# Synthesis and kinetic analysis of $\alpha$ -MnO<sub>2</sub> nanowires for supercapacitor electrode

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Abstract: As the electrode material of supercapacitor,  $MnO_2$  materials have attracted extensive concern and its electrochemical performance has been continuously optimized, but the kinetic analysis is rarely discussed. Herein,  $\alpha$ -MnO<sub>2</sub> nanowires with a uniform morphology were synthesized by hydrothermal method, which exhibits proven electrochemical property like outstanding circulation stability, demonstrated rate performance and high specific capacitance. In addition, diffusion-controlled Faradaic procedure and surface capacitance action were calculated and analyzed in detail.

**Keywords:** α-MnO<sub>2</sub>; Nanowires; Supercapacitor electrode; Kinetic study

## 1. Introduction

The supercapacitor, an energy storage devices with a future, has many strengths like environmental friendliness, high power density, superb cycling stability, which not only has been applied to hybrid electric vehicles and portable electronic devices, but has potential application prospects in solar cell board and electric vehicles, etc. [1-7]. Transition metal oxides (TMO) is a promising electrode material for supercapacitors in recent years, such as RuO<sub>2</sub>, Fe<sub>2</sub>O<sub>3</sub>, V<sub>2</sub>O<sub>5</sub>, Co<sub>3</sub>O<sub>4</sub>, MnO<sub>2</sub> and Mn<sub>3</sub>O<sub>4</sub>, etc. [8-11]. Among these TMOs, MnO<sub>2</sub> is widely favored because of its non-toxic, high theoretical capacitance and natural abundance [12-16]. MnO<sub>2</sub> has a variety of crystal structures in nature, such as  $\varepsilon$ -,  $\gamma$ -,  $\beta$ - and  $\alpha$ -types, etc. [17-18]. Ragupathy et al. pointed out that different structures of MnO<sub>2</sub> would have different electrochemical properties [19]. Especially, the  $\alpha$ -MnO<sub>2</sub> with its 2 × 2 tunnels are conducive to the storage of cations in the electrolyte (such as Li<sup>+</sup> and Na<sup>+</sup>, etc.) and promote the ion diffusion thus obtaining an ideal specific capacitance [20]. But the appliance of  $\alpha$ -MnO<sub>2</sub> in supercapacitors is limited by its unstable crystal structure and poor conductivity [21]. The electrochemical function of MnO<sub>2</sub> can be ameliorated adopt some measure include: controlling the morphology, and various nanostructured  $\alpha$ -MnO<sub>2</sub> (such as nanosheets, nanorods, nanowires) have been reported [22-24]. Among them, one-dimensional nanowire structure is the smallest dimension of effective electron transport and active site exposure, therefore it is hopeful to give free rein to an important role in electronic devices [25]. However, most of the previous works only reported the electrochemical properties of α-MnO<sub>2</sub> nanomaterials, the analysis and explanation of energy storage kinetics were relatively rare.

As known, Conway and Dunn reported that the supercapacitor can be divided into two categories, such as Faradaic pseudocapacitor and electric double layer capacitor (EDLC) [26-28]. In recent years, it has been found that the diffusion-controlled Faradaic behavior exists in the electrode materials of the supercapacitor. In fact, these two electrochemical behaviors working at the same time, but the proportions are different. Sarkar et al. reported MoS<sub>2</sub>/r-GO as electrode materials for supercapacitors. By changing the distance between MoS<sub>2</sub> layers and increasing the specific surface area, the diffusion-controlled Faradaic effect is enhanced, which helps to improve the diffusion of hybrid materials. The contribution values of diffusion-controlled Faradaic behavior and surface capacitive behavior are calculated in the scanning rate range of 10-500 mV s<sup>-1</sup>. At 10 mV s<sup>-1</sup>, the contribution of diffusion-controlled Faraday behavior to capacitance is only 15%, and it's observed that the contribution of surface capacitance behavior rises as the scanning rate rises [29]. Zhao et al. reported an electrochemical way to synthesis Li<sub>4</sub>Mn<sub>5</sub>O<sub>12</sub> nanoflakes on carbon cloth as supercapacitor electrode material. Based on CV kinetic analysis, it was found that the surface contribution proportions of Li<sub>4</sub>Mn<sub>5</sub>O<sub>12</sub> electrode were 44.1%, 44.3%, 47.2%, 49.9%, 52.8% and 58.5% at scanning rates of 2, 3, 4, 5, 6 and 8 mV s<sup>-1</sup>, separately. At low scanning rates, the diffusion-controlled Faraday behavior contribution of Li<sub>4</sub>Mn<sub>5</sub>O<sub>12</sub> electrode is dominant, but in the wake of adding the scan rates, the surface capacitance of Li<sub>4</sub>Mn<sub>5</sub>O<sub>12</sub> electrode contribution rate increases [30]. However, the kinetic analysis for pure MnO<sub>2</sub> nanowires as supercapacitors electrode materials is rarely covered.

Here, we reported a simple hydrothermal to prepare  $\alpha$ -MnO<sub>2</sub> nanowires with excellent electrode properties. The stable  $\alpha$ -MnO<sub>2</sub> nanowire structure electrode possesses high specific capacitance, at 0.1 A g<sup>-1</sup>, which reaches 540 F g<sup>-1</sup>, even the operating current increasing to 50 times, the supercapacitor material still has a satisfactory energy storage performance (the capacitance retention rate is 26%). In

addition, the material has excellent cycle stability (the capacitance retention is more than 120% after 15000 cycles). Furthermore, about the  $\alpha$ -MnO<sub>2</sub> nanowires electrode, we have analyzed and simulated the contribution of surface capacitive behavior effect and diffusion-controlled Faradaic process, revealing the energy storage kinetic analysis.

# 2. Materials and Methods

## 2.1. Preparation of $\alpha$ -MnO<sub>2</sub> nanowires

The typical process, firstly, 0.254 g MnSO<sub>4</sub> and 1 ml H<sub>2</sub>SO<sub>4</sub> (0.5 M) were dissolved in a beaker containing 30 ml DI water, and magnetic stirring for 10 minutes with 600 rpm of the speed. Then, 10 ml KMnO<sub>4</sub> (0.1 M) was added slowly under stirring condition, stirred for 1 h, and then treated with ultrasonic for 0.5 h. Finally, the compound was moved to an autoclave with 50 ml Teflon liner, then reacted at 120 °C for 12 hours. After cooling the product to room temperature, centrifugally wash with deionized water, and then lyophilized for further use.

# 2.2. Characterization

## 2.2.1. Morphology and chemical structure analysis

In this work, the morphology and lattice feature of the sample were investigated by SEM (Hitachi), TEM (JEM-2100F, JEOL), XRD (with Cu-Kα radiation). XS analytical balance (Mettler Toledo; 0.01 mg) and XPS (Thermo ESCALAB 250XI). Autolab (Metrohm, Nova 2.0 software).

#### 2.2.2. Electrochemical analysis

In this experiment, electrochemical performances of the electrodes were using an

Autolab (PGSTAT302N potentiostat) and the electrolyte is 0.5 M Na<sub>2</sub>SO<sub>4</sub> solution. The electrochemical performance was measured at room temperature (25 °C). The working electrode is composed of  $\alpha$ -MnO<sub>2</sub> nanowires, polytetrafluoroethylene (PTFE) and activated carbon with a mass ratio of 8:1:1, and the solvent was several drops of N-methylpyrrolidone and ethanol and then coating the formed slurry on graphite paper. After drying at 90 °C for 14 hours, it was immersed in electrolyte for 8 hours. The voltage window of GCD and CV tests were 0~0.8 V, GCD current density was 0.1, 0.2, 0.5, 1, 2, 5, 10, 20 A g<sup>-1</sup>, and CV scanning rates were 1, 2, 5, 10, 20, 50, 100, 200 mV s<sup>-1</sup>, respectively. The electrochemical impedance (EIS) frequency ranges from 10<sup>-2</sup> to 10<sup>5</sup> Hz. Specific capacitance by CV curves was computed by Formula (1):

$$C = Q / (m \cdot \Delta E) \tag{1}$$

In which Q, m and  $\Delta E$  are the integral of anode charge (C), the mass of active materials (~0.54 mg) and the voltage window (V), separately.

#### 3. Outcomes and discussion

#### 3.1. Chemical structure of the $\alpha$ -MnO<sub>2</sub> nanowires

XRD is a valid measurement to ascertain the crystal structure of synthesized material. Fig. 1 is the XRD pattern of the obtained product, which describes strong diffraction peaks at 20 angles of 60.3°, 28.8°, 37.5°, 42.0° and 18.1°, corresponding to (521), (310), (211), (301) and (200) crystal planes, respectively, of tetragonal  $\alpha$  - MnO<sub>2</sub> crystal (JCPDS No. 44-0141) [31]. The result illustrating that the synthesis route of this experimental scheme is mature and tetragonal  $\alpha$ -MnO<sub>2</sub> materials have been successfully synthesized.



Figure 1. XRD pattern of α-MnO<sub>2</sub> nanowires

The valence states and chemical composition of the elements were tested by XPS. The measured spectrum is shown in Figure 2a and the peaks of Mn 2p and O 1s are exhibited in Fig. 2b and 2c, separately. Figure 2b exhibits that the Mn 2p signal in MnO<sub>2</sub> is split into two spin orbitals, which are Mn  $2p^{1/2}$  and Mn  $2p^{3/2}$ , with binding energies of 642.8 and 653.8 eV, separately, belonging to the positive tetravalent manganese [32]. Figure 2c exhibits that the O 1s energy spectrum can be divided into three absorption peaks and the binding energies are 529.9, 532.0 and 533.6 eV, respectively, corresponding to the O 1s binding energies in different chemical environments of lattice oxygen (Mn-O-Mn), surface hydroxyl (Mn-O-H) and structural water (H-O-H). These results indicate that high purity  $\alpha$ -MnO<sub>2</sub> nanowires were fabricated employing the hydrothermal method.



**Figure** 2. (a) XPS survey spectrum of  $\alpha$ -MnO<sub>2</sub> nanowires. The high-resolution XPS spectra: (b) Mn 2p region, (c) O 1s.

# 3.2. Morphology of the $\alpha$ -MnO<sub>2</sub> nanowires

Figure 3a describes the SEM image of  $\alpha$ -MnO<sub>2</sub> products, which appeared with a typical one-dimensional nanowire morphology. Further analysis shows that the length of the nanowires is about 5  $\mu$ m. A large number of manganese dioxide nanowires are randomly interwoven together to form the network structure. Figure 3b is the TEM characterization of the one-dimensional manganese dioxide nanowires. It can be seen that the diameter of nanowires is very uniform which diameter is about 30-40 nm and the surface is very smooth. HR-TEM image of the manganese dioxide nanowire is

exhibited in Figure 3C, and the lattice structure is clear and regular. The *d*-spacing figuring out from the lattice fringes is 0.24 nm and corresponding to the crystal plane of (211). The illustration in Fig. 3c exhibits the FFT pattern of the corresponding lattice structure. These bright spots once again testify that the synthesized product is a single crystal with a regular crystal structure. It can be seen that the interplanar spacing of 0.24 nm and 0.31 nm correspond to the (211) and (310) crystal planes of  $\alpha$ -MnO<sub>2</sub> phase, separately. Simultaneously, Fig. 3d further authenticates the corresponding lattice spacing in Fig. 3c is 0.24 nm.



Figure 3. (a) SEM, (b) TEM, (c) HRTEM images of the  $\alpha$ -MnO<sub>2</sub> nanowires, the inset exhibits the corresponding FFT pattern, and (d) the corresponding lattice spacing obtained from (c).

# 3.3. Electrochemical property of $\alpha$ -MnO<sub>2</sub> nanowires

For obtaining the electrochemical performance of the prepared one-dimensional α-

MnO<sub>2</sub> nanomaterials, the electrode electrochemical property was tested by the potentiostat. Figure 4a exhibits the CV curve between 0~0.8 V, and the curves are analogue to rectangle, which confirms that the electrode with great reversibility and charge storage properties. Fig. 4b exhibits the GCD curve of the α-MnO<sub>2</sub> electrode under various current densities. Under each current density, the symmetry of the curve keeps excellent, indicating that the electrode features acceptable rate property and excellent Coulombic efficiency. Figure 4c exhibits that when at 0.1 A g<sup>-1</sup>, the specific capacitance can reach 540 F g<sup>-1</sup>, and when the current density is 0.2, 0.5, 1, 2, 5 A g<sup>-1</sup>, that corresponds to 396, 319, 280, 235 and 138 F g<sup>-1</sup>, separately. Resulting from the increased diffusion limitation at higher current densities, the specific capacitance drops as current density rises [33]. When the working current increases to 50 times (from 0.1 to 5 A g<sup>-1</sup>), the cell still keeps a satisfactory rate performance, and the capacitance retention rate is 26% (from 540 to 138 F g<sup>-1</sup>). Fig. 4d shows that at 50 mV s<sup>-1</sup>, the cyclic stability of the electrode. After 15,000 cycles, the performance could even maintain 120% of the initial specific capacitance and reach a relatively stable state without attenuation. As the electrolyte gradually permeates into MnO<sub>2</sub> nanowires, more and more nanowires are activated and leading to increased capacitance [34].



Figure 4. (a) CV and (b) GCD plots of  $\alpha$ -MnO<sub>2</sub> nanowire electrode at various scanning rates and current densities, separately. (c) rate property and (d) cycling stability of  $\alpha$ -MnO<sub>2</sub> nanowires electrodes.

For analyzing the electrochemical resistance behavior of  $\alpha$ -MnO<sub>2</sub> electrode material, we have conducted an electrochemical impedance test on  $\alpha$ -MnO<sub>2</sub> electrode material. And Fig. 5 exhibits the Nyquist curve before and after 15000 cycles. The illustration at the bottom right of the figure is an enlarged view of the high-frequency region of the curve and the illustration in the upper right corner is the equivalent circuit obtained by fitting with Nova 2.0 software equipped with the Autolab potentiostat. The fitting circuit consists of CPE  $R_{ct}$  (electric double layer capacitance), (charge transfer resistance), and  $R_s$  (internal resistance). The equivalent series resistance ESR  $R_s$  value of the  $\alpha$ -MnO<sub>2</sub> electrode before and after 15000 cycles are 1.10 and 0.56  $\Omega$ , separately. Moreover, the  $R_{ct}$  value (6.7  $\Omega$ ) of the  $\alpha$ -MnO<sub>2</sub> electrode after 15000 cycles is smaller than the value before cycling (17.6  $\Omega$ ), which may result from the more active centers



generated in the activation process, thus shortening the ion transfer path [35].

Figure 5 Nyquist diagram of the  $\alpha$ -MnO<sub>2</sub> electrode before and after 15,000 cycles. The insets are the corresponding equivalent circuit and the portion of the magnification pattern.

For better understanding the energy storage mechanism, the relation of the scan rates and the peak currents were plotted in Fig. 6a, and the relationship between the logarithm of the scanning rates and the logarithm of the oxidation peak currents is shown in Fig. 6b. As Fig. 6a shows the peak current values of redox peak changes linearly with the change of scanning rates, resulting from the limited diffusion rates of sodium ions. In the CV test, there are different peak current values at different scanning rates. By analyzing the logarithm of scan rate and corresponding peak currents, the surface capacitor behavior or diffusion-controlled Faraday behavior of the electrode in the charging and discharging process could be distinguished. For electrode materials, the value of b can be calculated by the formula (2) to judge whether there is diffusioncontrolled Faraday behavior in the process of charge and discharge.

 $i = av^b$  (2)

formula (2) can be further transformed into:

$$\log i = b \log v + \log a \tag{3}$$

In which a, b are tunable parameters, *i* represents the peak current (mA), v represents the scanning rate (mV s<sup>-1</sup>) and. b can be calculated by plotting log*i* and logv with different peak currents corresponding to different scan rates, and then a function fitting calculation is carried out to determine the charge storage mechanism. Generally, b = 0.5 refers to diffusion-controlled Faraday plication, whereas b = 1 indicates surface capacitive behavior processes. Through the fitting calculation, that b = 0.80 is between 1 and 0.5, and further verified that the two charge storage mechanisms coexist in the process of energy storage materials.

Surface capacitor contribution  $(K_1v)$  and diffusion-controlled Faradaic contribution  $(K_2v^{1/2})$  can be obtained employing the equation below [28,29,36].

$$i(V) = K_1 v + K_2 v^{1/2}$$
(4)

Transform formula (4) further into:

$$i(V) / v^{1/2} = K_1 v^{1/2} + K_2$$
 (5)

V is the specified voltage (V),  $K_1$  and  $K_2$  are adjustable parameters. The contribution value of surface capacitance at different potentials can be calculated from the  $K_1$  value under a specific voltage, so as to identify the contributions of diffusion-controlled Faradaic behavior and surface capacitive behavior in the electrochemical process. This method is widely used to determine whether the ion insertion process is surface controlled capacitive behavior or diffusion-controlled Faradaic behavior, and corresponding contribution values [29,36-38]. Fig. 6c shows the CV diagram at 2.0 mV s<sup>-1</sup>. The orange shaded area corresponds to the surface capacitive contribution. Each specific voltage corresponds to a fitted  $K_1$  value, which can be calculated by linear fitting  $i(V)/v^{1/2}$  and  $v^{1/2}$  in formula (5). The specific voltage (V) is linked with the

corresponding  $K_1$  (*i*, mA) through a smooth curve to carry out nonlinear fitting. Under the specific scan rate, the CV curve is integrated to calculate the area. And the contribution rate under the specific scan rate is the value obtained by dividing the fitting area by the area of CV is capacitive. Similarly, the contribution rate of surface capacitance under different scanning rate can be calculated, and the contribution value can be obtained. Fig. 6d shows that at the scanning rates of 1, 2, 5, 10 and 20 mV s<sup>-1</sup>, the surface capacitive contribution is 30%, 38%, 49%, 58% and 66%, respectively.



**Figure** 6 (a) CV plots of peak current value *vs.* scanning rate plots, (b) plots of logv *vs.* log I<sub>p</sub> for  $\alpha$ -MnO<sub>2</sub> electrode at diverse scan rates, (c) Separation of capacitive current and diffusion current measured at 2 mV S<sup>-1</sup>: total current (blue line) and capacitive currents (orange shaded), (d) Diffusion and capacitive current contribution of  $\alpha$ -MnO<sub>2</sub> electrode at different scanning rates.

# 4. Conclusions

The results show that  $\alpha$ -MnO<sub>2</sub> synthesized by the hydrothermal method has good electrochemical performance at 0.1 A g<sup>-1</sup>, it exhibits a high specific capacitance of 541 F g<sup>-1</sup> and when the current density increase 50 times to 5 A g<sup>-1</sup>, the capacitance retention rate is 26%, which provided a satisfactory rate performance. Besides, the material features proven cycling stability. After 15000 cycles, the capacity retention rate is 120%, and the performance is stable without attenuation. Based on the remarkable enhancement of the electrochemical property, we analyzed the contribution of surface capacitance effect and diffusion-controlled Faraday process to the total capacitance, namely, the energy storage kinetic analysis.

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