Electrochemical performance of Ce/Ni-MOFs electrode

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Abstract. A novel electrochemical capacitor electrode based on Ce/Ni-MOFs was prepared. During this process, we introduced hydrothermal method. However improper reaction conditions would cause the collapse of crystal structure which will do harm to the performance of the electrode. We explored the option reaction conditions including temperature and endurance time. Under the option condition, we performed a series of electrochemical testing and surface characterizations to explore and electrochemical performance and cycle life. We obtain the Ce/Ni-MOF electrode with the capacitance of 584 F/g and the retention of 95.5% after 1000 cycles of charging and discharging test. This indicate that Ce/Ni-MOFs might be a promising supercapacitor electrode for future use.

1. Introduction
With the rapid development of industry and the continuous growth of population, the demand for energy surges. The environmental pollution caused by traditional fossil fuels has caused great troubles to human beings and the ecological environment, and people have an increasingly urgent need for efficient, clean, environmentally friendly and sustainable new and renewable energy.[1] Supercapacitor is a new type of energy storage device between electrolytic capacitor and battery, which is a kind of energy storage device with high energy efficiency, economic utility and environmental protection.[2] Metal Organic Framework materials (MOFs) is a porous material with periodic network structure formed by self-assembly of metal ions and oxygen, nitrogen and other multidentate organic ligands.[3] Diaz et al. [4] replaced Zinc ions with Nickel ions and prepared Co8-MOF-5 electrode materials, and prepared slurry with acetylene black and PTFE in the weight ratio of 75:15:10. The material prepared has a higher conductivity than most of metal oxide electrode material. Fan Yang et al. [5] prepared a kind of amorphous metal frame material UiO-66 (Zr-MOF) and attained the capacitance of 920 F/g. In this work, we prepared a kind of Ce/Ni-MOF with promising electrochemical performance in hydrothermal method. We explore the option hydrothermal reaction temperature and endurance time. Under the option condition, we exert a series electrochemical testing and surface characterization methods. Finally, we observed the capacitance of a maximum of 584 F/g and the capacitance retention of 95.5% after 1000 cycles of charging and discharging, which proves that Ce/Ni-MOFs can be an ideal electrode with good electrochemical performance and great potential.

2. Experimental
All the reagents used in the experiment were analytically pure and were shown in Table 1(a) and instruments were shown in Table 1(b).
Table 1. Regent and Instrument

| Chemical formula | Molecular weight | Manufacturer |
|------------------|------------------|--------------|
| C₃H₇NO(N,N-dimethylformamide) | 73.09 | Tianjin Kemiou Chemical Reagent Co., Ltd. |
| C₈H₆O₄ | 166.131 | Aladdin |
| Ni(NO₃)₂·6H₂O | 290.79 | Tianjin Fuchen Chemical Reagent Co., Ltd. |
| CeO₂ | 172.11 | Tianjin Beichen Fangzheng Chemical Regent Co., Ltd. |
| CH₃CH₂OH | 46 | |

(b)

| Instruments | Manufacturer |
|-------------|--------------|
| ME104E Electronic balance | Beijing Zhongyi Co., Ltd. |
| DF-101S Concentrated type constant temperature heating magnetic stirrer | Shijiazhuang Yangxing Instrument Co., Ltd. |
| DZF-6020 Vacuum drying box | Shanghai Qixin Science Instrument Co., Ltd. |
| AP-9925N Vacuum filter | Tianjin automatic Science Instrument Co., Ltd. |

Experiment materials is prepared by hydrothermal method. At room temperature, nickel nitrate (Ni(NO₃)₂·6H₂O, 3.8g, 0.01mol), cerium oxide (CeO₂, 0.34g, 0.002mol) and terephthalic acid (0.32g, 0.05mol) were first weighed and placed in a beaker. Secondly, anhydrous ethanol, N, n-dimethylformamide and deionized water were each taken in a quantity of 1:1:1, and then poured into a beaker and mixed with the weighed substance. Then, put the mixed beaker on the magnetic stirrer with constant temperature heating for stirring. Thirdly, put the liquid after stirring for a period of time into the hydrothermal reactor; Finally, the hydrothermal reactor was put into the vacuum drying oven, which was then vacualized and heated at 100°C for 48h.In addition, after the reaction was completed, the prepared material was repeatedly washed with anhydrous ethanol solution for 2-3 times, and then the filtered material was put into a vacuum drying oven for drying at 100°C for 60min to obtain the final required material, and the final material was grinded for use.

Figure 1. Three electrodes testing system
The materials were made into electrodes in the following steps. First, according to the mass ratio of 8:1:1, the electrode material, acetylene black and polytetrafluoroethylene (PTFE) were put into the mortar and added an appropriate amount of anhydrous ethanol for grinding. Secondly, the above materials are uniformly coated on the foam nickel, and then put into a vacuum drying oven for drying at a certain time and temperature. Finally, the coated nickel foam slices are pressed into 7 MPa pieces to make the final working electrode. The test was conducted with a three-electrode test system composed of platinum extremely auxiliary electrode, saturated calomel extremely reference electrode, and 6 mol/L potassium hydroxide solution as electrolyte.

3. Results and discussion

Scanning Electron Microscope (SEM) is an effective method to study the microstructure of solid surface. In order to explore the influence of the surface microstructure of MOFs materials, Ce/Ni-MOFs materials were prepared and characterized, the results are presented in Figure 2.

![Figure 2. Scanning Electron Microscope figure of Ce/Ni-MOFs](image)

It can be vividly shown in Figure 2 that Ce/Ni-MOF’s surface presents the surface exhibits a uniform layered structure. This can be significantly decrease ion diffusion distance and improve energy storage condition of the electrode. [6]

The research methods of electrochemical properties of electrode materials in this experiment mainly include: cyclic voltammetry, Galvano static charge-discharge measurements and cycling charge-discharge testing. All electrochemical properties were tested on CHI760E (Shanghai Chenhua Co., Ltd.). The specific capacitance were calculated with Eq (1).

\[ C = \frac{I \cdot \Delta t}{m \cdot \Delta V} \]  

In Eq (1), C, I, m, Δt and ΔV represents specific capacitance, currents, the mass of the testing sample, discharging time and voltage window, respectively. In this part, we discuss the influence of hydrothermal temperature and endurance time. The electrochemical performance is represented in Figure 3.
Figure 3. Influence of hydrothermal (a) temperature; (b) endurance time to the specific capacitance.

It can be vividly shown in Figure 3(a) that Ce/Ni-MOFs exhibits the highest specific capacitance with 584 F/g. Meanwhile there is obvious redox peak, which indicates that there is highly reversible redox reaction taking place on the electrode and forms pseudo capacitance. The electrochemical performance improves with the range of 50°C and 100°C. While the temperature increases over 100°C, the performance decreases with the increase of the temperature. The reason and principle of this shall be the high hydrothermal temperature do contribution to the collapse of the holes in the materials.

Figure 3(b) indicates that while the reaction time is 48h, the material exhibit the highest specific capacitance of 564 F/g. The increase of hydrothermal time will increase the crystallinity of the sample, and the grain gradually increases. When the hydrothermal temperature remains unchanged, the electrochemical properties of the sample first increase and then decrease with the increase of hydrothermal time. When the time is 48h, the electrochemical performance of the sample is the best. This is because the short time of water heating will lead to the crystallization of the remaining organic matter on the surface of the sample, which will reduce the site participating in the reaction activity, while the longer time of calcination will destroy the porous structure and specific surface area of the sample.

Figure 4. (a)CV and (b) GCD curves of Ce/Ni-MOFs and (c) specific capacitance calculated from GCD.

Figure 4 respects electrochemical performance of Ce/Ni-MOFs. (a) Shows the cyclic voltammetry curves of this kind of materials. The scanning rate ranges from 10 mV/s to 30 mV/s. It can be analyzed from the figure that the oxidation and reduction potential are approximately 0.18V and 0.55V respectively. This might be explained by difference of the surface structure and pore distribution in the redox reaction. [6]Figure 3 (b) and (c) respect the GCD testing result of Ce/Ni-MOFs. While the current
density increases from 1A/g to 10A/g, the capacitance are 422, 324, 230, 184, 162 and 127F/g respectively, showing the trend of decreasing. Besides, specific capacitance decreases when the current density increases and tends to be gentle. The option current density is 1A/g, and the capacitance reaches 422F/g.

![Figure 5. Cycling charge and discharge test of the Ce/Ni-MOF electrode](image)

**Figure 5.** Cycling charge and discharge test of the Ce/Ni-MOF electrode

Figure 5 presents the results of the cycling charge and discharge test of the Ce/MOF electrode. The specific capacitance of the electrode keeps over 95.5% after 1000 cycles of charge and discharge, exhibiting excellent cycle life. This is mainly because the porous channel can ensure the electrolyte and solid surface have enough contact surface, so it can shorten the ion transfer/diffusion channel and increase the dynamic characteristics. In this way, the resistance of the supercapacitor can be reduced and the capacitance can be improved.

4. Conclusion

In this work, we prepared Ce/Ni-MOFs in hydrothermal methods. To acquire the optimal hydrothermal conditions, we designed a series of experience and obtained the ideal temperature and reaction time is 100°C and 48h respectively. Besides, we operate on the Ce/Ni-MOFs with cyclic voltammetry, Galvano static charge-discharge measurements and cycling charge-discharge testing, and obtain the highest capacitance of 584F/g, and the retention ratio of the capacitance over 95.5% after 1000 cycling. This indicates that Ce/Ni-MOFs might be a potential electrode material in capacitance.

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