Recrystallization-induced capacity fading of birnessite-type MnO₂ nanosheets for pseudocapacitors

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Keywords: MnO₂, nanosheets, pseudocapacitor, birnessite, capacity fading

Abstract
Birnessite-type MnO₂ materials are widely studied as electrodes for pseudocapacitors. However, the poor cycling stability limits their applications. Here, wrinkle birnessite-type MnO₂ nanosheet array has been synthesized and taken as an example to discover the reason of capacity fading for pseudocapacitors. It is discovered that in the galvanostatic charge-discharge process, the small nanosheets blocking the macropores of the array framework have been dissolved and recrystallized on the large wrinkle birnessite nanosheet array framework, finally forming a hierarchical structure of nanosheets@nanosheets of birnessite. The recrystallization of the small birnessite nanosheets may decrease the specific capacity through the decrease of the surface area of the electrode.

1. Introduction
The global climate change and environmental pollution originated from fossil energy consumption have pressurized people to find new clean energy [1, 2]. No matter what type of new energy used (nuclear, wind, tide or others), batteries are usually needed to storage the energy by charge transfer in, for example, electric vehicle, where gasoline engine is replaced by electromotor [3, 4]. However, batteries (such as lithium ion battery, fuel cell and others) usually have poor power density, which is very important for speeding up and braking of electric vehicles [5, 6]. Therefore, pseudocapacitors have drawn much of attention due to their higher power density than batteries [7–10]. Different from traditional electrochemical double-layer capacitors (EDLCs), pseudocapacitors not only store energy based on the electrostatic double layer in the interface of electrolyte and electrode, but also engaged in fast and reversible surface redox reactions like batteries. Apart from conducting polymers, transition metal oxides with higher cycling stability and specific capacitance are more attractive as the electrode materials for pseudocapacitors [1]. In transition metal oxides, RuO₂ and Ni-Co oxides have excellent performance but expensive [11–13]. Cheaper metal oxides such as MnO₂ are also widely studied. The drawbacks of MnO₂ are their poor conductivity and cycle stability. To conquer these drawbacks, various composites and architectures are designed, which usually introduce carbon, mesopores and arrays to enhance the conductivity and electrolyte penetration in MnO₂ electrodes [14–16]. MnO₂ array electrodes on conductive substrates are favoured for their binder-free 3D architecture and good performance [17, 18]. However, at larger current densities and long cycles, the contact between MnO₂ array and substrate may be relaxed, resulting in capacity fading [19]. Therefore, the deepgoing understanding of the fading mechanism is very important for the further design of MnO₂ array electrodes.

In this paper, galvanostatic charge-discharge technique is applied to study the long cycling on the structure and morphology evolution of the MnO₂ array electrodes. Because of the recrystallization of the small birnessite nanosheets in the galvanostatic charge-discharge cycling process, the interfacial contact between the birnessite nanosheets and the nickel foam substrate becomes loosened, leading to the capacity fading of the electrodes. Meanwhile, the recrystallization of the small birnessite nanosheets on large ones may decrease the surface area of the electrode, which is another reason for the capacity fading.
2. Experimental

2.1. Syntheses

The birnessite-type MnO₂ nanosheet arrays grown on nickel foam substrate were prepared as previously with a little modification [19]: 158 mg KMnO₄ was dissolved in 20 ml distilled water by stirring, which was poured into a 25 ml Teflon-lined autoclave. Afterwards, a piece of 1 × 3 cm² nickel foam was immersed into the above KMnO₄ solution. The nickel foam has been etched with 6 M HCl for 10 min and washed by abundant water. The sealed autoclave was put into a 160 °C oven for 4 h. Finally, the autoclave was cooled down in air naturally to room temperature. The nickel foam grown by birnessite was then taken out, sonicated with distilled water and dried in a 60 °C oven by sequence.

2.2. Characterization

The surface morphologies of the electrodes were observed by a scanning electron microscopy (SEM) named Hitachi SU8020. The phase information was investigated with x-ray powder diffraction (XRD) using a Rigaku D/Max-RB x-ray diffractometer (λ = 1.5418 Å). Transmission electron microscopy (TEM) and high-resolution transmission electron microscopy (HRTEM) were carried out on a Tecnai G2 F20 S-TWIN (200KV) transmission electron microscope with the energy dispersive x-ray spectroscopy.

2.3. Supercapacitve property study

The cycling performance of the birnessite nanosheets was studied by a three electrode system in a 0.5 M Na₂SO₄ aqueous solution. The nickel foam (nominal area: 1 × 1 cm²) grown with birnessite nanosheets was used directly as the working electrode. A Pt wire and a SCE electrode were used as counter and reference electrodes, respectively. Galvanostatic charge-discharge tests were conducted on a LANHE CT2001A galvanostatmeter. The nickel foam substrate with a nominal area of 1 × 1 cm² (ca. 0.0335 g) is used all through the experiments. The mass loading of birnessite on the nickel foam is ca. 1.0 mg cm⁻². All the calculations of capacitance (F g⁻¹) and current density (A g⁻¹) are based on the active materials of birnessite.

3. Results and discussion

Figure 1 shows the surface morphology and atom arrangement of the as-grown birnessite on nickel foam observed by SEM and HRTEM, respectively. Figure 1(A) gives a photograph of the bare nickel foam etched with 6 M HCl, displaying a concave surface structure. After the hydrothermal reaction, a uniform layer of tiny nanostructures has been grown on the nickel foam surface (figure 1(B)). Further high magnification SEM image of the as-grown layer presents many thin nanosheets with remarkable surface fluctuations (figure 1(C)).
width and thickness of the nanosheets are around 500 nm and several nm, respectively. The phase of the grown nanosheets determined by XRD (figure S1 is available online at stacks.iop.org/ MRX/6/126002/vmmedia) is birnessite-type MnO₂ (JCPDS 80–1098). Further HRTEM image shown in figure 1 (D) depicts the observed lattice fringe of 0.20 nm, which can be attributed to the (112) plane of birnessite.

The cycling stability of the birnessite nanosheets has been examined by the galvanostatic charge-discharge measurements conducted at current densities of 2 Å g⁻¹, 5 Å g⁻¹ and 10 Å g⁻¹ within a potential window of 0.0–1.0 V versus SCE, as shown in figure 2. When cycled at 2 Å g⁻¹, the birnessite electrode exhibits ca. 25% capacity loss after the first 50 cycles. In the ongoing cycling process, the specific capacity exhibits a steady slow decrease up to 4600 cycles, where the birnessite electrode stands still for one month. Re-starting of the cycling makes a sharp drop of the specific capacity, suggesting falling of the birnessite nanosheets from the nickel foam substrate. When cycled at 5 Å g⁻¹, the birnessite electrode works very well till 4200 cycles with ca. 17% loss of the initial specific capacity. Afterwards, the fading of specific capacity is faster than before as evidenced by the larger slope the curve. When cycled at 10 Å g⁻¹, the birnessite electrode can only run for ca. 700 cycles and then fail. It can be deduced that the birnessite nanosheet array electrode has been run the best at 5 Å g⁻¹, because for the same cycle numbers, it needs more time at 2 Å g⁻¹, and a current density of 10 Å g⁻¹ is too large here for the birnessite-type MnO₂ with poor conductivity. Therefore, the cycle time and current density are both factors affecting the cycling stability of the birnessite array.

Figure 3 presents the corresponding representative charge–discharge voltage profiles at specific cycle numbers for the birnessite electrodes at current densities of 2 Å g⁻¹, 5 Å g⁻¹ and 10 Å g⁻¹, respectively. The charge–discharge curves are approximately symmetric for the initial cycles at 2 Å g⁻¹. For long cycles of 5000 cycles, the increased iR drop leads to asymmetric charge–discharge curves. More severe asymmetry of the charge–discharge curves is found for the 10000 cycles. The increasing iR drop with cycling process could suggest the bad contact between the birnessite nanosheets and the nickel foam substrate. When cycled at 5 Å g⁻¹, the iR drop is larger than that of 2 Å g⁻¹ at initial cycles. However, around 5000–10000 cycles, the iR drop is smaller than that of 2 Å g⁻¹. This indicates that a current density of 5 Å g⁻¹ is favorable by this birnessite electrode, which is in agreement with the cycling performance shown in figure 2. When cycled at 10 Å g⁻¹, the curve of the first charge–discharge cycle is severely asymmetric. The charge-discharge curve is changed a lot at the second cycle, indicating the unstable of the electrode at 10 Å g⁻¹. When cycled up to 700 cycles at 10 Å g⁻¹, the big iR drop indicates the contact between the birnessite and nickel foam is very bad.

Electron microscope technique is carried out to discover the structure and morphology evolution underneath the capacity fading of the birnessite electrodes. Figure 4 shows the SEM images of the birnessite electrodes after cycling at current densities of 2 Å g⁻¹, 5 Å g⁻¹ and 10 Å g⁻¹, respectively. Compared with the primitive birnessite nanosheets, all the cycled birnessite nanosheet arrays in figure 4 generate larger macropores between the nanosheets; meanwhile, the nanosheets have become thicker and straight, which is more evident in the samples cycled at 2 Å g⁻¹ for 300 times as shown in figure S2. For the samples of cycled at 2 Å g⁻¹ and 5 Å g⁻¹ for long cycle numbers (figures 4(A)–(D)), the nanosheets blocking the macropores have been dismissed, and meanwhile, the surfaces of nanosheets have been grown with smaller nanosheets, indicating the dissolution and recrystallization of small birnessite in the macropores in the cycling process. Conspicuous hierarchical structures of nanosheets/nanosheets have been found in some region of the electrodes (figures 4(B) and (D)). Fig. S3 further shows the SEM images of the product after cycled at 2 Å g⁻¹ for 300 times in 40 °C electrolyte.
solution. The nanosheet@nanosheet structure grew larger forming flower-like morphology. Therefore, the growing process of the hierarchical structures of birnessite can be accelerated by a higher temperature of 40 °C. The morphology of the product (figures 4(E) and (F)) after cycled at 10 A g\(^{-1}\) is changed little compared with the primitive nanosheets, but the failing of the electrode is faster than that of cycling at 2 A g\(^{-1}\) and 5 A g\(^{-1}\), respectively. Therefore, the dissolving the birnessite may start at the interface of birnessite and the substrate; and large current densities can accelerate the dissolving rate.

TEM and EDS measurements have been applied to discover the structure and composition variations of the nanosheets after cycling. Figure 5 shows the results detecting on the initial birnessite nanosheets and a sample after cycling at 2 A g\(^{-1}\) for 300 cycles, respectively. Figure 5(a) displays the full view of a selected nanosheet of the initial sample. The nanosheet has a flat surface with some fluctuation regions. After cycled at 2 A g\(^{-1}\) for 300 cycles, it can be seen in figure 5(E) that there are lots of tiny nanosheets on the initial large one. The observed hierarchical structure is in agreement with the SEM images (figure S2). Elemental mapping of K Mn Na of the above samples discover that Na/Mn mole ratio of the final sample is increased, indicating that K is basically replaced by Na. Na is uniformly distributed in the observed sample (figure 5(D)), indicating the inserting of Na\(^{+}\) into the birnessite.

Based on the above observations, the electrochemical cycling on the structure and morphology evolution of the birnessite electrode for a pseudocapacitor has been illustrated in Scheme 1. Before the cycling, the initial wrinkled birnessite nanosheets are distributed randomly on the nickel foam substrate. The macroporous channels between the basic nanosheets are occupied by other smaller nanosheets. After short cycles of 300 times, the wrinkled birnessite nanosheets become straight and the macroporous channels between the nanosheets are
opened. In this process, it may involve the fracture of the smaller nanosheets in the macropores and their recrystallization on the interconnected birnessite nanosheet frameworks, which is similar to the Ostwald ripening process usually happened in the crystal growth process of manganese oxides \[20\]. Indeed, it has been

Figure 4. SEM images of the birnessite nanosheets after cycling at different current densities. (A), (B) 2 A g\(^{-1}\) for 10000 cycles; (C), (D) 5 A g\(^{-1}\) for 10000 cycles; (E), (F) 10 A g\(^{-1}\) for 1700 cycles.

Figure 5. (A) TEM image and EDS mappings on (B) K, (C) Mn and (D) Na of the initial birnessite nanosheets; (E) TEM image and EDS mappings on (F) K, (G) Mn and (H) Na of the birnessite nanosheets after cycled at 2 A g\(^{-1}\) for 300 cycles.
discovered that birnessite-type pseudocapacitive electrodes undergoes phase transformation in the charge-discharge process in Na₂SO₄ aqueous solution [21, 22]. In the full charging state, hexagonal phase of H₂O intercalated MnO₆ octahedral layers are formed; in the full discharging state, monoclinic phase of Na⁺/H₂O intercalated MnO₆ octahedral layers appears. Therefore, the charge-discharge process is accompanied by the volume change and symmetry transformation of the birnessite, which also usually exist in battery materials [23], leading to the instability of the electrodes. As for birnessite, previous reports have demonstrated that the interlayer expansion process can introduce vacancies in the MnO₆ octahedral layers [24, 25]. Although our HRTEM studies have not found out visual vacancies, they may exist on the surface and edges of the nanosheets and form fracture at the edges of the nanosheets (figure S4). Smaller particles with more active surface and edges could be divided into sub-particles, which move with the electrolyte flow in the macroporous channels to further grow on the larger nanosheet framework. Repeating this recrystallization process finally results in the nanosheet@nanosheet hierarchical structures. Therefore, the volume change may induce the recrystallization process. Volume change and recrystallization are both factors that affect the capacity fading. At large current densities, recrystallization is suppressed for the short charge-discharge time not enough for the solute to migrate and grow; and volume change is the major reason for the capacity fading for a short time. In the previous reports, capacity fading is usually discovered in birnessite and also other transition oxide pseudocapacitive electrodes [21, 26]. We propose that recrystallization mechanism may be responsible for the capacity fading of transition oxide pseudocapacitive electrodes for a long cycle time. The nature of recrystallization process is to increase the particle sizes and decrease the surface active sites, which lower the total surface energy of the electrode.

### 4. Conclusion

In this work, birnessite-type MnO₂ nanosheet arrays grown on nickel foam substrate have been taken as an example to investigate the influence of long-cycles on the structure stability of pseudocapacitive electrode materials. It has been found that after long cycles, the birnessite nanosheets have the tendency to drop off the substrate due to the recrystallization of the birnessite nanosheets, leading to the fading of the electrode. Therefore, suppression of the recrystallization by coatings and tailored hierarchical structures may be helpful for the enhancement of the cycling stability of birnessite-type MnO₂ pseudocapacitive electrodes.

### Acknowledgments

This work is supported by the National Natural Science Foundation (NSFC) of China (no. 21601127) and Doctoral Research Start-up Funding of Shenyang Agricultural University (no. 880416019).

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