Manganese oxides-based composite electrodes for supercapacitors

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Abstract. In recent, nanostructured transition metal oxides as a new class of energy storage materials have widely attracted attention due to its excellent electrochemical performance for supercapacitors. The MnO₂ based transition metal oxides and their composite electrode materials were focused in the review for supercapacitor applications. The researches on different nanostructures of manganese oxides such as Nano rods, Nano sheets, nanowires, nanotubes and so on have been discovered in recent years, together with brief explanations of their properties. Research on enhancing materials’ properties by designing combination of different materials on the micron or Nano scale is too limited, and therefore we discuss the effects of different components’ sizes and their synergy on the performance. Moreover, the low-cost and large-scale fabrication of flexible supercapacitors with high performance (high energy density and cycle stability) have been pointed out and studied.

1. Introduction

Supercapacitors are regarded as a new promising type of device for energy storage and conversion, due to its high power density, rapid charging and discharging, and long cycle life. In the actual research, however, those problems such as low energy density and low capacitance is the bottleneck, limiting its development. Therefore, it’s essential to develop new type of supercapacitor electrode materials to resolve these problems [1-3]. Transition metal oxides (e.g. MnO₂) are regarded as the most promising supercapacitor materials due to their high theoretical capacitances, excellent cycling performance, abundance, low cost and environment friendliness. But weak conductivity and low specific surface area of the materials make their capacities far less than the theoretical values. Usually designing a unique morphology is used to increase the materials’ specific surface area, and inducing other highly conductive materials is used to enhance the conductivity [4-6]. However, most of the reports only focus on the influence of one of these two factors. These researches are rare that enhance materials’ property by designing the combination between capacitor materials with different activity under the micro or Nano scale, therefore it’s still not clear about the synergy effect of different components neither size effect on the performance[7-8]. It is a great challenge to realize low-cost and large-scale fabrication of flexible SCs with high performance.
2. MnO₂ and MnO₂-based composite electrode materials

2.1. MnO₂ electrode material

A great deal of studies has been attained in developing fabrication different types of MnO₂ nanostructures. The key factors influencing the electrochemical capacitance are conductivity and specific surface area. However, MnO₂ has poor conductivity which couldn’t be changed. So designing different nanostructures of MnO₂ electrode materials is the key to improve the capacitance. A summary of pure MnO₂ obtained with different nanostructures and their supercapacitor performances are discussed in Table 1.

As show in Table 1, MnO₂ can be synthesized in dozens of crystalline and disordered forms with variety structures, which were determined by the synthesis methods and nanostructures. Various MnO₂ with different crystalline structures, morphologies, pore structures, microstructures, and unique architectures have been synthesized by changing the parameters or using different reactions. Also, the specific capacitance of MnO₂ could be affected by its specific surface area, such as, Nano flake, particle size, urchin-like nanostructures with different specific surface area, contributing to various specific capacitances.

| Synthesis methods                  | Nanostructure             | Capacitance         | Ref. |
|------------------------------------|---------------------------|---------------------|------|
| Carboxylic acid-mediated           | Hollow sphere amorphous   | 281 F g⁻¹ at 0.5 mA cm⁻² | 6    |
| Template engaged redox             | Hollow structures         | 366 F g⁻¹ at 5 mV s⁻¹ | 7    |
| Hydrothermal                       | Hierarchical Nano flower  | 347 F g⁻¹ at 5 mV s⁻¹ | 8    |
| Hydrothermal route                 | Crystalline porous        | 275 mAh g⁻¹ at 40 mA g⁻¹ | 9    |
| Chemical deposition                | Mesoporous                | 173 F g⁻¹ at 0.25 A g⁻¹ | 10   |
| Microwave-assisted reflux          | Urchin-like nanostructures| 311 F g⁻¹ at 0.2 A g⁻¹ | 11   |
| hydrothermal method                | Nano flake films          | 2.3 mF cm⁻² at 0.025 mA cm⁻² | 12   |

2.2. MnO₂-based composite electrode materials

According to the categories of electrode materials, different types like carbon materials, transition metal oxides and conductive polymers also can be used as the doping materials with MnO₂, which has been widely reported, as shown in Table 2.

In addition, there are also many reports about some other metal oxides doped with MnO₂, as shown in Figure 1. Zhu et al [21] reported that hierarchically porous yet densely packed MnO₂ microspheres doped with Fe₃O₄ nanoparticles via a one-step and low-cost ultrasound assisted method. The results show that single-crystalline Fe₃O₄ particles of 3-5 nm in diameter are homogeneously distributed throughout the spheres and none are on the surface. The specific capacitance is optimized at an Fe/Mn atomic ratio of r = 0.075 to be 448 F/g at a scan rate of 5 mV/s, which is nearly 1.5 times that of the extremely high reported value for MnO₂ nanostructures. MnO₂ based with polymer such as PPy also has been studied. The composites formed by electrochemical polymerization of pyrrole deposited onto MnO₂ particles, have a big specific surface area for excellent performance.

In terms of materials design and preparation of MnO₂, the high specific surface area and good conductivity should be taken into the consideration. However, many reports only focus on the influence of one of these two factors, which improves the capacitance in limitation. Therefore, the choice of doped materials and design of nanostructure are very important for the capacitance improvement.

In addition, electrolyte optimization has been emphasized consistently for enhancing capacitance. The choice of electrolyte is much close to the increase of potential window, which can achieve highly desirable resulting in higher energy density and power density. Up to now, the electrolyte becomes the major cost factor and limitation of the next generation of supercapacitors.
In summary, choosing suitable component and reaction methods to build composite structures with rational design has a pivotal role in electrochemical properties. The synergistic effect and unique structure of composites should be taken full advantages. Due to the pure MnO₂-based pseudo capacitor with poor conductivity and cycle performance, supercapacitor materials should be designed basing on synergistic effect between the electrical double layer capacitor component and pseudo-capacitor component.

### Table 2. Methods and performances of MnO₂-based composites electrodes

| Synthesis methods | Nanostructure       | Composite materials       | Capacitance          | Ref. |
|-------------------|---------------------|---------------------------|----------------------|------|
| Vacuum filtration | Ultrathin Nano sheets | MnO₂/Graphene            | 267 F/g at 0.2 A/g   | 13   |
| Hydrothermal      | Core-shell          | PPy/MnO₂                  | 141.6 F g⁻¹ at 2 mA cm⁻² | 14   |
| Wet chemical      | Core-Shell Nanowire | α-Fe₂O₃/MnO₂              | 838 F g⁻¹ 2 mV s⁻¹   | 15   |
| Chemical agents   | Nano needle structure | Graphene/MnO₂            | 327.5 F g⁻¹ 10 mV s⁻¹ | 16   |
| Hydrothermal      | Core/Shell Nano sheet | Co₃O₄ Nanowire@MnO₂     | 480 F g⁻¹ 2.67 A g⁻¹ | 17   |
| Hydrothermal      | Core/shell Nano sphere | Carbon@MnO₂               | 175 F g⁻¹ 100 mV s⁻¹ | 18   |
| Hydrothermal      | Core/porous         | MnO₂/CNT                  | 205 F/g 2 mV/s       | 19   |
| Hydrothermal      | Nano architectures  | Co₃O₄@MnO₂                | 1224 F/g 5 mV/s      | 20   |

#### Figure 1. Scheme of the composites of MnO₂ and other metal oxides

3. Summary

In this review, we have systematically pointed out that the recent researches and progress on MnO₂ and MnO₂-based composites as energy storage materials for supercapacitors. And the important of synergistic effect and size effect have been given an explanation. It is crucial to synthesize materials with suitable morphology and good conductivity since that have a profound influence on the storage capacity. So, the further detail explanations for the relationship between different materials should be researched in future.

#### Acknowledgments

This work was jointly supported by the Qing Lan Project, the Advanced Access Engineers for Higher Vocational Colleges Teachers of Jiangsu Province (2015FG032), the Natural Science Foundation of Jiangsu Province (BK20161289), the Research Innovation Program for College Graduates and Students of Jiangsu Province (KYZZ15_0043), the Foundation of Nantong Vocational University
1512102), the College Students Innovation and Entrepreneurship Training Program of Jiangsu Province, Nantong Research Project (GY12015020).

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