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Investigation of electrochemical calcium-ion energy storage mechanism in potassium birnessite

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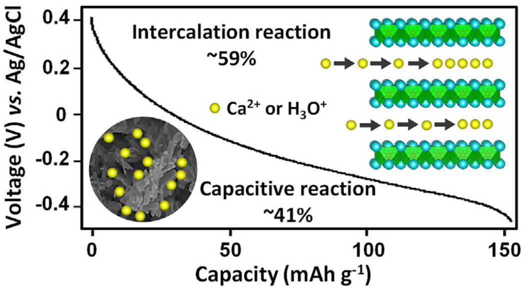
HIGHLIGHTS

- Potassium birnessite is presented as a cathode material for Ca-ion batteries.
- The discharge capacity is 153 mAh g^{-1} with a voltage of 2.8 V (*vs.* Ca/Ca^{2+}).
- The storage mechanism is a combined intercalation and adsorption reaction.

GRAPHICAL ABSTRACT



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ABSTRACT

Calcium-ion intercalation-based batteries receive attention as one type of post lithium-ion battery because of their potential advantages in terms of cost and capacity. A birnessite-type manganese oxide, $K_{0.31}MnO_2{\cdot}0.25H_2O$, is characterized by a layered structure with interlayer distances of ~7 Å. Here, we demonstrate for the first time the electrochemical Ca^{2+} ion intercalation capability of K-bir, and elucidate the calcium-ion storage mechanism. A reversible electrochemical reaction is observed in cyclic voltammograms and galvanostatic cycles. The initial specific discharge capacity is 153 mAh g^{-1} at 25.8 mA g^{-1} (0.1 C) in a 1 M $Ca(NO_3)_2$ aqueous electrolyte, with the average discharge voltage of 2.8 V (*vs.* Ca/Ca^{2+}). X-ray diffraction, transmission electron microscopy, and elemental analyses confirm that Ca^{2+} ion transport is mainly responsible for the electrochemical reaction. A kinetic analysis using CVs with various scan rates indicates that the reaction mechanism can be described as a combined reaction of a surface-limited capacitance and a diffusion-controlled intercalation. In addition, 3D bond valence sum difference maps show the 2D network for conduction pathways of calcium ions in the structure. This work demonstrates that birnessite-type manganese oxide could be a potential cathode material for calcium-ion batteries.

1. Introduction

Demands for efficient and safer energy storage are increasing alongside the recent development of smart energy grids and renewable energy technologies, which include specific applications such as portable electrical devices and electric vehicles [1–3]. To satisfy these requirements, next generation battery systems are being actively investigated [4]. For over two decades, rechargeable lithium-ion batteries (LIBs) have been the most successful energy storage systems [5]. However, cost and safety issues with lithium have induced the emergence of post-LIB technologies [6,7].

Recently, multivalent calcium-ion batteries (CIBs) have received attention as one of the post LIBs. The abundance of calcium resources can make CIBs cost effective. Calcium has a standard reduction

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potential of 0.17 V above lithium ($E^\circ = -2.869$ V *vs.* SHE for Ca^{2+}/Ca) that makes CIBs capable of a higher energy density compared to other multivalent ions such as magnesium, aluminum, and zinc [8]. In addition, calcium ion have a lower charge density than other multivalent ions, which may lead to relatively faster diffusion in a host material [9,10]. Ponrouch et al. reported the feasibility of calcium plating and stripping using conventional organic electrolytes at elevated temperatures [8]. To use calcium metal as a negative electrode in a cell, suitable cathode materials that store calcium ions are required. However, only a few cathode materials are reported so far to show electrochemical activity in calcium-containing electrolytes, such as V_2O_5 [11–13], $CaCo_2O_4$ [13], WO_3 [14], and Prussian-blue analogues [9,15–18].

Birnessite is one of the polymorphs of manganese oxides with a layered structure, and has a general chemical formula, $A_xMnO_2{\cdot}nH_2O$ (A = alkali or alkaline earth metals). Birnessite consists of bi-dimensional sheets of edge-shared MnO_6 octahedra, with cations and crystal water located in the interlayer space [19,20]. Owing to its structural characteristics, it has been studied as a capacitor [20–22] or battery host material capable of intercalating various cations such as lithium [23], sodium [24], potassium [25], magnesium [26–28], and zinc [29] ions. Birnessite is able to provide low toxicity, low cost, and a relatively high capacity as a result of a structure that is close-packed but nonetheless has a wide interlayer spacing of ~7 Å [23,24,30]. In addition, birnessite containing crystal water show facile ionic diffusion kinetics as well as structural stability [24,27,31]. Depending on the interlayer cations, birnessite can be called ‘A’ birnessite, where ‘A’ is a metal, such as lithium, sodium, magnesium, potassium, or calcium [23–28,32–34]. The presence of chemically synthesized calcium birnessite [33,34] implies a possibility of electrochemical calcium insertion into this structure, and motivated us to study the properties of this reaction.

In this work, we investigate a potassium birnessite, $K_{0.31}MnO_2{\cdot}0.25H_2O$ (K-bir), as an electrochemical calcium-ion storage host material. Calcium birnessite requires a complicated synthetic process, but a potassium birnessite has a relatively simple process [34]. Consequently, potassium birnessite was selected as a host material for this work. Preliminary studies suggested that the electrochemical reaction did not involve pure intercalation but a combined reaction of capacitance and intercalation. Kinetic analysis based on cyclic voltammograms (CVs) was performed to quantitatively estimate the relative contributions of the surface-limited capacitive reaction and the diffusion-controlled intercalation, elucidating the mechanism of the calcium-ion storage. Evidence of calcium-ion intercalation is provided by X-ray diffraction, elemental analyses, and transmission electron microscopy. Bond-valence-sum mapping calculations are used to provide additional support for calcium-ion diffusion in the structure. This is the first demonstration, to the best of our knowledge, of electrochemical intercalation of calcium ions into birnessite.

2. Experimental

2.1. Preparation of K-bir

Potassium birnessite $K_{0.31}MnO_2{\cdot}0.25H_2O$ was prepared from $KMnO_4$ (Sigma-Aldrich, 99%) by thermal decomposition at 350 °C for 10 h in air, as described previously [35]. After being cooled to room temperature, the obtained products were washed with deionized (DI) water and dried at 80 °C in air for 4 d.

2.2. Materials characterization

The structure of the synthesized birnessite was analyzed using powder X-ray diffraction (XRD, Rigaku Miniflex 600) with Cu Kα radiation ($\lambda = 1.5418$ Å) and a secondary graphite (002) monochromator. XRD patterns were collected between 5° and 70° in 2θ angles with a scanning step of 0.05° and a step duration of 1.2 s. Rietveld refinement of XRD data was carried out using GSAS software [36]. The chemical formula was identified by inductively coupled plasma optical emission spectroscopy (ICP-OES, Varian 700-ES). The structural water content of the birnessite was confirmed by thermogravimetric analysis (TGA, Rigaku Thermo plus EVO2) at a heating rate of 10 K min^{-1} under a N_2 flow. The morphology of the samples was verified using a high-resolution field-emission scanning electron microscope (HR FE-SEM, Hitachi SU-8020) equipped with an energy-dispersive X-ray spectrometry (EDX) detector, and field-emission transmission electron microscope (FE-TEM, Hitachi HF-3300). The structural and elemental analysis of the birnessite after electrochemical cell cycles were also carried out using a FE-TEM equipped with an EDX detector.

2.3. Electrochemistry

The electrochemical measurements of the birnessite were carried out using laboratory-fabricated cells with three electrodes (Fig. S1). An activated carbon (Daejung Chemical) pellet and Ag/AgCl (saturated) were used as the counter and reference electrodes, respectively. A slurry for the working electrode was made with 80 wt% birnessite as the active material, 10 wt% super P carbon black (Timcal Graphite & Carbon) as a conductive carbon, and 10 wt% polyacrylonitrile (PAN, Sigma-Aldrich, average Mw 150,000) as a binder, that were mixed and dispersed in 1-methyl-2-pyrrolidinone (NMP, Sigma-Aldrich, 99.5%). This slurry was cast onto a 20 μm stainless steel foil (Wellcos Co., SUS-316L) and dried in air at 80 °C. After drying, the birnessite electrode was roll-pressed and punched into disks. The loading of the active material on each electrode was ~1.5 mg cm^{-2}. A glass fiber filter (Whatman, GF/A) was used as a separator. The aqueous electrolyte used was 1 M $Ca(NO_3)_2{\cdot}4H_2O$ (Alfa-Aesar, 99%). Potentiostatic CV and galvanostatic discharge/charge measurements were performed using the EC-Lab software on a VMP3 multichannel potentiostat (BioLogic Science Instruments SAS) at room temperature.

3. Results and discussion

3.1. Synthesis

$KMnO_4$ is thermally decomposed at 350 °C [35], into compounds such as K_3MnO_4, K_2MnO_4, MnO_2, and O_2. Products from this reaction are soluble in water except for MnO_2 having a birnessite structure (Fig. 1a), which has potassium ions and water intercalated between the layers. Thus, the birnessite is easily separated from the other products by vacuum filtration with deionized (DI) water. The synthesized material is confirmed to have the birnessite structure by the powder X-ray Rietveld refinement (Fig. 1b). All the diffraction peaks match well with those for the previously known monoclinic structure (space group *C2/m*, no. 12) [30]. The crystal and atomic parameters determined by the Rietveld method are summarized in Table S1. The first peak, (001) at 12.4° (2θ), indicates the interlayer spacing (~0.71 nm) between MnO_2 sheets. The (001) *d*-spacing is also confirmed by the TEM image (Fig. 1d). Homogeneous particle sizes are observed in the range of 100–300 nm through SEM image (Fig. 1c), and BET surface area is measured as 13 m^2/g (Fig. S2). The exact chemical formula—particularly the potassium and crystal water content—is determined to be $K_{0.31}MnO_2{\cdot}0.25H_2O$ by combined analyses of ICP (Table S2) and TGA (Fig. S3) data.

3.2. Electrochemical studies

In the calcium aqueous electrolyte, K-bir delivers the first discharge and charge capacities of 153 mAh g^{-1} and 130 mAh g^{-1}, respectively, when cycled between −0.45 and 0.85 V (*vs.* Ag/AgCl) at 0.1 C rate (Fig. 2a). The rate of 1 C is defined as 258 mA g^{-1} based on one electron transfer per $K_{0.31}MnO_2{\cdot}0.25H_2O$ formula unit, where the “n C rate” is defined as the rate of discharges (or charges) that is completed in 1/n h. In addition, the discharge and charge are defined as reduction (calcium