Electrochemical Performance of Ni-MOFs for Supercapacitors

Yujuan Li¹, Lili Song¹, Yinghui Han¹, Guangyou Wang¹

¹School of Mathematics & Physics, North China Electric Power University; Baoding, China

Abstract. In this work, the Ni-MOFs of electrode material has been synthesized, characterized and studied for the electrochemical properties of electrode materials. The effects of the doping amount of Ni, calcination temperature and time were studied in detail. The results suggested that the electrochemical properties were obviously improved by the Ni-MOFs of electrode material and the best preparation conditions can also improve the electrochemical properties of electrode materials. These results open a way for the design of tailored MOFs as electrode materials for supercapacitors.

1. Introduction

Supercapacitors are considered as one efficient renewable energy storage device because of their high power density, rapid charging-discharging rate and long cycle life [1-3]. Thus, research efforts on supercapacitors are focused on achieving higher energy densities, and the development of new materials is of paramount importance to achieve this goal [4-6].

Currently, metal organic frameworks (MOFs) or porous coordination polymers, as a new type of electrode material, have attracted more and more attention. MOFs are new porous materials with high surface area, tunable pore size and incorporated redox metal centres, which are emerging as novel supercapacitor electrodes [7]. Díaz R [6] et al. pointed out that Co8-MOF-5 show electrical conductivities which are good enough to result in electrodes with nearly ideal supercapacitive behavior at rates up to 200 mV s⁻¹ in an electrolyte composed of 0.1 M tetrabutylammonium hexafluorophosphate (TBAPF₆) in acetonitrile. Yuan Xia [8] et al. reported the energy storage performances of the as-prepared double-layer nanospheres were further investigated in lithium ion battery and supercapacitor systems. Zhang et al. [9] obtained a hierarchical Co₃O₄ material by heating a Co-based MOF in air which exhibited an initial specific capacitance of 208 F g⁻¹ at 1 A g⁻¹. However, to the best of our knowledge, metal organic frameworks are rare in supercapacitors [10-12].

In the present work, it provided a method for the preparation of the Ni-MOFs of electrode material. The influence of the molar ratio of Ni-MOFs on the electrochemical properties was also investigated in this work. The preparation conditions had great influence on the electrochemical activity, such as the hydrothermal temperature, hydrothermal time and so on. In addition, it also studied the effect of reactive power on electrochemical activity.

2. Experimental section

2.1. Material

All chemicals reagents were analytical grade and were used without further purification. Nickel(II) nitrate hexahydrate [Ni(NO₃)₂·6H₂O] was provided by the Fuchen chemical reagent factory, in Tianjin, China. P-phthalic acid (H₂BDC) was supplied by the Guangfu institute of fine chemical engineering,
in Tianjin, China. N, N-dimethylformamide (DMF), ethanol (C₂H₅OH) and other reagents were purchased from the Huaxin Reagents Co., in Tianjin, China. Ni-MOFs samples were prepared using hydrothermal method.

2.2. Methods
The material was prepared by the hydrothermal process. Ni(NO₃)₂·6H₂O (3.8g, 0.01mol) and p-phthalic acid (0.32g, 0.05mol) were dissolved in 60 ml solvent of C₂H₅OH, DMF and deionized water at room temperature with a given solvent volume ratio of C₂H₅OH : DMF : deionized water = 1:1:1. The mixture was stirred for three hours on a magnetic stirrer. The mixture was transferred into a 100 mL Teflon-lined autoclave, which was sealed and maintained at a certain temperature and time.

The electrochemical measurements using a three-electrode electrochemical system, a 6 M/L KOH aqueous solutions as the electrolyte, Pt plate acted as the counter electrode and Ag/AgCl electrode served as the reference electrode. The working electrode consisted of active material, acetylene black and polytetrafluoroethylene (PTFE) with the mass ration of 8:1:1. Cyclic voltammetry and galvanostatic charge-discharge investigation were implemented using a CHI760E electrochemical workstation (ChenHua, Shanghai). The specific capacitance was calculated from the galvanostatic charge-discharge curves using the following equation [13-15]:

$$C = \frac{l \cdot \Delta t}{m \cdot \Delta V}$$

where I is charge-discharge current at a discharge time Δt (s), ΔV is dropout voltage, and m is the mass of active electrode materials.

3. Result and discussion

3.1. The effect of the hydrothermal time on the electrochemical property
The increase of hydrothermal time will increase the crystallization degree of the sample, and the grain will increase gradually. A series of experiments were carried out to reveal the relationship between the hydrothermal time and the electrochemical properties, the result was shown in figure 1. The representative cyclic voltammetry (CV) curves are shown in figure 1(a) with the hydrothermal time.

When the hydrothermal temperature was changeless, the electrochemical properties of the prepared samples increased first and then decreased with the increasing of the hydrothermal time. The specific capacitance values at different hydrothermal times are shown in figure 1(b). When the time was 48h, the electrochemical properties of the sample was the best. This is because the hydrothermal time shorter would lead the crystal particles surface of the sample covered by some residual organic matter and reduce participation reaction active sites; while the calcination time is too long, the porous structure and specific surface area of the sample would be destroyed. So in terms of the researched electrode materials, the optimal amount of hydrothermal time was 48h.

![Figure 1. (a) The CV curves at different hydrothermal times; (b) The specific capacitance values at different hydrothermal times.](image)
3.2. The effect of the hydrothermal temperature on the electrochemical property
The hydrothermal temperature of material not only affects the final particle size, but also influences the crystal structure and crystal structure of the material. The effect of different hydrothermal temperature on the activity of the prepared catalyst was shown in figure 2. The materials were calcined for 48 hours. A series of experiments were carried out to reveal the relationship between the hydrothermal temperature and the electrochemical properties, which are shown in figure 2(a) and figure 2(b). The result was shown that the hydrothermal temperature would influence the degradation rate significantly, the electrochemical properties increased with the increase of hydrothermal temperature within the range of 50°C~200°C, however, when more than 100°C, the electrochemical properties will decline. This indicates that the electrochemical reaction rate of Ni-MOFs prepared at 100°C is faster, the storage charge is more, and the specific electrical capacity is larger.

![Figure 2](image1.png)

Figure 2. (a) The CV curves at different hydrothermal temperatures; (b) The specific capacitance values at different hydrothermal temperatures.

3.3. The effect of the scan rates and cycle life on the electrochemical property
The plot of potential versus time at current densities is shown in figure 4. The electrochemical performance of the Ni-MOFs was evaluated in a three-electrode configuration with 6 M/L KOH electrolyte. The representative cyclic voltammetry (CV) curves are shown in Fig. 3(a) with the scan rates from 10 to 30 mV s⁻¹. So in terms of the researched electrode materials, the optimal amount of scan rates was 10 mV s⁻¹. Fig. 3(b) is the variation of specific capacitance retention of Ni-MOFs electrodes versus cycle number in two electrode system. The capacitance retention of Ni-MOFs remains at 95.5% after 1000 charge-discharge cycles, showing excellent cycle stability [16].

![Figure 3](image2.png)

Figure 3. (a) The cyclic voltammetry curves at different scan rates; (b) Capacitance retention of Ni-MOFs electrode versus cycle number.

4. Conclusion
Ni-MOFs, a green and multifunctional material, promises to be a new technology for high-performance supercapacitors. Multiple factors affect the electrochemical properties of electrode materials. The best preparation conditions will lead to better electrochemical properties. Industrial
feasibility analysis indicates that Ni-MOFs electrode material could be a promising alternative to conventional methods.

References
[1] Wang Y, Xia Y, 2013 Adv. Mater. 25 5536.
[2] Simon P, Gogotsi Y 2008 Nat. Mater. 7 845.
[3] Yan J, Wang Q, Wei T, Fan Z 2014 Adv. Energ. Mater. 4 157-64.
[4] Wang L, Chen D, Wang J, Liu G, Wu W, Liang G 2015 Rsc. Adv. 5 99856-65.
[5] Venkateswara Rao Ch, Rambabu B 2010 Sol. State Ion. 181 839-43.
[6] Diaz R, Orcajo M G, Botas J A, Calleja G, Palma J 2012 Mater. Lett. 68 126-8.
[7] Xu J, Yang C, Xue Y, Wang C, Cao J, Chen Z 2016 Electrochim. Acta. 211 595-602.
[8] Xia Y, Wang G, Zhang X, Wang B, Wang H 2016 Electrochim. Acta. 220 643-53.
[9] Zhang F, Hao L, Zhang L, Zhang X 2011 Int. J. Electrochem. Sci. 6 2943-54.
[10] Guo B, Yang Y, Hu Z, An Y, Zhang Q, Yang X, et al. 2017 Electrochim. Acta. 223 74-84.
[11] Ke F S, Wu Y S, Deng H 2015 J. Solid State Chem. 223 109-21.
[12] Ma L, Liu R, Liu L, Wang F, Niu H, Huang Y 2016 J. Pow. Sour. 335 76-83.
[13] Yu L, Zhang G, Yuan C, Lou X W 2013 Chem. Commun. 49 137-9.
[14] Zhang J, Jiang J, Li H, Zhao X S 2011 Energ. Environ. Sci. 4 4009-15.
[15] Peng H, Ma G, Sun K, Mu J, Luo M, Lei Z 2014 Electrochim. Acta. 147 54-61.
[16] Yu M, Zhang L, He X, Yu H, Han J, Wu M 2016 Mater. Lett. 172 81-4.

Acknowledgements
This research was supported by the Fundamental Research Funds for the Central Universities of China (NO.2015ZZD3), the National Natural Science Foundation of China (No. 51308212) and the Fundamental Research Funds for the Central Universities of China (No.13ZD18).