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Carbon-coated manganese dioxide nanoparticles and their enhanced electrochemical properties for zinc-ion battery applications

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ABSTRACT

In this study, we report the cost-effective and simple synthesis of carbon-coated α -MnO₂ nanoparticles (α -MnO₂@C) for use as cathodes of aqueous zinc-ion batteries (ZIBs) for the first time. α -MnO₂@C was prepared via a gel formation, using maleic acid (C₄H₄O₄) as the carbon source, followed by annealing at low temperature of 270 °C. A uniform carbon network among the α -MnO₂ nanoparticles was observed by transmission electron microscopy. When tested in a zinc cell, the α -MnO₂@C exhibited a high initial discharge capacity of 272 mAh/g under 66 mA/g current density compared to 213 mAh/g, at the same current density, displayed by the pristine sample. Further, α -MnO₂@C demonstrated superior cycleability compared to the pristine samples. This study may pave the way for the utilizing carbon-coated MnO₂ electrodes for aqueous ZIB applications and thereby contribute to realizing high performance eco-friendly batteries.

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1. Introduction

Since manganese dioxide (MnO₂) is relatively cheap, environmentally benign, and electrochemically active, it is considered as a promising energy storage electrode material. Different crystallographic polymorphs of MnO₂ namely α , β , γ , δ , and λ can be obtained by different synthetic routes [1]. Among all these polymorphs, α -MnO₂ has a distinctive [2 × 2] tunnel structure and it has received much attentions. In our previous report, α -MnO₂ nanorods were investigated as zinc-ion battery (ZIB) cathodes. This electrode showed a first discharge capacity of 233 mAh/g at 83 mA/g current density [2]. However, capacity fading under prolonged cycles, which has also been reported by many other groups, is a major drawback of this electrode [3,4]. Additionally, the intrinsically poor electrical conductivity of MnO₂ impedes the electronic path way and consequently, limits its electrochemical performance [4,5].

Naturally abundant, low-cost, and environmentally benign highly conducting materials, such as carbon can be used to overcome the aforementioned limitation of MnO₂. Carbon-coated electrode materials such as transition metal oxides have been widely studied to obtain high performance electrodes [6–9]. Hashem et al. prepared carbon-coated rod-shaped MnO₂ in order to achieve an electrode material with enhanced electrochemical performance for lithium-ion battery (LIB) application [10]. Incorporation of carbon

materials including carbon nanotubes, graphene, and fullerene into MnO₂ increases its surface area and enhances its conductivity because of the formation of a MnO₂/C composite. Hence, these composite materials have been used in high performance supercapacitors and LIBs [11,12]. Mesoporous MnO₂/C spheres with a very large surface area (324 m² g⁻¹) have been synthesized and investigated as an active electrode by Pan et al. [13]. Kim et al. demonstrated the electrochemical performance of an electrode-posit mesoporous MnO₂/C composite electrode for advanced supercapacitors [14]. Moreover, Li et al. reported on carbon coated MnO₂ nanorods obtained via a facile solid state grinding and low temperature calcination as a high performance electrode for supercapacitors [6]. Therefore, from the above discussion, it is clear that the carbon coating strategy is an effective method of improving conductivity and increasing the stability of electrode materials.

Here, for the first time, we report the enhanced electrochemical performance of carbon-coated α -MnO₂ nanoparticles for ZIBs. We have successfully prepared carbon-coated α -MnO₂ nanoparticles by just stirring α -MnO₂ nanoparticles in an ethanolic solution of maleic acid at a mild temperature until a gel is formed and finally it is annealed at lower temperature under Ar atmosphere. The carbon coatings on the electrode material not only increase the electrical conductivity and discharge capacity but also improve the electrode cycleability and capacity retention by preventing manganese dissolution from the active material during electrochemical discharge reaction. Higher discharge capacity and improved cycleability were obtained for the prepared carbon-coated MnO₂ sample.

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53 2. Experimental

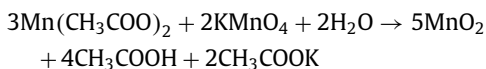
54 The pristine α -MnO₂ nanoparticles were synthesized before
 55 preparing the carbon-coated α -MnO₂ nanoparticles (α -MnO₂@C).
 56 First, 150 mmol of Mn(CH₃COO)₂·4H₂O was dissolved in 30 mL of
 57 distilled water (denoted: solution A). Then, a 50 mL solution of
 58 100 mmol KMnO₄ was added dropwise to solution A. A dark brown
 59 precipitate was obtained immediately after the addition of KMnO₄
 60 solution followed by continuous stirring for 5 h. The resultant
 61 products were then filtered, washed with distilled water followed
 62 by ethanol, and dried at 80 °C for 12 h. Finally, the as-prepared
 63 sample was ground using an agate mortar and annealed at 450 °C
 64 for 5 h before characterization. For preparing α -MnO₂@C, maleic
 65 acid was used as the carbon source. 100 mg α -MnO₂ nanoparticles
 66 were added slowly to a 5 mL ethanolic solution of 25 mg maleic
 67 acid and stirred at a mild temperature (50 °C) until gel formation
 68 was obtained. Then, the obtained gel was heated at 270 °C for 3 h
 69 under Ar atmosphere.

70 The crystalline nature of the powder samples was characterized
 71 using X-ray diffraction (XRD, Shimadzu X-ray diffractometer, Chon-
 72 nam National University, Republic of Korea) with Cu-K α radiation
 73 ($\lambda = 1.54056 \text{ \AA}$) operating at 40 kV and 30 mA over the 2θ range of
 74 10° to 80° in steps of 0.01°. The morphology and elemental distri-
 75 bution of the final products were characterized by scanning elec-
 76 tron microscopy (SEM, Hitachi, Chonnam National University, Repu-
 77 blic of Korea), field-emission transmission electron microscopy
 78 (FE-TEM, Tecnai-F20) with an accelerating voltage of 200 kV, and
 79 energy dispersive X-ray (EDX) spectroscopy (EX-200, Hitachi, Chon-
 80 nam National University, Republic of Korea). For FE-TEM studies,
 81 the samples were dispersed in ethanol by ultrasonication before a
 82 few drops of the dispersion were put on copper grids and held un-
 83 til the solvent evaporated at room temperature.

84 Both pristine and carbon-coated MnO₂ electrodes in this study
 85 were prepared by mixing the active materials, Ketjen black, and
 86 teflonated acetylene black (TAB) with a ratio of 7:2:1, and were
 87 then pasted onto a stainless-steel mesh. The prepared cathodes
 88 were then vacuum-dried at 120 °C for 12 h. The anode was a Zn
 89 metal foil with a thickness of 0.25 mm and 1 M ZnSO₄ (pH 4.0)
 90 aqueous solution was used as the electrolyte. To assemble 2032-
 91 type coin cells, a glass fiber was sandwiched between the cathode
 92 and the Zn foil in the electrolyte. The coin cells assembled in an
 93 open-air atmosphere were aged overnight before electrochemical
 94 measurements. Cyclic voltammetry (CV) was performed at a scan
 95 rate 0.5 mV/s in the voltage range 1.0–1.8 V and electrochemical
 96 impedance spectroscopy (EIS) was performed with an amplitude
 97 of 5 mV at frequencies varying from 100 mHz to 10 kHz using a
 98 Bio Logic Science Instrument (VSP 1075). The electrochemical dis-
 99 charge/charge measurements at room temperature were performed
 100 using a BTS 2004H (Nagano Keiki Co. Ltd., Ohta-ku, Tokyo, Japan)
 101 analyzer.

102 3. Results and discussion

103 In this study, α -MnO₂ was prepared by a simple redox reaction
 104 in DI water between manganese acetate and potassium perman-
 105 ganate and the reaction can be described as follows:



106 A dark brown precipitate was formed immediately after the ad-
 107 dition of the KMnO₄ solution. This simple redox reaction is widely
 108 used to prepare MnO₂ nanoparticles. MnO₂ exhibits poor electri-
 109 cal conductivity, thereby limiting electronic transport and hence
 110 its performance for electrochemical applications. The techniques
 111 of utilizing highly conductive materials such as carbon to improve
 112 the electronic transport and hence electrochemical performance in

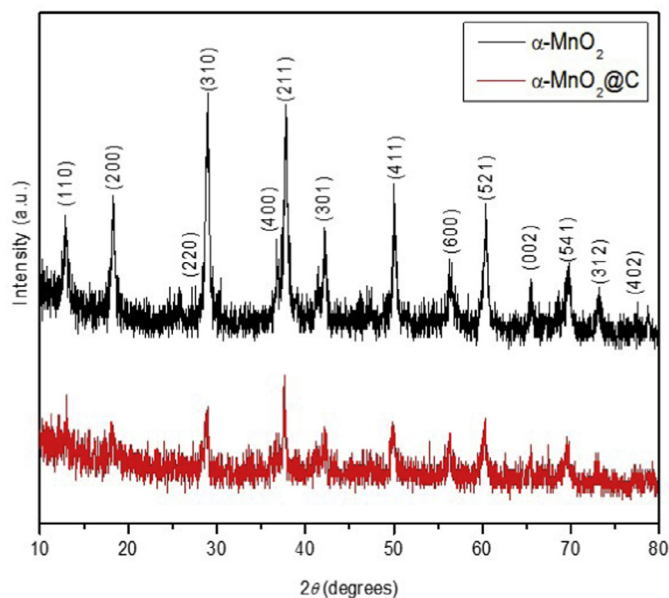


Fig. 1. XRD pattern of the pristine and carbon-coated α -MnO₂ powder.

MnO₂ electrodes are well recorded in previous studies. Recently, Li et al. have prepared carbon-coated MnO₂ nanorods by solid-state grinding and annealing at lower temperature using malic acid as the carbon source [6]. In the present study, we have slightly modified that method for preparing carbon-coated MnO₂ by using maleic acid as the carbon source.

Fig. 1 shows the XRD patterns for both pristine α -MnO₂ and α -MnO₂@C samples. Both of the patterns match well with the pattern of α -MnO₂ (JSPDS card no. 44-0141). This observation suggests that carbon coating does not influence the structure of α -MnO₂ [10]. The calculated values of the pristine α -MnO₂ unit cell parameters were $a = 9.837 \text{ \AA}$ and $c = 2.860 \text{ \AA}$. On the other hand, the lattice parameters of the α -MnO₂@C were $a = 9.731 \text{ \AA}$ and $c = 2.814 \text{ \AA}$. The peak intensities appear relatively low for the α -MnO₂@C sample [5,6].

The surface morphologies of the pristine α -MnO₂ and α -MnO₂@C samples were studied using electron microscopy. The FE-SEM images of the pristine α -MnO₂ and α -MnO₂@C are shown in Fig. 2(a) and (b), respectively. Uniform particles with spherical shaped sizes ca. 20 nm for α -MnO₂ and α -MnO₂@C were observed from these images. Similar SEM images were obtained for the pristine α -MnO₂ and α -MnO₂@C, indicating that no obvious change in morphology occurred after carbon coating [6]. Furthermore, in order to investigate the carbon coating, the sample was characterized by FE-TEM as well. The FE-TEM images recorded for α -MnO₂@C at different magnifications are presented in Fig. 2(c) and (d). The relatively dark shade regions appear to indicate the presence of the clustered α -MnO₂@C. The high resolution TEM image presented in Fig. 2(d) displays distinct fringes with interplanar spacing values of approximately 0.49 nm, corresponding to the (200) planes of α -MnO₂ (JCPDS card no. 44-0141). HR-TEM image recorded for α -MnO₂@C also reveals that the nanoparticles are coated with a thin carbon layer.

EDX mapping for the chemical elements in the sample was also performed and the obtained images in Fig. 3 showing the distribution of C, Mn, and O confirm the presence of carbon in the sample. Also, it is worth noting that the carbon distribution is uniformly spread throughout the selected area of study. This observation appears to suggest that the carbon is uniformly wrapped on the α -MnO₂ particles. Moreover, the EDX analysis estimated the carbon percentage to be 7.9%, the amount being adequate for

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