0.2 M, respectively. After the precipitation reaction completed, the mixture was aged overnight without stirring. The black product was filtered and rinsed with distilled water and ethanol to remove any chemical impurities. The resultant sample was dried in an oven at 70 °C overnight, which is listed as

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