Origin of storage capacity enhancement by replacing univalent ion with multivalent ion for energy storage

Junlin Wu [a, b], Qian Yang [a, b], Jia Li [a], Lixiang Zhong [a, b], Liubing Dong [a, b], Wenbao Liu [a, b], Jian Mou [a, b], Chengjun Xu [a, *]

[a] Graduate School at Shenzhen, Tsinghua University, Shenzhen 518055, China
[b] School of Materials Science and Engineering, Tsinghua University, Beijing 100084, China

ARTICLE INFO

ABSTRACT

The storage capacity or capacitance of a material could be enhanced significantly by replacing univalent ion with multivalent ion in the energy storage field. However, the mechanism of the enhancement is unknown. Here, we dedicate to understand the origin of the enhancement on the storage capacity of multivalent ions over univalent ions. The experimental results show that the specific capacitance and charge-discharge rate of α-MnO$_2$ are doubled by using Ca^{2+} cation to replace Na$^+$ cation in the electrolyte as the energy storage medium. The First-principles calculations are used for a further understanding for the enhancement on the capacity, charge rate and the insertion mechanism. The given number of cations (two Na$^+$ or Ca^{2+} ions) can be preferably stabled in one α-MnO$_2$ unit cell to decrease the irreversible tetragonal-orthorhombic deformation caused by John-Teller effect. Because the insertion of Ca^{2+} triggers double electron transfer than Na$^+$, the capacity and charge-discharge rate of α-MnO$_2$ using Ca^{2+} cation as storage medium are doubled. The result pave a path to understand the enhancement on the storage capacity by replacing the univalent ions (such as Li$^+$, Na$^+$, K$^+$, etc.) with multivalent ions (such as Ca^{2+}, Mg^{2+}, Zn^{2+}, Al^{3+}, etc.).

1. Introduction

Manganese dioxide (MnO$_2$) has been widely investigated in electrochemical applications, such as Li-ion batteries [1,2], Li-O$_2$ batteries [3,4], Na-ion batteries [5,6], supercapacitors [7,8], etc., due to its low cost, nontoxicity and high capacity [9—13]. α-MnO$_2$ is one of the polymorphs which are able to accommodate protons [14,15], univalent cations [16,17] and multivalent cations [18,19] in 2 × 2 tunnel with appropriate size and stable structure [20—23]. The storage capacity or capacitance of α-MnO$_2$ could be enhanced significantly by replacing univalent ion with multivalent ion in the energy storage field.

First-principle density functional theory (DFT) calculation is widely accepted and utilized to verify and predict the property of electrode materials in experiment, such as Li-ion, Na-ion, Mg-ion battery, etc [17,18,24]. For instance, it is reported that α-MnO$_2$ can achieve the initial capacity as high as 360 mAh g^{-1} in rechargeable

Li-ion batteries [25]. The calculated charge-discharge process and potential profile through First-principle DFT calculation agree well with the experimental data [16,17]. With the development and demand of large scale systems such as electric vehicles and grid systems, the Na-ion batteries have gained considerable renewed interest due to their low-cost advantage [26,27]. The insertion of Na ion into MnO$_2$ delivers a capacity over 200 mAh g^{-1} [5]. The insertion of Na ion in Na$_{0.44}$MnO$_2$ was studied by using DFT calculations for Na-ion batteries, in which seven intermediate phases were found and the calculated potential plateaus agreed well with experiments [24]. α-MnO$_2$ has also been used as cathode materials in Mg-ion batteries with the initial capacity of 280 mAh g^{-1} [28], and its magnesiation has been studied recently [18]. In addition, because of the high pseudocapacitance of α-MnO$_2$, it is a promising electrode material for the high energy density of supercapacitors. The amorphous α-MnO$_2$ nanosheets of controllable width could achieve a specific capacitance over 500 F g^{-1} [7,8,29—31].

However, compared to the extensively theoretical study of lithium capture in α-MnO$_2$ for Li-ion batteries, the structure of α-MnO$_2$ when used as supercapacitor electrodes is rarely characterized. In our previous works, charge storage mechanism of α-MnO$_2$

* Corresponding author.
E-mail address: vivaxuchengjun@163.com (C. Xu).

was explored in the aqueous electrolytes containing univalent and bivalent cations [32,33].

In this work, we explored the charge storage mechanism of α-MnO$_2$ in electrolytes containing Na$^+$ and Ca^{2+} cations by both experiment and DFT calculations. The experimental results show that the capacity and charge-discharge rate of α-MnO$_2$ is doubled by simply replacing the electrolyte containing Na$^+$ cations with the electrolyte containing Ca^{2+} cations with the similar cation activity. Meanwhile, the DFT calculations prove that two Na$^+$ or Ca^{2+} cations can be stored in one unit cell of α-MnO$_2$. But more cations than two in the tunnel will lead to strong John-Teller effect, which will cause irreversible distortion of the structure. The calculated results compensate for and agree well with the experimental findings from the atomic scale, which enlighten us to understand the enhancement on the storage capacity by replacing the univalent ions (such as Li$^+$, Na$^+$, K$^+$, etc.) with multivalent ions (such as Ca^{2+}, Mg^{2+}, Zn^{2+}, Al^{3+}, etc.).

2. Methods

2.1. Experimental

MnO$_2$ powder was prepared by self-reacting micro-emulsion method. The details of preparation can be referred to in our previous work [34]. Electrodes were prepared by mixing as-prepared MnO$_2$ powder (the active material), acetylene black and polytetrafluoroethylene (PTFE) with weight ratio of 7:2:1. 70 mg MnO$_2$ powder and 20 mg acetylene black were first mixed and dispersed in ethanol for 30 min under ultrasound atmosphere. Then the ink was dried at 80 °C for 4 h to get dark mixed powder and 10 mg PTFE was added to get a paste. Then the paste was dried at 80 °C and turned into syrup after 1 mL 1-methy-2-pyrrolidinone (NMP) was added into it. The syrup was cold rolled into a thick film with the thickness of ~40 μm. 1 × 1 cm^2 pieces (usually 3 mg) were cut and then hot-pressed on a titanium plate under 100 MPa at 80 °C.

X-ray diffraction (XRD) measurement of MnO$_2$ sample was operated on TW3040/60 diffractometer (Tanalygical Company, Holland) using Cu-Kα radiation. Electrochemical tests were performed at a Bio-Logic VMP3 electrochemical station. A piece of platinum and the saturated calomel electrode (SCE) were used as the counter and at the reference electrode respectively. Cyclic voltammetry (CV) tests were performed with the scan rate of 2 mV s^{-1} and the potential of 0.1–0.7 V. The specific capacitance (C) of MnO$_2$ was calculated according to Equation (1):

$$C = \frac{\int idV}{2v\Delta V} \qquad (1)$$

where i is the specific current (A g^{-1}), $\int idV/2$ is half of the integrated area of the CV curve, v (V s^{-1}) is the potential scan rate, ΔV (V) is the potential window.

2.2. Computational

DFT calculations were performed with the Vienna ab-initio simulation package (VASP) with projector augmented wave (PAW) pseudopotentials. The Perdew-Burke-Ernzerhof (PBE) exchange-correlation functional is used with the Hubbard U-corrections to correct the self-interaction error introduced by the highly localized d orbitals [35–37]. Numerical convergence to less than 3 meV per α-MnO$_2$ unit was ensured by using cutoff energy 520.0 eV and appropriate Gamma centered k-point mesh with the density of at least 0.03 Å^{-1}. The energy converges to 1 × 10^{-5} eV per atom and the force converges to 0.02 eV Å^{-1}. In the dilute limit, a

1 × 1 × 2 supercell of α-MnO$_2$ was employed to calculate the preferred insertion site. And a single cell was returned to beyond the dilute limit. We used the PBE + U method to treat the static correlations by introducing a Hubbard type potential to describe the d-part of the Hamiltonian. The value of U is set to be 3.9. This value works well for a number of Mn oxides in previous reports [17,18,24].

3. Results and discussion

3.1. Experimental

Fig. 1a shows the XRD pattern of the as-prepared MnO$_2$ sample. The broad and low-intensity peaks indicate the amorphous nature and small size of particles. Broad peaks at 2θ = 37.0° and 65.8° can be indexed to characteristic peaks of α-MnO$_2$ (JCPDS No. 44-0141). According to our previous work [34], the as-prepared α-MnO$_2$ presents as individual particle with size of about 4 nm. In this work, this amorphous nano-sized α-MnO$_2$ is used in the following electrochemical tests. Fig. 1b shows the SEM image of as-prepared MnO$_2$. The sample is composed by nanostructured particles, on which the surface is wrapped by tiny nanosheets. Because of the nano size of these nanosheets, only two broad peaks are shown in the XRD pattern. Also, the huge specific surface area of nanosheets has provided many active sites for the adsorption and insertion of cations, which contributes to the excellent electrochemical performance of α-MnO$_2$ electrode. As the characterization of Na$^+$ in α-MnO$_2$ has widely been investigate in Ref. 5, 6, 12, 24 and 27, some fundamental characterization of α-MnO$_2$ electrode in Ca(NO$_3$)$_2$ electrolyte is provided in Supplementary Materials. Fig. S1a shows the CV curves of the electrode under fast scanning rate, and Fig. S1b shows the variation of the specific capacity of α-MnO$_2$ with the scan rate, which proved that α-MnO$_2$ has good high-current discharge characteristics. Fig. S2a is the constant current charge-discharge curve of α-MnO2, as well as Fig. S2b shows the cycle life of α-MnO$_2$ electrode in 0.1 mol dm^{-3} Ca(NO$_3$)$_2$, which means α-MnO$_2$ electrode has good cycle life in electrolytes containing divalent ions.

The impact of cations on the capacity of α-MnO$_2$ is investigated in experiments. The CV curves shown in Fig. 2 were measured in 0.2 mol dm^{-3} NaNO$_3$ aqueous electrolyte and 0.1 mol dm^{-3} Ca(NO$_3$)$_2$ aqueous electrolyte at the scan rate of 2 mV s^{-1}. The pH value (pH = 6.0) and the concentration of anion (NO$_3^-$) are equal in both electrolytes so that the performance of α-MnO$_2$ is driven by the two different cations. As depicted in Fig. 2, the shape of both CV curves is quasi-rectangular, which illustrates the pseudocapacitive storage mechanism of α-MnO$_2$. Obviously, the area encircled by the CV curve in the Ca(NO$_3$)$_2$ solution is much larger than that in the NaNO$_3$ solution. The C values of α-MnO$_2$ are 336.32 and 194.17 F g^{-1} in Ca(NO$_3$)$_2$ and NaNO$_3$ electrolytes, respectively. Although the concentration of Na ions is twice of that of Ca-ions, the C value of α-MnO$_2$ in 0.1 mol dm^{-3} Ca(NO$_3$)$_2$ electrolyte is still 1.7 times higher than that in 0.2 mol dm^{-3} NaNO$_3$ electrolyte. Therefore, though the diffusion and the mobility through the α-MnO$_2$ tunnel may be different for the two cations in corresponding electrolyte, two electrons are stored when one Ca^{2+} comes into the α-MnO$_2$ tunnel whereas only one electron is stored when one Na$^+$ comes into the tunnel. In other words, the capacity of α-MnO$_2$ in Ca(NO$_3$)$_2$ is doubled by replacing the Na$^+$ with Ca^{2+} cation.

According to our previous work, the electrochemical performance of α-MnO$_2$ is only affected by the properties of cations [32,33] (i.e. species, concentration, etc.). Considering the slight solution of CaSO$_4$, the performance of α-MnO$_2$ is investigated by the CV test in Na$_2$SO$_4$ and Ca(NO$_3$)$_2$ electrolytes with various concentrations. The calculated C values are shown in Table 1, in which we