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NaMnO$_{2-x}$ thin nanosheets assembled microspheres as electrode for aqueous asymmetric supercapacitor

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Abstract

This study proposes MnO$_2$ thin nanosheets assembled microspheres with oxygen vacancies and pre-insertion of Na ions (NaMnO$_{2-x}$) as highly capable supercapacitor electrodes. The NaMnO$_{2-x}$ electrode can reach a stable potential window of 1.2 V without oxygen evolution reactions in three-electrode configuration. The voltage window of the assembled aqueous ASC device can be expanded to 2.4 V (1 M Na$_2$SO$_4$) by using NaMnO$_{2-x}$ electrode and activated carbon electrode as positive and negative electrodes, respectively. The NaMnO$_{2-x}$ electrode delivers a good specific capacitance of 215 F · g$^{-1}$ at current density of 1 A · g$^{-1}$. It displays high-rate capability and an excellent cycling stability, maintaining 95.5% of its initial specific capacitance at 2 A · g$^{-1}$ after 2500 cycles. The ASC device shows a high energy density and power density of 28.56 W · h · kg$^{-1}$ and 1246 W · kg$^{-1}$, respectively, at a current density of 1 A · g$^{-1}$.

Introduction

Manganese oxide (MnO$_2$) has the desired attributes as the most promising pseudocapacitive electrodes for supercapacitors. Over the past decades, MnO$_2$ has been widely investigated due to a series of attractive properties, being abundant, non-toxic, low-cost, and with a high theoretical capacitance ($\sim$1370 F · g$^{-1}$), etc [1–5].

However, the practical capacitance of MnO$_2$ is smaller than its theoretical capacitance and goes lower as the mass loading increases. Normally, the capacitance is less than 600 F · g$^{-1}$ when loaded amounts higher than 1 mg cm$^{-2}$ [6, 7]. Numerous experiments have shown that the poor conductivity including electronic and ionic conductivity is the major issue for MnO$_2$ to achieve dramatic capacitive performance. To address this issue, many measures have been used to improve the conductivity, thus boosting electrochemical performance of MnO$_2$, including intrinsically and extrinsically modifies. Intrinsically modifies mainly consist of crystallinity tuning, crystal structure adoption, nanostructural construction and oxygen vacancy introduction [8, 9]. Concerning crystallinity, the low crystallinity of MnO$_2$ means a porous structure and good ionic conductivity but also means a low electronic conductivity. A high crystallinity does the opposite [10–12]. For example, Wei et al calculated the obtained MnO$_2$ films at 200 °C to improve its crystallinity and reduce its porosity and the heat treated films exhibited lower specific capacitance (SC) at scan rates below 10 mV s$^{-1}$ and higher SC at scan rates above 10 mV s$^{-1}$ compared to the non-calcinated MnO$_2$ films [13].

With respect to the crystal structure, a large amount of MnO$_2$ allotrope phases with different crystallographic pathways (one-demention channels (1D), two-demention (2D) layers and three-demention (3D) interconnecting channels) have been well studied and evaluated based on supercapacitors (SCs) [14]. It turns out that an increase in channel size and connectivity resulted in improved electrochemical performance.
At the same time, different morphologies of MnO₂ have been synthesized such as nanowires, nanoflowers, nanorods, nanospheres and nanosheets, etc [2, 15, 16]. The nanostructured MnO₂ electrodes can offer more faradic active sites in the electrolyte with high surface area. Also, the charge and ion transfer efficiency and material utilization can be enhanced compared to the bulk materials which resulting in improved electrochemical performance since the faradic reaction only happen in the surface or near-surface regions when used in SCs [12, 17].

Of all the methods of improving conductivity, the introduction of oxygen vacancies is taken as the most advantageous method. Researchers found that oxygen vacancies is good at enhancing electrochemical performances by promoting electrons to move to the reaction sites and accelerating the kinetics of the surface redox reactions [10, 18–20]. Doping with lower valence state impurity (Zn, Al, Ag, Fe, B, V, Cu, etc) [18, 21–26] and annealing in de-oxygen are two major approaches to bring oxygen vacancies into MnO₂. For extrinsically modifies, the most common way is to combine MnO₂ with highly conductive materials to enhance the electronic conductivity of the electrode [27–30].

As we know, for ASC devices, voltage window (V) is another important parameter on improving energy density (E) according to the equation $E = 1/2CV^2$. Broadening of the potential window of ASC in aqueous electrolytes beyond 2.0 V is still a significant challenge [31].

Based on the above considerations, herein, high Na content NaMnO₂ thin nanosheets assembled microspheres were formed via hydrothermal method. Then the oxygen vacancies were introduced into the surface of NaMnO₂ thin nanosheets by annealing treatment in N₂. The existence oxygen vacancies increase the amount of Mn⁴⁺ in NaMnO₂ and they can improve the activity of the electrode reactions by drawing the electrons to the surface of electrode where reaction sites are [10]. At the same time, the pre-insertion of metal ions into the MnO₂ lattice contributes to broaden the working potential [32–34].

**Experimental section**

**Preparation of NaMnO₂**

NaMnO₂ thin nanosheets assembled microspheres were synthesized by hydrothermal method. In experimental procedure, 3 mmol of potassium permanganate (KMnO₄), 5 mmol of manganese chloride (MnCl₂) and 2 g of sodium hydroxide (NaOH) were mixed in 40 ml of distilled water as a medium. The mixture was then transferred into a 100 ml Teflon-lined stainless steel autoclave liner. The liner was sealed and maintained at 120 °C for 10 h. After the reaction, the brown precipitates were collected via centrifugation and washed several times with deionized water to remove possible impurities or excess ions. The obtained powder was dried in oven at 80 °C for 12 h.

**Preparation of NaMnO₂ thin nanosheets assembled microspheres with oxygen vacancies (NaMnO₂₋ₓ)**

The NaMnO₂₋ₓ were obtained by annealing the as-prepared NaMnO₂ in N₂ at 300 °C for 3 h.

**Characterization**

The structures and morphologies of the as-prepared samples were characterized using field emission scanning electron microscope (FE-SEM, ZEISS, Germany) and high-resolution transmission electron microscopy (TEM, JEM-2100F, Japan). The crystallographic and chemical compositions characterizations of the as-prepared samples were performed by D8 advance diffractometer (Bruker, Germany) and Raman spectroscopy (LabRAM HR 800). X-ray photoelectron spectroscopy (XPS) was further used to investigate the Mn valence of the samples.

**Electrochemical Measurement**

Cyclic voltammetry (CV), galvanostatic charge-discharge (GCD) and Electrochemical impedance spectroscopy (EIS) experiments were performed to determine the electrochemical properties of the NaMnO₂₋ₓ electrodes using a three-electrode configuration in Na₂SO₄ (1.0 M) solution. The working electrode was prepared by painting and pressing slurry on Ni foam and the slurry was produced by mixing the NaMnO₂₋ₓ, carbon black (Super P), and polyvinylidene fluoride (PVDF) in N-methyl-2-pyrrolidone (NMP) at a weight ratio of 75:15:10. The loading mass of the NaMnO₂₋ₓ on the working electrode was in the range of 1.5–2.5 mg cm⁻². A Pt plate and a saturated calomel electrode were used as the counter electrode the reference electrode, respectively. The performances of as-prepared ASC device were tested in the two-electrode electrochemical system.

The specific capacitance($C$, F·g⁻¹), energy density($E_p$, W·h·kg⁻¹) and power density($P_p$, W·kg⁻¹) were calculated from the galvanostatic discharge curves according to the following equation:

$$C = \frac{\Delta t}{\Delta V \cdot m}$$  \hspace{1cm} (1)
The CV curves of NaMnO₂ show two major peaks at binding energies of 653.7 and 641.9 eV with a spin-energy separation of 11.8 eV, which was assigned to Mn⁴⁺. The fitting peaks at binding energies of 653.4 and 641.7 eV were assigned to Mn⁵⁺ [36].

It is generally accredited that the existence of oxygen vacancies can increase the quantity of Mn³⁺ in MnO₂ [37]. The high energy electron in e.g. orbit can jump between Mn⁴⁺ and Mn³⁺ according to double-exchange interaction through O²⁻ ion, where the as formed Mn³⁺–O–Mn⁴⁺ route enhance the electrical conductivity of mixed valence state MnO₂ [17].

The morphologies of NaMnO₂ and NaMnO₂₋ₓ were investigated by scanning electron microscopy (SEM) and transmission electron microscopy (TEM). Figure 2 displays that the microspheres have a diameter less than 300 nm and thin nanosheets make up all these microspheres. Scanning electron microscopy (SEM) studies revealed that there were no obvious morphological changes for NaMnO₂ during the thermal treatment in N₂. Figures 3(a) and (b) exhibits the TEM images of the NaMnO₂₋ₓ. The HRTEM image analysis also showed the presence of NaMnO₂. Clear lattice fringes were observed in figure 3(c) and measured to be 0.24 nm, which can be assigned to (−111) plane of NaMnO₂ (JCPDS 25–0845). Moreover, figure 3(d) shows the corresponding EDS elemental maps. It can be seen that the Mn, O and Na atoms were homogeneously distributed over the structure.

In order to study the effects of oxygen vacancies and ions pre-insertion on the electrochemical performances, CV and GCD were carried out in a three-electrode configuration. Note that NaMnO₂ and NaMnO₂₋ₓ electrodes both have a stable potential window of 1.2 V which is higher than the ordinary potential window of MnO₂. The CV curves of NaMnO₂₋ₓ exhibited nearly rectangular shape at various scan rates from 5 to 50 mV s⁻¹ as shown in figure 4(a), implying the good capacitive behavior. The figure 4(b) displayed the nearly symmetric and linear GCD curves of NaMnO₂₋ₓ at various current densities from 1 to 5 A g⁻¹. As shown in figures 4(c) and (d), the CV integrated areas and discharge time of NaMnO₂₋ₓ is much larger and longer than NaMnO₂ at a scan rates of 30 mV s⁻¹ and a current density of 1 A g⁻¹ respectively, indicating that the NaMnO₂₋ₓ has a higher specific capacitance than NaMnO₂. The CV curves and GCD curves of NaMnO₂ in 1 M Na₂SO₄ at various scan rates (5–50 mV s⁻¹) and various current densities (1–4 A g⁻¹) respectively are shown in figure S1 is available online at stacks.iop.org/REP/7/035508/mmedia. Figure 4(e) presented that the specific capacitance of NaNaO₂ and NaMnO₂₋ₓ decreased as the scan rates increased.

\[
E_g = \frac{1}{2} \times \frac{C_{g,\text{cell}} \times \Delta V^2}{3.6} \quad (2)
\]

\[
P_E = \frac{3600 \times E_g}{\Delta t} \quad (3)
\]

where \(I\) is the discharge current (A), \(\Delta t\) is the discharge time (s), \(\Delta V\) is the applied potential window (V), and \(m\) is the loading mass of the active material (g); \(C_{g,\text{cell}}\) is the capacitance of the as-prepared ASC [35].

Results and discussion

As shown in figure 1(a), the XRD diffraction signals of NaMnO₂ and NaMnO₂₋ₓ were consistent with the standard diffraction patterns of monoclinic NaMnO₂ (JCPDS 25–0845). This indicated that there was no phase transition for NaMnO₂ during the process of annealing in N₂ at 300 °C for 3 h. The x-ray photoelectron spectroscopy (XPS) analysis was carried out to investigate the Mn valence of NaMnO₂. As we can see in figure 1(b), the Mn 2p spectrum was fitted to two major peaks at binding energies of 653.7 and 641.9 eV with a spin-energy separation of 11.8 eV, which was assigned to Mn⁴⁺. The fitting peaks at binding energies of 653.4 and 641.7 eV were assigned to Mn⁵⁺ [36].
Figure 4. The smaller semicircle radius of the NaMnO$_2$ at high frequency revealed lower charge transfer resistance. Moreover, the more vertical plot at lower frequency range of the NaMnO$_2$ demonstrated a better capacitive behavior than NaMnO$_2$ [38, 39].

The cycle stability of the NaMnO$_2$ and NaMnO$_2$ at a current density of 2 A·g$^{-1}$ is shown in figure S2. The specific capacitance of NaMnO$_2$ electrode retained 95.5% after 2500 cycles and NaMnO$_2$ electrode retained 88.9% which is lower.

An aqueous ASC device consisting of NaMnO$_2$ (NaMnO$_2$/NF) and AC (AC/NF) as the positive and negative electrode was assembled to rate the electrochemical performance of NaMnO$_2$ [40]. The electroactive material mass ratio of the positive electrode to the negative electrode was calculated according to the charge balance relation: $m^+/m^- = (C^- \times V^-)/(C^+ \times V^+)$, which was set to 0.46. The CV, GCD, and EIS tests of AC electrodes are shown as curves in figure S3 and 4 [34]. Within the potential window of −1.2～0 V, the CV curves of AC/NF electrodes maintained rectangular at a scan rate of 30 mV·s$^{-1}$ just like NaMnO$_2$/NF did in 0～1.2 V (figure 5(a)) [41]. Figure 5(b) showed the CV curves of the NaMnO$_2$/NF//AC/NF ASC device at
different voltage windows at a scan rate of 40 mV·s⁻¹. As we can see, a stable voltage window of 2.4 V could be achieved on this as-prepared ASC device. With an increase of the operating voltage to 2.4 V, the curve starts to turn sharp at the high voltage area, indicating some irreversible reactions happen when the voltage window is higher than 2.4 V. CV curves of the ASC device at different scan rates ranging from 5 to 100 mV·s⁻¹ and GCD curves at different current densities ranging from 1 to 5 A·g⁻¹ are given in figures 5(c) and (d). The ASC device exhibited rectangular-shaped CV curves and linear GCD curves which suggested a good capacitive behavior. The calculated specific capacitance of ASC device was 35.7 F·g⁻¹ at current densities of 1 A·g⁻¹. The specific capacitance reached 26.9 F·g⁻¹ when current densities increased to 5 A·g⁻¹. It demonstrated that the electrodes have a good rate capability (figure S3). The EIS of the NaMnO₂−x/NF//AC/NF ASC device was conducted and the Nyquist plot was shown in figure S4.
internal resistance ($R_s$) is around 6 $\Omega$. The diameter of semicircle represents the charge transfer resistance ($R_{ct}$) and the value is around 2 $\Omega$.

A schematic diagram is shown in figure 6(a) of the ASC device using the NaMnO$_{2-x}$/NF as the cathode and AC/NF as the anode in a 1 M Na$_2$SO$_4$, with a piece of cellulose paper as the separator [40]. As shown in figure 6(b), at a power density of 1246 W · kg$^{-1}$, the ASC device showed an energy density of 28.56 W · h · kg$^{-1}$, the energy density still maintained at 21.512 W · h · kg$^{-1}$ (75.3% retention). Remarkably, the obtained energy density is significantly higher than the asymmetrical SCs such as CNTs@DNA–MnO$_2$ // CNTs@DNA (~11.6 W · h · kg$^{-1}$) [41], RGO/MnO$_2$/fFWNT and AC/fFWNT (~24 W h kg$^{-1}$) [42], MnO$_2$/AG (~22.5 W · h · kg$^{-1}$) [43], MnO$_2$/AC (~21 W · h · kg$^{-1}$) [44]. Long-term cycling stability is also a critical parameter for practical application of supercapacitors. At current density of 3 A · g$^{-1}$, the specific capacitance of NaMnO$_{2-x}$/NF // AC/NF ASC device retained 90.85% after 5000 cycles which demonstrated an outstanding cycling performance (figure 6(c)). The discharge curves of the initial 10 cycles were almost identical with its corresponding charge counterpart, implying excellent electrochemical reversibility and Coulombic efficiency of the device.

**Conclusion**

In this study, MnO$_2$ with pre-insertion of Na ions and oxygen vacancies is prepared and applied as electrode for high-performance electrochemical capacitors. In this case, the structure of thin nanosheets assembled microspheres increase the active sites between the active materials and the electrolyte, the pre-insertion of metal ions enlarges the potential window and the oxygen vacancies improve the conductivity of active material. This work demonstrated that the introduction of pre-insertion ions and oxygen vacancies can greatly increase the practical application possibility of aqueous asymmetric supercapacitors. We also believe that these strategies can
be applied on other transition metal oxides and used for improve their properties which is attractive for energy storage devices.

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Author contributions

Data curation, Song. Xu and Tao Wan; funding acquisition, Song Xu; methodology, Kaibin Zhou, Guangming Zhu, Zhiqiang He and Haibo Huang; writing—original draft, Ting Zhou, Wenqi Mao, Jiejun Wu and Shangkun Gong; writing—review and editing, Yanxin Qiao.

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Conflict of interest

The authors declare no conflict of interest.
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