



## Full Length Article

# Ambient redox synthesis of vanadium-doped manganese dioxide nanoparticles and their enhanced zinc storage properties



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## ARTICLE INFO

## Article history:

Received 26 August 2016  
Received in revised form 26 January 2017  
Accepted 2 February 2017  
Available online 4 February 2017

## Keywords:

Manganese dioxide  
Transition metal doping  
Electrode  
Electrochemical properties  
Zinc-ion batteries

## ABSTRACT

In this work, we demonstrate the first use of a V-doped MnO<sub>2</sub> nanoparticle electrode for zinc-ion battery (ZIB) applications. The V-doped MnO<sub>2</sub> was prepared via a simple redox reaction and the X-ray diffraction studies confirmed the formation of pure MnO<sub>2</sub>, accompanied by an anisotropic expansion of MnO<sub>2</sub> lattice, suggesting the incorporation of V-ions into the MnO<sub>2</sub> framework. V doping of MnO<sub>2</sub> not only increased the specific surface area but also improved the electronic conductivity. When Zn-storage properties were tested, the V-doped MnO<sub>2</sub> electrode registered a higher discharge capacity of 266 mAh g<sup>-1</sup> compared to 213 mAh g<sup>-1</sup> for the pure MnO<sub>2</sub> electrode. On prolonged cycling, the doped electrode retained 31% higher capacity than that of the bare MnO<sub>2</sub> electrode and thereby demonstrated superior cycling performance. This study may pave the way towards understanding the enhancement of the energy storage properties via doping in electrodes of aqueous ZIB applications and also furthers the efforts for the practical realization of a potential eco-friendly battery system.

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## 1. Introduction

The vast developments in devices, such as laptop computers, mobile phones, digital cameras and electric vehicles, have increased the demands for energy storage devices. Presently, lithium-ion batteries (LIBs) play an important role in meeting this demand; however, it is well known that LIBs have safety issues as their components are toxic and flammable [1]. Therefore, researchers are seeking alternative battery systems that are safe, eco-friendly, non-corrosive, non-toxic, and low cost. In 2011, Xu et al. proposed a zinc-ion battery (ZIB) that utilized an environmentally benign electrode and electrolyte to deliver high storage capacities at high current densities (rate capabilities) [2]. Since then, ZIBs have attracted huge attention as one of the most interesting candidates for replacing LIBs [3–8].

Manganese dioxide (MnO<sub>2</sub>) is one of the most widely used electrode materials for battery applications due to its outstanding electrochemical behavior, low cost, and environmental compati-

bility [9]. Depending on the synthetic route used, MnO<sub>2</sub> can form into one of several crystallographic polymorphs, including α-, β-, γ-, δ-, and λ-MnO<sub>2</sub>. The α-, β- and γ-polymorphs possess 1D tunnels in their structures, the δ-MnO<sub>2</sub> has a 2D layered structure, while the λ-polymorph has a 3D spinel structure [9]. Of these, α-MnO<sub>2</sub> has received much interest in energy storage applications owing to its (2 × 2) tunnel structure that facilitates the hosting/release of multi-valent charge carrier ions. Our previous study showed that α-MnO<sub>2</sub> nanorod electrode showed an initial impressive zinc storage capacity of 233 mAh g<sup>-1</sup> at a current density of 83 mA g<sup>-1</sup> [6]. However, during long-term cycling, this electrode showed gradual capacity fading, which is suspected to arise from manganese dissolution and structural degradation related to the Jahn-Teller distortion [4,10]. Further, the high charge-transfer resistance and hence low intrinsic electronic conductivity limits the electrochemical performance of MnO<sub>2</sub> electrodes during cycling [10,11]. In addition, although the eco-friendly storage technology holds promise, just a few materials have been studied as cathodes for ZIB applications. From this viewpoint, the research on improving the performance of already known materials or identifying new materials towards the progression of the ZIB technology gains huge significance.

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One of the established strategies to improve the electronic transport in MnO<sub>2</sub> when used as electrode for LIBs and supercapacitors is transition metal (TM) doping [11–15]. Liu et al. reported that the anisotropic changes in the unit cell lattice parameters introduced by Fe-doping in MnO<sub>2</sub> facilitated enhanced lithium storage capacities at high discharge/charge rates [13]. Hu et al. utilized the first principle calculations and four-probe method to report the significant enhancement of the electronic conductivity in MnO<sub>2</sub> by V-doping [14]. When tested for supercapacitor applications, the V-doped MnO<sub>2</sub> electrode demonstrated excellent cycling stability and improved electrochemical properties. Gulbinska et al. studied the lithium intercalation properties of V-doped MnO<sub>2</sub> prepared by microwave-assisted synthesis. They concluded that the comparable ionic radii of V<sup>5+</sup> (0.53 Å) and Mn<sup>4+</sup> (0.54 Å) ions facilitate the easy inclusion of the V-ion into the MnO<sub>2</sub> lattice [15]. Another comprehensive study on a high-capacity V-doped MnO<sub>2</sub> electrode for primary lithium batteries LIBs demonstrated higher structural stability arising from the stronger Mn-O bonds and limited cell volume expansion during the electrochemical discharge reaction. These features ultimately contribute to their enhanced electrochemical properties [16]. Bearing these in mind and on the basis that there have been no attempts to improve the electrochemical performance of MnO<sub>2</sub> electrodes in ZIBs by TM-doping (to the authors' best knowledge), we herein examine the V-doping into MnO<sub>2</sub> with the aim of improving its electrochemical properties for ZIB applications.

In this work, the bare and V-doped MnO<sub>2</sub> nanoparticles were successfully synthesized via a simple ambient temperature redox reaction. As anticipated, the obtained V-doped MnO<sub>2</sub> electrode revealed an improvement in the electrical conductivity and hence the electrochemical zinc-storage properties of MnO<sub>2</sub>. Moreover, the doped electrode exhibited reduced capacity fading and better cycling ability during galvanostatic measurements.

## 2. Experimental

The samples in the present study were synthesized via a simple ambient redox reaction [5,16]. For the V-doped MnO<sub>2</sub>, 150 mmol of Mn(CH<sub>3</sub>COO)<sub>2</sub>·4H<sub>2</sub>O was dissolved in 30 mL of H<sub>2</sub>O (denoted: Solution A). An optimum amount of V<sub>2</sub>O<sub>5</sub> (0.5 mmol) was dissolved in 20 mL of H<sub>2</sub>O (denoted: Solution B). After this, Solution B was added dropwise to the Solution A (to give Solution C), which was then stirred for 30 min. Meanwhile, 100 mmol of KMnO<sub>4</sub> was dissolved in 50 mL of H<sub>2</sub>O and added dropwise to Solution C. After stirring for 5 h, a dark brown precipitate of MnO<sub>2</sub> was obtained. For comparison purposes, bare MnO<sub>2</sub> was prepared in a similar manner but without the addition of Solution B. The products were filtered, washed with distilled water and ethanol, and dried at 80 °C overnight before annealing at 450 °C for 5 h. The samples were then thoroughly ground using an agate mortar before characterization.

The powder was characterized using X-ray diffraction (XRD, Shimadzu X-ray diffractometer, Chonnam National University, Republic of Korea) with Cu-Kα radiation (λ = 1.54056 Å) operating at 40 kV and 30 mA between 2θ values of 10–80° in steps of 0.01°. Field emission scanning electron microscopy (FE-SEM S-4700 Hitachi, Chonnam National University, Republic of Korea) and energy dispersive X-ray (EDX) mapping (EX-200 Hitachi, Chonnam National University, Republic of Korea) studies were carried out to analyze the morphology and elemental distribution of the particles, respectively. The inductively coupled plasma atomic emission spectroscopy (ICP-AES) was performed using OPTIMA 4300 DV from PerkinElmer (Chonnam National University Center for Research Facilities, Republic of Korea). The synchrotron X-ray absorption near edge structure (XANES) was performed using BL7D beam line at the Pohang Light Source (PLS), a third-generation

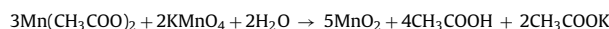
synchrotron radiation source. The K-edge position of a Mn foil at 6539 eV was used to calibrate the monochromator energy. ATHENA software was then used to analyze the obtained spectra.

Nitrogen adsorption and desorption measurements were carried out using a Micromeritics ASAP 2020 (Norcross, GA, USA). The surface areas of the powders were determined using the Brunauer-Emmet-Teller (BET) method. The powders were also examined by XPS (Thermo VG Scientific instrument, Multilab 2000, Chonnam National University Center for Research Facilities, Republic of Korea) using Al Kα as the X-ray source. The spectrometer was calibrated with respect to the C 1s peak binding energy of 284.6 eV.

Both bare and V-doped MnO<sub>2</sub> cathodes were prepared by mixing 70 wt.% of active material, 20 wt.% of Ketjen black, and 10 wt.% of teflonated acetylene black (TAB) into a paste and pressed onto a stainless-steel mesh. Before assembling coin cells, the prepared cathodes were dried overnight under vacuum at 120 °C. Zn metal foil (0.25 mm) was used as the anode and an aqueous solution of 1 M ZnSO<sub>4</sub> (pH 4.0) was used as the electrolyte. The 2032-type coin cells were assembled in an open-air atmosphere by stacking a glass fiber filled with the electrolyte between the prepared cathode and the zinc foil anode. The cells were aged overnight before the electrochemical measurements. Cyclic voltammetry (CV) and electrochemical impedance spectroscopy (EIS) were performed using Bio Logic Science Instrument (VSP 1075). Discharge/charge measurements were carried out at room temperature using a BTS 2004H (Nagano Keiki Co., Ltd, Ohta-ku, Tokyo, Japan). The recovered electrodes were analyzed using X'Pert Pro PANalytical Model X-ray diffractometer (Chonnam National University, Republic of Korea).

## 3. Results and discussion

In this work, the samples were prepared via a simple redox reaction which can be represented as follows:



This redox reaction process is commonly used to prepare both bare and TM-doped MnO<sub>2</sub> samples [17]. The XRD patterns of the V-doped MnO<sub>2</sub> sample compared to that of the bare MnO<sub>2</sub>, in Fig. 1(a), can be well indexed to α-MnO<sub>2</sub> (space group *I4/m*, JCPDS card No. 44-0141) with tetragonal symmetry. This observation confirms that after vanadium doping, the tetragonal crystal structure of α-MnO<sub>2</sub> is largely retained. The (211) peak of the V-doped MnO<sub>2</sub> sample shows a slight shift towards lower scanning angles and is most likely related to the incorporation of V-ions into the MnO<sub>2</sub> structure, as can be seen in Fig. 1(b), resulting in anisotropic changes to the unit cell parameters, which will be beneficial for guest-ion insertion [19]. The unit cell parameters of the V-doped MnO<sub>2</sub> were calculated to be *a* = 9.832 Å and *c* = 2.863 Å. However, the calculated unit cell parameters of the bare MnO<sub>2</sub> sample were slightly lower (*a* = 9.739 Å and *c* = 2.839 Å), as anticipated. Further, the unit cell volumes of the V-doped MnO<sub>2</sub> was determined to be 276.76 Å<sup>3</sup>, compared to 269.27 Å<sup>3</sup> for the bare sample. These observations appear to support the conclusion by Hu et al. that, on V-doping, vanadium ions were located in the tunnels of α-MnO<sub>2</sub> [14]. Another recent study also suggested the possibility of incorporating bigger cations as Ce<sup>3+</sup>, with 0.10 nm of ionic radius, in the tunnels of α-MnO<sub>2</sub> [18]. Nevertheless, in the present case, the average crystallite sizes (*d*) of the V-doped and bare MnO<sub>2</sub> samples calculated from the (310) X-ray line width using the Scherrer equation,  $d = 0.9\lambda / \beta_{1/2} \cos \theta$  (where λ is the X-ray wavelength, β<sub>1/2</sub> is the full width at half maximum, and θ is the diffraction angle) were determined to be 21 and 31 nm, respectively. The XRD studies thus confirmed that V-doping does not significantly change the parent MnO<sub>2</sub> structure.

ICP measurement was performed to measure the vanadium content in the V-doped MnO<sub>2</sub> sample and the results confirmed the

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