Manganese-Containing Supercapacitors for Future Energy Storage

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ABSTRACT

Due to the fast developing demand for storing new energy, as well as the practical need of the growing smart grid technologies, many researchers engage in nanoparticles to explore their energy storage potential. Supercapacitors become very popular in the past two decades for their high power density and long-term cycling stability. Manganese-containing electrode materials show many advantages in asymmetric supercapacitor devices. In this review, we will both provide a facile practice of building asymmetric supercapacitors in the lab and list some latest results in the field of Mn-containing electrode materials and find out the challenges that still lie there. From the review work, we hope to attract more material and energy system researchers to pay attention to these materials, make our contribution together and bring a brighter future to energy storage.

Keywords: Supercapacitor, energy storage, smart grid, metal oxide, manganese.

INTRODUCTION

Energy is the material basis for the survival and development of humankind. With the economic development of industrial civilization, people consume more and more coal, petroleum and natural gas. However, the reserves of these energies on the earth are limited. Energy shortage and environmental destruction have drawn more attention from worldwide. Protecting the natural environment on which humankind depends for survival, seeking a right balance between economy and the environment, and building a resource and environment friendly country are essential tasks in the 21st century.

Given the extensive market demand of smart grid for intrinsically safe, long service life and low cost advanced energy storage technology, electrochemical energy storage devices are developed to meet the requirements of high energy density, large power density and long-term cycling stability. The task of researching high-performance solid-state batteries and supercapacitor materials for hybrid energy storage and energy management in power grids is becoming more pressing.

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Electric double layer capacitors (EDLCs) and pseudocapacitors are distinguished by the faradaic reactions[1]. Materials with pseudocapacitance are more attractive to researchers for their potential in energy storage, which primarily depend on their fast and reversible redox reaction[2, 3]. Manganese-containing electrode materials have mainly received increasing attention owing to their high specific capacitance, low cost, natural abundance, and environmental benignity[4].

In this paper, we provide a facile practice of how to make better electrodes and build asymmetric supercapacitors (ASCs), as well as the calculation of average performances. Then some published papers about manganese-containing electrodes will be listed. From them, we can find out the current situation and some urgent challenges.

METHODS

Experiments

The three electrodes and two electrodes test devices were illustrated in Figure 1, respectively. Active electrode materials, electrodes are prepared by mixing the active material with carbon black and PTFE in ethanol with the weight ratio 8.5:1:0.5, and then the slurry is pasted onto nickel foam. The prepared samples are heated at 105°C overnight to evaporate the solvent entirely and pressed at 20 MPa for 30 s to avoid the mass loss of active materials in the test. During the three electrodes test, the typical mass loadings are 4 to 4.5 mg cm$^{-2}$ for all active materials. The three electrodes system has a nickel foam loading with active materials as the working electrode, a platinum electrode as the counter electrode, a saturated calomel electrode (SCE) as the reference electrode, and 1 M KOH or 1 M Na$_2$SO$_4$ as the electrolyte.

For the two electrodes test, coin-type ASCs are needed. The charge balance should be finished firstly, which will follow the equation $q_+ = q_-$, $q = C \times \Delta V \times m$. So that the mass loading ratio of positive and negative electrodes should be determined after getting the three electrodes capacitance (C) and voltage range ($\Delta V$), and the cell mass loading is about 6 mg cm$^{-2}$[5]. The ASCs are fabricated by 2025 coin type full cells with nickel foam electric collectors, cellulose paper separators and neutral or alkaline aqueous solution electrolyte[6]. Each cell is left to stay overnight before the test.

Both three and two electrodes tests are finished by an electrochemical workstation to collect the raw data such as electrochemical impedance spectroscopy, cyclic voltammetry curve and galvanostatic charge discharge curve.

Figure 1. Three electrodes test and two electrodes tests. a) Three electrodes beaker battery. b) Two electrode button-battery type supercapacitor.
Calculations

After finishing the electrodes measurements, the electrode specific capacitance was calculated from the galvanostatic charge discharge curves according to the equation (1):

\[ C_s = \frac{I \Delta t}{m} \]  

\( C_s \) (F g\(^{-1}\)) is the electrode specific capacitance, I (mA) the discharge current, and m (g) the designated mass of active materials, \( \Delta V \) (V) potential drop during discharge, \( \Delta t \) (s) discharge time respectively.

For ASC devices, the cell specific capacitance was derived by equation (2):

\[ C_{cell} = \frac{I \Delta t}{m \Delta V} \]  

\( C_{cell} \) (F g\(^{-1}\)) is the cell specific capacitance, I (mA) the discharge current, and m (g) the total mass of active materials pasted on both electrodes, \( \Delta V \) (V) and \( \Delta t \) (s) are the same as described above.

The cell energy density and power density are calculated from the following equations:

\[ E = \frac{C_{cell}(\Delta V)^2}{7.2} \]  
\[ P = \frac{3600E}{\Delta t} \]

where E (Wh kg\(^{-1}\)) is the energy density, P (W kg\(^{-1}\)) the power density[7-9].

RECENT PROGRESS

MnO\(_2\) Materials

We found in our previous work that the specific capacitance for MnO\(_2\) is 195 F g\(^{-1}\) at 1 A g\(^{-1}\) in a voltage window from -0.4 to 0.45 V in 1 M KOH, 70 F g\(^{-1}\) at 1 A g\(^{-1}\) in a voltage window from 0 to 1 V in 1 M Na\(_2\)SO\(_4\)[10]. Brousse and his co-workers prepared amorphous MnO\(_2\) by fumaric acid and KMnO\(_4\) and it shows 150 F g\(^{-1}\) specific capacitance in 0.1 M K\(_2\)SO\(_4\)[11]. This kind of MnO\(_2\) was made by hydrothermal method with the reaction of KMnO\(_4\) and MnCl\(_2\). Commercially available cryptomelane-type \( \alpha \)-MnO\(_2\) was used as positive electrode material in Olivier Crosnier’s research on FeWO\(_4\)[6]. This kind of MnO\(_2\) shows 100 F g\(^{-1}\) electrode specific capacitance in 5 M LiNO\(_3\). It is well known that the theoretical specific capacitance value of MnO\(_2\) is 1233 F g\(^{-1}\). The main limiting issues of MnO\(_2\) lie in poor electronic conductivity because of its wide band gap, low ionic diffusion constant, and low structural stability[12].

To solve these problems, Yat Li tried to enhance the rate capability of MnO\(_2\) electrode via the Ostwald ripening process. After treatment, the electrode exhibits an areal capacitance of 618 mF cm\(^{-2}\) at a high scan rate of 200 mV s\(^{-1}\), which is three times higher than that of the untreated sample. The method of hydrothermal treatment is noteworthy, for it improves the electrical conductivity and ion diffusion rate, gives a feasible idea to improve the ability of energy storage and makes us interested in nanomaterial surfaces[13].

Other people combined MnO\(_2\) with carbon materials such as graphene, nanoparticle, nanosheet, nanowire, graphene oxide and mesoporous carbon and got new composites with better specific capacitances[4]. Nanocomposite of needle-like MnO\(_2\) nanowires arrays sandwiched between graphene nanosheets was synthesized by a simple chemical method, a. In 1 M Na\(_2\)SO\(_4\) aqueous electrolyte (pH=9) at room temperature, it shows 33 Wh kg\(^{-1}\) energy density at 1000 W kg\(^{-1}\) power density[14]. Carbon nanotubes (CNT) also met nice use, Jian Yang got MnO\(_2\) and CNT nanocomposite, which reaches 162.2 F g\(^{-1}\) at the current density of 0.2 A g\(^{-1}\) with excellent cycling stability with 90% of its specific capacitance left after 2000 cycles[15]. Junlei Qifabricated vertically standing graphene-MnO\(_2\) nanoparticle hybrids as electrode materials, exhibits a high specific capacitance of 1176 F g\(^{-1}\) at 2 mV s\(^{-1}\), and a long
cycling lifetime with negligible capacitance loss after 10000 cycles. This work almost reaches the theoretical specific capacitance value of MnO$_2$, for their effort on the 3D structure which provides electron transport superhighways[16].

These efforts work to enhance the conductivity of the MnO$_2$ material and give us some credible ideas about the performance of supercapacitors for manganese materials. However, for large-scale applications of supercapacitor materials in smart grids and energy storage systems, we should take other factors, such as yield and cost, into consideration, then accept these ideas critically and selectively.

MnO$_2$ Materials

In addition to MnO$_2$, other manganese oxides, Mn$_3$O$_4$ and MnO have been known as significant candidates with unique properties for application in supercapacitors. They share a similar energy storage mechanism. Aghazadeh prepared Mn$_3$O$_4$ nanorods with secondary plate-like structures by adopting electrochemical deposition method[17]. Using a 1 M Na$_2$SO$_4$ solution as the electrolyte, they get potential window 1 V. This material was evaluated to be as high as 279 F g$^{-1}$ specific capacitance, but after 1000 cycles CV scan only 81.4% capacitance remains. Gund synthesized graphene oxide and Mn$_3$O$_4$ material with specific capacitance 344 F g$^{-1}$ in 1 M Na$_2$SO$_4$ solution[18]. Mn$_3$O$_4$ thick film electrodes have been manufactured by spray pyrolysis method and exhibit capacitance 187.79 F g$^{-1}$. The calculated energy density and power density for the same sample were 26 Wh kg$^{-1}$ and 1000 W kg$^{-1}$[19]. Sun researched the MnO and carbon composite as cathode and Fe$_2$O$_3$ and carbon composite material as the anode, using the aerogel as the precursor, achieving the performance of 48.7 Wh kg$^{-1}$, 1000 Wh kg$^{-1}$ in 1 M Na$_2$SO$_4$ electrolyte[20]. Although many MnO$_x$ materials were appropriately synthesized and got good capacitance, there are still some problems. For example, the mechanism of rapid redox reactions in different electrolytes and the phase change situation during long-cycling ought to be made clear.

MnS Materials

Manganese sulfides is a new member of supercapacitors family. Based on the different valence states of Mn element as well as higher conductivity, these materials should be potentially used for energy storage. Yongfu Tang obtained monodispersed hollow spindle-like nanosphere through a facile hydrothermal process. It displayed a high specific capacitance of 704.5 F g$^{-1}$ in 2 M KOH, energy density 11.7 Wh kg$^{-1}$ even at the high power density of 4450 W kg$^{-1}$[21]. Hongying Quan finished their work and got $\alpha$-MnS on nitrogen-doped reduced graphene oxide with long-term cycling stability. The most significant bright spot in this article is the device excellent rate capability with 16.1 Wh kg$^{-1}$ at a power density of 20000 W kg$^{-1}$[22].

MnOOH Materials

Manganese oxyhydroxide (MnOOH) is a trivalent stable polymorph hydroxide under ambient conditions[23]. Feng Li reported the one-pot synthesis of MnOOH nanorods on graphene and made it into asymmetric supercapacitors. In 6 M KOH, it performs a power density of 12800 W kg$^{-1}$ at energy density of 10.7 Wh kg$^{-1}$, with no decay of specific capacitance after cycling for 5000 times[23]. Lujun Pan fabricated polyaniline and $\gamma$-MnOOH composite on a buckypaper, it shows a maximum specific capacitance of 567.5 F g$^{-1}$ at a current density of 0.5 A g$^{-1}$[24]. However, after 5000 cycles charging and discharging, only 77.2% specific capacitance remains. MnOOH material is abundant in natural storage and a
competitive candidate as an electrode material. However, like the abovementioned results showing, more work is needed to make it better in overall electrochemical performance, especially energy density and cycling stability research. Zhongai Hu used electrodeposition to fabricate thin-wall MnOOH on carbon cloth, measured its performance in 0.5 M LiNO₃ solution. They finally come up with a symmetric supercapacitor with an energy density of 32.5 Wh kg⁻¹ at power density of 850 W kg⁻¹, the cycling stability is 84.6% of the initial capacitance after 10000 cycles, which is excellent among similar aqueous devices[25].

Other Mn-containing Materials.
Mn₃(PO₄)₂[26], MnCO₃[27], MnSiO₃[28]are also reported to serve as supercapacitor material. These powdery materials share similar advantages like simple synthesis methods, cheap and abundant raw materials, unique porous structures. However, our understanding of these supernova electrode materials is inadequate, that need more experiments to improve their performances. In addition to the synthesis work, we should select suitable test systems to assemble them into devices, which include current collectors, electrolytes, and separators. Particularly suitable electrolytes, it is important to test the performance of a new electrode material in aqueous solutions of different acids, bases and salts. Devaraj and his colleagues tried their best to find a better electrolyte for MnCO₃ material. He chose aqueous solution of 0.1 M Na₂SO₄, 0.1 M Mg(ClO₄)₂ and 6 M KOH for tests. Finally, he found it perform better in 0.1 M Mg(ClO₄)₂, 216 F g⁻¹ and much stability[27].

<table>
<thead>
<tr>
<th>Electrolyte</th>
<th>Specific capacitance (F g⁻¹)</th>
<th>Cycles (stability)</th>
<th>Maximum energy density (Wh kg⁻¹)</th>
<th>Maximum power density (W kg⁻¹)</th>
<th>Ref.#</th>
</tr>
</thead>
<tbody>
<tr>
<td>MnO₂</td>
<td>1 M KOH</td>
<td>195/ 1 A g⁻¹</td>
<td>1200 (90%)</td>
<td>17.2</td>
<td>[10]</td>
</tr>
<tr>
<td>MnO₂</td>
<td>5 M LiNO₃</td>
<td>100/ 1 A g⁻¹</td>
<td>40000 (100%)</td>
<td>-</td>
<td>[6]</td>
</tr>
<tr>
<td>MnO₂</td>
<td>0.1 M K₂SO₄</td>
<td>150/ 0.53 A g⁻¹</td>
<td>1200 (88%)</td>
<td>3.3</td>
<td>[11]</td>
</tr>
<tr>
<td>MnO₃-h</td>
<td>5 M LiCl</td>
<td>618 mF cm⁻²/ 200 mV s⁻¹</td>
<td>10000 (96%)</td>
<td>5 mWh cm⁻³</td>
<td>-</td>
</tr>
<tr>
<td>MnO₂/G</td>
<td>1 M Na₂SO₄ (pH=9)</td>
<td>276/ 0.5 A g⁻¹</td>
<td>1200 (100%)</td>
<td>37</td>
<td>20000</td>
</tr>
<tr>
<td>MnO₂/CNT</td>
<td>0.5 M Na₂SO₄</td>
<td>162.2/ 0.2 A g⁻¹</td>
<td>2000 (90%)</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>MnO₂/G</td>
<td>1 M Na₃SO₄</td>
<td>1176/ 2 mV s⁻¹</td>
<td>10000 (98%)</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>MnO₃O₄</td>
<td>1 M Na₂SO₄</td>
<td>298/ 2 mA cm⁻²</td>
<td>1000 (95%)</td>
<td>-</td>
<td>26</td>
</tr>
<tr>
<td>Mn₃O₄/GO</td>
<td>1 M Na₂SO₄</td>
<td>344/ 5 mV s⁻¹</td>
<td>3000 (85%)</td>
<td>93</td>
<td>10000</td>
</tr>
<tr>
<td>MnO/NCA</td>
<td>1 M Na₂SO₄</td>
<td>188/ 1 A g⁻¹</td>
<td>1000 (100%)</td>
<td>26</td>
<td>1010</td>
</tr>
<tr>
<td>MnO/GO</td>
<td>1 M Na₂SO₄</td>
<td>553/ 10 mV s⁻¹</td>
<td>5000 (96.8%)</td>
<td>48.7</td>
<td>10000</td>
</tr>
<tr>
<td>MnS</td>
<td>2 M KOH</td>
<td>704.5/ 1 mV s⁻¹</td>
<td>5000 (62.6%)</td>
<td>11</td>
<td>6000</td>
</tr>
</tbody>
</table>
MnS/N-rGO       3 M KOH    933.6/ 1 A g⁻¹    2000 (95%)    27.7    20000 [22]
MnOOH/G         1 M Na₂SO₄ 268/ 0.5 A g⁻¹  5000 (98.3%)  41.1  12800 [23]
Mn₃(PO₄)₂       2 M KOH    360/ 0.5 A g⁻¹  2000 (56%)     -     -   [26]
MnCO₃           0.1 M Mg(ClO₄)₂ 216/ 0.33 A g⁻¹  500 (90.3%)   -     -   [27]
MnSiO₃          1 M KOH    281/ 1 A g⁻¹    1000 (74.7%)  -     -   [28]

CONCLUSIONS

Mn-containing materials including MnOₓ, MnOOH, MnS, MnCO₃, Mn₃(PO₄)₂, MnSiO₃ are introduced here for energy storage use. In the previous works, many people used smart methods, for example, increasing the specific surface area of materials, increasing the conductivity of materials, designing 3D hierarchical structures, improving the surface microstructure, and attempting different electrolytes to enhance the performance of electrode materials of Mn-containing supercapacitors. Researchers have yielded good results because of their continuous efforts, some of the materials are promising in practical application.

We have reviewed some recent experimental results and provide a facile method for assembling ASCs and data analysis. Mn-containing supercapacitors materials have been developed for two decades, yet most commercial companies still choose to double-layer capacitive activated carbon material supercapacitors. We should not only accept the inspirations from these experiments but also criticize them and make continuous innovation. Mn-containing supercapacitor electrode material has rich chemical valences, changing morphologies, many energy saving and environmentally friendly synthesis methods so that it has great application prospects. More efforts need to be made on reducing costs, increasing yields, improving the assembling process of the devices, and studying the interaction between the electrolytes and the active materials. Under the continuous efforts of many researchers, the energy storage mechanism and performance degradation mechanism of supercapacitors are sure to be more precise. With the development of theoretical knowledge, we can find the path to industrialize the supercapacitor devices more easily. Therefore the application of supercapacitors in smart grids and new energy will meet a brighter future, the implementation of smart grids and new energy will make a better world.

REFERENCES


