Study on the preparation of composite MnO₂

Hui Qing¹,², Su Xu¹,⁴, Huizi Kuang¹,², WenChao Liao³, Xiaodong Huang¹ and Xiuxiu Zhang¹

¹ School of Environmental Science and Engineering, Xiamen University of Technology, Xiamen, 361024, PR China;
² College of Environmental Science and Engineering, North China Electric Power University, Beijing, 102206, PR China;
³ College of Health and Environmental Engineering, Shenzhen Technology University, Shenzhen, 518118, PR China
⁴ Email: schnell19@qq.com

Abstract. The manganese dioxide (MnO₂) is a material that has broad application prospects and economic value, which is used in various fields. However, the poor conductivity, less active sites and the easy collapse of the structure during the reaction, limit application. In this paper, three kinds of MnO₂ were prepared by simple method, α-MnO₂, β-MnO₂, and γ-MnO₂. And the properties of the sample were further analyzed by Brunauer–Emmett–Teller (BET), X-ray diffractometer (XRD), scanning electron microscopy (SEM), Energy Dispersive X-Ray Spectroscopy (EDX) and fourier transform infrared spectroscopy (FTIR). Then α-MnO₂ was chosen as the precursor of this study. Three different ratios of transition metal Ni and Co are respectively loaded with α-MnO₂. Electrodes made of 7 different samples including α-MnO₂, complete cyclic voltammetry test. Results show that: (1) α-MnO₂ is not easy to collapse and suitable for precursor; (2) the addition of metal Ni and Co increases the specific surface area of the material to varying degrees. Co@a-MnO₂-2 has the highest specific surface area and porosity, which can provide more active sites when applied; (3) all seven samples have good capacitance characteristics. The best is Co@a-MnO₂-0.5, but Co@a-MnO₂-2 is very close to Co@a-MnO₂-0.5. Comprehensive analysis, the best ratio for this study is Co@a-MnO₂-2.

1. Introduction

MnO₂ has tantalum capacitance behavior [1]. Due to abundant resources, environmental protection, and high theoretical value of capacitance, the application of supercapacitors has been rapidly promoted.

However, the single MnO₂ electrode has some drawbacks, such as poor conductivity, short cycle life and low specific capacitance. Study at the present stage mainly focuses on doping modification or compounding with other materials to improve the overall performance by the synergistic effect between the doping elements and the composite components.

Doping metal elements in MnO₂ electrode materials can improve many properties of materials, such as conductivity, specific capacitance, cyclic stability, etc. At present, the metal elements doped into MnO₂-based electrodes have been studied, such as Co, Fe, Bi, Pb, Ni, V, Al, Cr, etc. After fabricating, impurities will enter into the MnO₂ structure and act as a branch lattice, which keeps the MnO₂ lattice an "open" structure and greatly reduces the resistance of protons and electrons to move between the lattices [2].
Gan et al. fabricated two double-layer composite electrodes, which are onto activated carbon electrodes by coating anion exchange resin (A520E) and carboxyl functionalized multi-walled carbon nanotubes (MWCNTs-COOH) [3]. Liu et al. Deposited MnO₂ on the surface of graphene to obtain graphene-MnO₂ composite via pulse electrodeposition under the supergravity field, which is enhanced supercapacitive performance [4]. The specific capacitance is 595.7 F g⁻¹, which is not decay after 1000 cycles of testing. Myint et al. Prepared electrodes by loading zinc oxide (ZnO) micro/nano materials (nanoparticles, nanorods, microsheets, and microspheres) on activated carbon cloth (ACC) [5]. The results of desalination experiments show that nanorods and microsheets have the best effect. Ryoo et al. used metal alkoxide to dope heavy metals on activated carbon cloth, Al, Zn, Ti and Zr. The results of characterization and desalination experiments show that Ti not only reduces the physical adsorption capacity but also improves the electroabsorption capacity [2].

The objective of this paper is to develop the new active material that the fabrication of electrodes grafted with different proportions of transition metals Co or Ni (1:0.5, 1:1 and 1:2) on alpha-MnO₂. Before screening out α-MnO₂, three crystalline forms of MnO₂, α-MnO₂, β-MnO₂, and γ-MnO₂, were prepared by simpler method. After further testing by XRD BET and FSEM, α-MnO₂ is the most suitable precursor for this study.

This paper aims to: (i) on the basis of α-MnO₂, increase the active site of the material while expanding the specific surface area; (ii) by the doping of transition metals Co and Ni, the metal-free electrons are used to improve the electronic distribution of MnO₂ and enhance its conductivity; and (iii) improve the electrochemical performance of the electrode and the catalytic efficiency of the redox reaction, and better apply to the actual water treatment problem.

2. Results and discussion

Figure 1. XRD pattern of as-prepared MnO₂ samples.
2.1. Material fabrication and characterization
The MnO$_2$ were prepared through a hydrothermal reaction [6]. Samples have different mass ratios and hydrothermal reaction time. The label is consistent with the crystal plane determined by the standard card after the X-ray diffraction (XRD) analysis, which are α-MnO$_2$, β-MnO$_2$ and γ-MnO$_2$ respectively.

The XRD patterns of the three composites shown in Figure 1 are almost identical and all of the lines can be indexed to α-MnO$_2$, β-MnO$_2$ and γ-MnO$_2$ in the tetragonal structure, confirming that three kinds basic structure of samples α, β and γ have been successfully synthesized.

Scanning electron microscopy (SEM) was conducted to confirm the microstructures of materials (Figure 2). Combining previous studies, it can be seen that the α shows flocculent morphology, which structure is more fluffy and nanowire morphology obviously. Besides, β and γ are similar in appearance for closely arranged. Through further analysis, α is less likely to collapse than β and γ, that is, α is more suitable as a precursor for further study.

![Figure 2. SEM images of as-prepared MnO$_2$ samples.](image)

By hydrothermal reaction, Co and Ni were loaded into α-MnO$_2$ with transition metal-ion: MnO$_2$ molar ratio of 0.5:1, 1:1 and 2:1. Labeled as Co@α-MnO$_2$-0.5, Co@α-MnO$_2$-1, Co@α-MnO$_2$-2 and Ni@α-MnO$_2$-0.5, Ni@α-MnO$_2$-1, Ni@α-MnO$_2$-2, respectively.

By scanning SEM shows that the crystallization degree of powder is more obvious, the structure is clearer and more stable, and the gap can accommodate ions is more abundant with the increase of Co ions concentration. However, the structure formed by loading Ni is blocky or flaky, which makes it difficult to give ion attachment space (Figure 3). The XRD patterns of all composites shown in Figure 4 are almost identical, which can be indexed to α-MnO$_2$ as all samples retained the characteristic peaks of α-MnO$_2$. While EDX detector was used to determine the composition of elements (Figure 5), it can see metals Co, Ni have successfully doped into α-MnO$_2$.

Brunauer–Emmett–Teller (BET) analyses of the α-MnO$_2$ that had been ground into a powder revealed a surface area of only 5.026 m$^2$·g$^{-1}$, which is less than 5% of the Co@α-MnO$_2$-2 composites. Co@α-MnO$_2$-2 composites had a large surface area of 171.642 m$^2$·g$^{-1}$ while Ni@α-MnO$_2$-2 is 93.109 m$^2$·g$^{-1}$. Table 1 shows that the fabricated of metals Co and Ni increases the specific surface area of α-MnO$_2$ to a certain extent. As the doping concentration increases, Co@α-MnO$_2$ is greater than Co@α-MnO$_2$. This means that Co@α-MnO$_2$ can provide more electroactive sites in the electrochemical reaction, which is more conducive to degradation. Therefore, in the two metal ions, Co ions loaded on the substrate will have higher degradation efficiency.

2.2. Electrochemical performance in a three-electrode system
Cyclic voltammetry (CV) was used to determine the capacitances of all composites electrodes, with the gravimetric capacitance (F·g$^{-1}$) being calculated from
Figure 3. SEM images of as-prepared MnO₂ composite samples.

Figure 4. XRD pattern of as-prepared MnO₂ composite samples.

Figure 5. EDX images of as-prepared MnO₂ composite samples.
where \( S \) is the geometric surface area of the working electrode, \( v \) is the sweep rate, \( m \) is the mass of the active material, and \( \Delta U \) is the potential of the scan.

The performance of all composites was compared to that of \( \alpha \)-MnO\(_2\) and \( \beta \)-MnO\(_2\) electrode of the same geometric area. At a scan rate of 50 mV\( \text{s}^{-1} \), areal capacitances of 27.272, 21.502, 39.339, 36.877, 32.560, 10.015, 32.839, 24.550 F\( \text{g}^{-1} \) were recorded for the \( \alpha \)-MnO\(_2\), \( \beta \)-MnO\(_2\), Co@\( \alpha \)-MnO\(_2\)-0.5, Co@\( \alpha \)-MnO\(_2\)-1, Co@\( \alpha \)-MnO\(_2\)-2, Ni@\( \alpha \)-MnO\(_2\)-0.5, Ni@\( \alpha \)-MnO\(_2\)-1, and Ni@\( \alpha \)-MnO\(_2\)-2 samples, respectively (Figure 6). Mesopore has larger specific surface area, where the pores are well interconnected and distributed, which shows better ion storage capacity, thus explaining the improvement capacitance.

![Figure 6](image)

**Figure 6.** CV curves of different MnO\(_2\) samples in 1mol\( \text{L}^{-1} \) Na\(_2\)SO\(_4\) solution with scanning potential width of 0.6V and potential scanning rate of (A)50mV\( \text{s}^{-1} \), (B)100 mV\( \text{s}^{-1} \).

### 3. Conclusions

A hydrothermal approach to deposit transition metal-ion (Co and Ni) on \( \alpha \)-MnO\(_2\) nanoparticles has been successfully demonstrated. There are three different proportions of metal Ni and metal Co were respectively loaded, namely Co@\( \alpha \)-MnO\(_2\)-0.5, Co@\( \alpha \)-MnO\(_2\)-1, Co@\( \alpha \)-MnO\(_2\)-2, Ni@\( \alpha \)-MnO\(_2\)-0.5, Ni@\( \alpha \)-MnO\(_2\)-1, and Ni@\( \alpha \)-MnO\(_2\)-2.

Under the same conditions, the performance of \( \alpha \)-MnO\(_2\)/Co ions and \( \alpha \)-MnO\(_2\)/Ni ions in terms of the surface area and gravimetric capacitance show a great improvement in comparison with \( \alpha \)-MnO\(_2\).

The resulted composite was then tested as electrodes for CV. Based on cyclic voltammetry, the composite Co@\( \alpha \)-MnO\(_2\)-0.5 has the largest capacitance, but Co@\( \alpha \)-MnO\(_2\)-2 is very close to Co@\( \alpha \)-MnO\(_2\)-0.5. Meanwhile, Co@\( \alpha \)-MnO\(_2\)-2 has the highest specific surface area and porosity, which can provide more active sites when applied. Therefore, the conclusion of this study is that Co@\( \alpha \)-MnO\(_2\)-2 is the optimal ratio.

### 4. Experimental section

#### 4.1. Material synthesis

The MnO\(_2\) powders were prepared via a hydrothermal reaction [6]. The precursor solution was prepared by adding 0.2g MnSO\(_4\) and 0.5g KMnO\(_4\) dropwise 60 mL deionized water with continuous stirring by Ultrasonic Cleaner over a period of 10 min. Then the mixed solutions were transferred into a 200 mL Teflon-lined stainless steel autoclave, which placed in the furnace at 150 \( ^\circ \text{C} \) for 12 h. After cooling naturally, solution solid-liquid separation is obvious, the reaction liquid becomes colorless, that is to say, all purple MnO\(_4\) ions vhave been reduced during this period. From the comparison of
the weights of the Titanium plate before and after deposition, the amount of deposition of MnO$_2$ can be obtained. Labeled as α-MnO$_2$.

The procedure of sample synthesis is similar, the difference lies in the dosing of chemicals, reaction temperature and reaction time. The samples with 0.2g MnSO$_4$ and 0.5g KMnO$_4$, reaction time 12 h and reaction temperature 150°C is labeled as α-MnO$_2$, whereas the other, obtained from 0.2g MnSO$_4$ and 0.4g KMnO$_4$, 180°C and the 10 h process, is labeled as β-MnO$_2$; 0.2g MnSO$_4$ and 0.1g KMnO$_4$, 150°C and the 5 h process, is labeled as γ-MnO$_2$.

Co and Ni were loaded into α-MnO$_2$ with transition metal-ion: MnO$_2$ molar ratio of 0.5:1, 1:1 and 2:1. Based on the chemical dosage of sample α-MnO$_2$, 0.0005mol, 0.001mol and 0.002mol of chemical Co(NO$_3$)$_2$·6H$_2$O or NiSO$_4$·6H$_2$O were added to the solution, labeled as Co@α-MnO$_2$-0.5, Co@α-MnO$_2$-1, Co@α-MnO$_2$-2 and Ni@α-MnO$_2$-0.5, Ni@α-MnO$_2$-1, Ni@α-MnO$_2$-2, respectively.

The α-MnO$_2$, β-MnO$_2$ and all composite samples as an electrode active material made into a working electrode, used for comparison purposes. So, eight beakers were prepared. Eight different samples, 0.3g superconducting carbon black and 0.1g PVDF were added to each beaker. After mixing, about 10mL of 1-methyl-2-pyrrolidone was added to form a flowable concentrated slurry. Then, the mixture was stirred at room temperature for 48h with 2000 rad·min$^{-1}$ on a magnetic stirrer. The mixture was evenly transferred to the titanium plate (3 cm × 3 cm) by coating. The titanium plate was then placed in an oven at 80 °C for 3 hours until the evaporation of NMP. The working electrode was fabricated.

4.2. Material characterization
The structure and morphology of the resulting composites were characterized by XRD (Cu Ka radiation $\lambda = 0.15418$nm) over the two-theta range 10–90°and SEM (JSM700F-JEOL) at 10 kV. The specific surface area was determined by the Bennet–Emmett–Teller (BET) method (WBL-830 specific surface area and porosity analyzer).

4.3. Electrochemical measurements
The electrochemical experiments were performed on with the aid of a Zennium 2.0 electrochemical workstation (Zahner). Cyclic voltammetry (CV) measurements were carried out in 1 M Na$_2$SO$_4$ electrolyte using a three-electrode system with 3 cm × 3 cm sheets of MnO$_2$, MnO$_2$/Co or MnO$_2$/Ni as the working electrode, a platinum counter electrode, and a saturated calomel reference electrode (SCE) with a potential range of −0.6− 0.6V versus SCE.

| composites powers | surface area (m²·g$^{-1}$) |
|-------------------|-----------------------------|
| alpha-MnO$_2$     | 5.026                       |
| beta-MnO$_2$      | 27.222                      |
| Co@α-MnO$_2$-0.5 | 43.476                      |
| Co@α-MnO$_2$-1   | 49.127                      |
| Co@α-MnO$_2$-2   | 171.642                     |
| Ni@α-MnO$_2$-0.5 | 6.140                       |
| Ni@α-MnO$_2$-1   | 86.132                      |
| Ni@α-MnO$_2$-2   | 93.109                      |

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