

Application research of MOF and its Ni-doping materials in supercapacitor

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Abstract. With the development of the technology and the automation of the modern industry, finding a new kind of energy storing device gradually occupies a significant position. The supercapacitor takes up scientists' eyes, because of its advantages of high watt density, long servicing life and non-pollution. However, there is also some barriers blocking the way of the forward development. In this project, we use MOF-5 as the electrode material, combining with some other metal atoms to enhance its specific capacitance. Through researching, we found that using Ni as the adding atom has a markable difference. It can improve the conductivity of the electrode effectively, then enhancing the specific capacitance. Finally, we measured the data of the supercapacitor using Ni-MOF-5 as the electrode materials under different scanning speed. Then we got the specific capacitance respectively: $105\text{F} \cdot \text{g}^{-1}$ under $50\text{mV} \cdot \text{s}^{-1}$, $78\text{F} \cdot \text{g}^{-1}$ under $100\text{mV} \cdot \text{s}^{-1}$, $44\text{F} \cdot \text{g}^{-1}$ under $500\text{mV} \cdot \text{s}^{-1}$, $35\text{F} \cdot \text{g}^{-1}$ under $1000\text{mV} \cdot \text{s}^{-1}$.

Keywords: Pseudocapacitor; MOF-5 materials; Ni-MOF-5 composites; Specific capacitance.

1. Introduction

The constant progress of modern industry and innovation of automation has led to many issues caused by oil, coal and fossil fuels, and such environment problems as ozone hole, haze and greenhouse effect have had significant impact on the global ecological system. Therefore, the exploration of renewable clean energy has received growing attention. Owing to relatively high production and extraction costs of clean energy resources and less developed technologies, however, the controllability of clean energy is far from unsatisfying, and how to improve the storage efficiency of electricity has become the focus of researchers.

At present, the most typical two forms of high performance energy storage devices are batteries and capacitors. The batteries are small in size and easy to carry, but are low in power density; while the supercapacitors have the advantages of high power density, flexible capacity configuration, long service life, wide working temperature range and being eco-friendly, which have made them a favorable supplement for secondary batteries. The supercapacitors would have been applied in much wider fields were it not for their relatively low energy density. Generally, two methods are optional for improving the energy density: to improve the specific capacitance of the electrodes, or to improve the electrochemical window of the electrolyte.

The supercapacitor is a new form of energy storage device which lies somewhere in between the traditional capacitor and the rechargeable battery, and can be classified into two types based on the charge-recharge mechanism, namely the double-layer capacitor and the pseudocapacitor. It has unique advantages of high power density and super-long service life over traditional capacitors. Of the two types, the pseudocapacitor has more favorable features compared with the double-layer capacitor. The pseudocapacitance is generated not only at the electrode surface, but inside the whole electrode, through which higher capacity and energy density are obtained than in the double-layer capacitor. With the same electrode area, the pseudocapacitor has a capacitance 10-100 times that of the double-layer capacitor. Those supercapacitors prepared with metal-organic frameworks (MOFs) can especially give play to the electrochemical performance advantages. Due to the Faraday-effect of charge-transfer transition, the pseudocapacitor has encountered the bottleneck of low power density, that's why constructing a capacitor with both high energy density and power density is of such vital importance.

Metal-organic frameworks (MOFs) is a kind of self-assembled metal-organic framework material formed by organic bridging ligands and transition metal ions, and has a periodic network structure.

With features of rich, diverse and designable frame patterns and pore structures, as well as high specific surface area and ease of functionalization, MOFs can be considered as a hybrid material between inorganic materials and organic materials. Different from traditional porous materials, MOF has flexible pore structures with its metal centers regularly arranged in space, which enables regional selectivity or shape and size selectivity for guest molecules, and the active centers are evenly distributed. The mechanism of the significant electrochemical advantages of MOF materials is that unsaturated coordination metal centers, i.e. active metal sites, can be created after removing the coordinated solvent molecules by heating under high vacuum. When the metal center is bound to organic ligands with a low coordination number, the coordination polymer may exhibit significant electrochemical activity. The main research direction of our group is MOF-5, a three-dimensional metal-organic skeleton material created by $[\text{Zn}_4\text{O}]^{6+}$ and $(\text{OOC}_6\text{H}_4\text{COO})^{2-}$, with a simple cubic structure as shown in Figure 1.

In this paper, MOF-5 was prepared using the hydrothermal method in conjunction with addition of nickel nitrate into the reactant. The electrochemical properties of the two MOF materials were studied from the aspects of material structure and energy density. The detailed preparation procedures are as follows:

(1) MoF-5 was prepared with the hydrothermal method. Dissolve terephthalic acid and zinc nitrate in DMF and transfer the mixture into an autoclave, then put the autoclave into the oven at 120°C for 720 minutes. After the reaction, the solution in the reactor was vacuum-filtered to obtain the white solid, and dried for 720 minutes in a vacuum drying oven at 80°C .

(2) Add nickel nitrate into DMF during the preparation process, and adjust the temperature and heating time of the oven according to the literatures. After the reaction, Ni-MOF-5 was obtained by suction filtration and drying.

2. Experiment design and process

2.1. Experiment design

The focus of this experiment is on improving the performance of electrode materials, for example, to improve the energy density of the supercapacitor by increasing the specific capacitance of the electrode material. According to the literatures, specific capacitance is mainly related to the pore structure: larger porosity and specific surface area, as well as ion doping will facilitate better ion adsorption on the electrode material. Therefore, MOF is selected as the experiment material. MOF is a metal-organic framework composite with large specific surface area and porosity, adjustable pore structure, abundant active sites for binding heteroatoms and other characteristics, which combined meet the requirements of this experiment to improve the specific capacitance. MOF-5 is a three-dimensional skeleton structure formed by octahedral binding of Zn as the metal site and terephthalic acid as the organic ligand, which has the advantages of strong adsorption, thermal stability, large specific surface area and regular pore size structure. At the same time, considering the evaporation of Zn at high temperature, more vacancy sites can be created which leave space for addition of other metal ions. According to the actual conditions and operation difficulty, the synthesis method of MOF-5 was determined with the hydrothermal method.

2.2. Experiment process

2.2.1 Preparation of MOF-5 and Ni-MOF-5 with the hydrothermal method

Detailed preparation procedure with the hydrothermal method:

Dissolve 0.2g zinc nitrate and 0.08g terephthalic acid respectively in 30mL DMF with two separate glass tubes. Then put these two solutions in teflon-lined autoclave and add 5mL more DMF. Next, the reaction mixture was heated at 100°C for 12 hours to get the white crystals. Filter and wash with deionized water.

2.2.2 Calcination of MOF-5 and Ni-MOF-5

Calcination procedure with the tube furnace

Appropriate amount of MOF-5 was put into an alumina boat and placed in the tube furnace. The air was drained by argon gas flow at room temperature for 30min, after which the temperature was raised to the target temperature with a $5^{\circ}\text{C}/\text{min}$ step. Then the temperature was kept constant for a period of time at the target temperature, and finally the calcined product was obtained under natural cooling to below 100°C .

The table below is obtained with multiple experiments to determine the target temperature and time.

Table 1. Determination of calcination temperature and time

	Temperature T/ $^{\circ}\text{C}$	Time t/h
MOF-5	400	6
	600	10
	600	6
Ni-MOF-5	400	6
	600	10
	600	6

The final optimal calcination temperature is determined as 600°C , and the optimal time is 6h.

2.3. Electrodes prepared with the binding method

First, 50mL/mg binder was prepared, which was later fully blended with 50mg conductive material through thorough oscillation and mixing. The mixture was uniformly dropped on 10 units of Ni foam with the pipette gun, before drying at 100°C for 12h in the atmospheric oven, followed by drying at 100°C for 12h in the vacuum oven.

3. Results and discussions

3.1 Analysis of the electrochemical performance

In order to study the electrochemical performance of MOF-5 and Ni-MOF-5 materials as the working electrode, CV test was performed in this experiment. Figures 1 to 8 below show the CV curves of MOF-5 and Ni-MOF-5 at different sweep rates ($50\text{mV} \cdot \text{s}^{-1}$, $100\text{mV} \cdot \text{s}^{-1}$, $500\text{mV} \cdot \text{s}^{-1}$ and $1000\text{mV} \cdot \text{s}^{-1}$) in a voltage window of 0-1V, respectively.

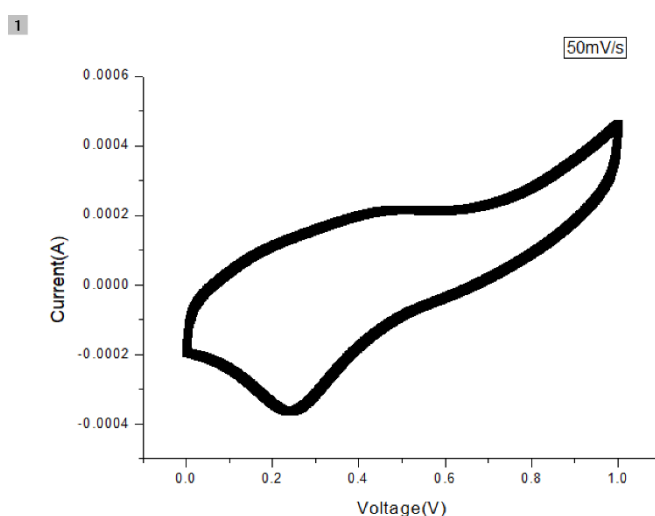


Fig.1 Cyclic voltammetry curve of Ni-MOF-5 electrode material at a sweep rate of $50 \text{ mV} \cdot \text{s}^{-1}$

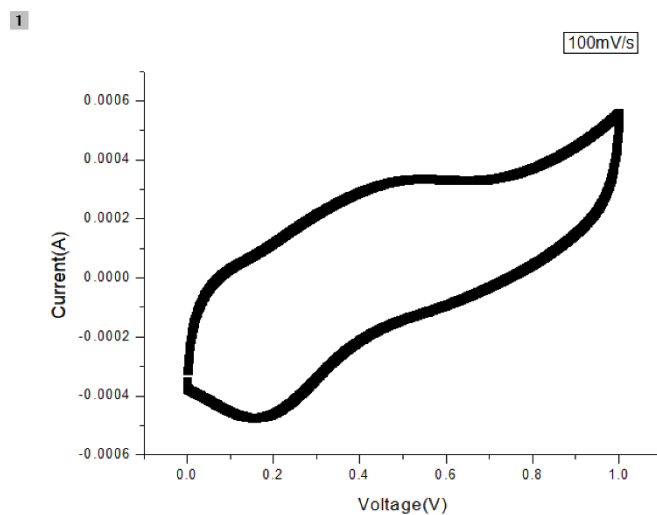


Fig.2 Cyclic voltammetry curve of Ni-MOF-5 electrode material at a sweep rate of $100 \text{ mV} \cdot \text{s}^{-1}$

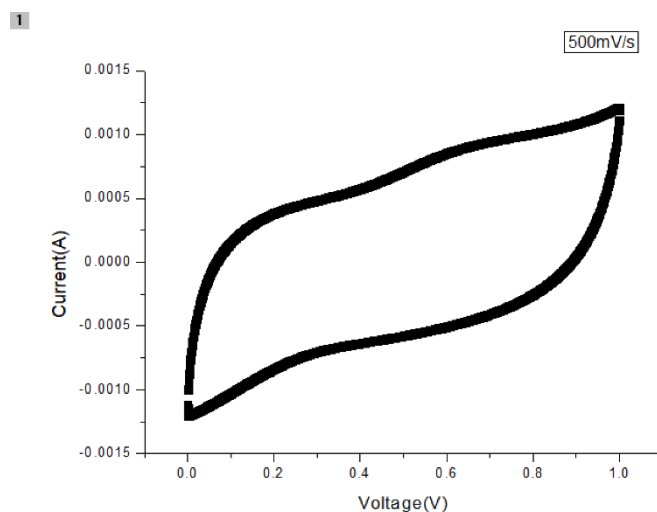


Fig.3 Cyclic voltammetry curve of Ni-MOF-5 electrode material at a sweep rate of $500 \text{ mV} \cdot \text{s}^{-1}$

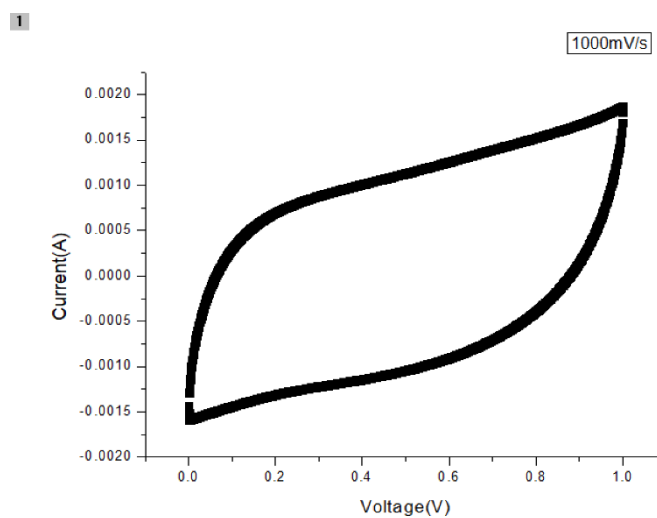


Fig.4 Cyclic voltammetry curve of Ni-MOF-5 electrode material at a sweep rate of $1000 \text{ mV} \cdot \text{s}^{-1}$

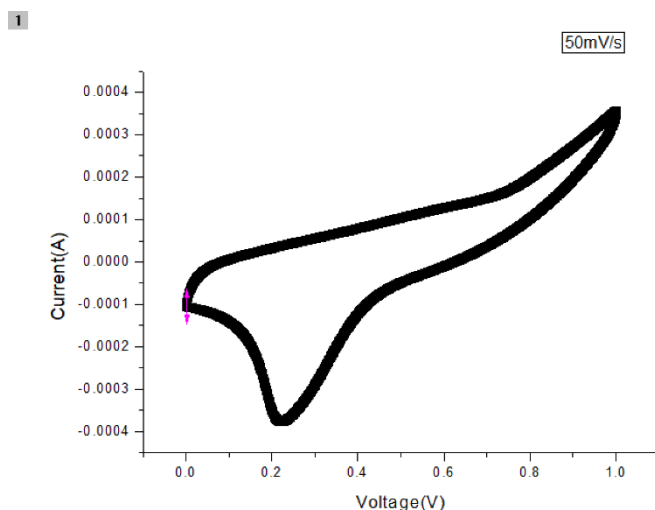


Fig.5 Cyclic voltammetry curve of MOF-5 electrode material at a sweep rate of $50 \text{ mV} \cdot \text{s}^{-1}$

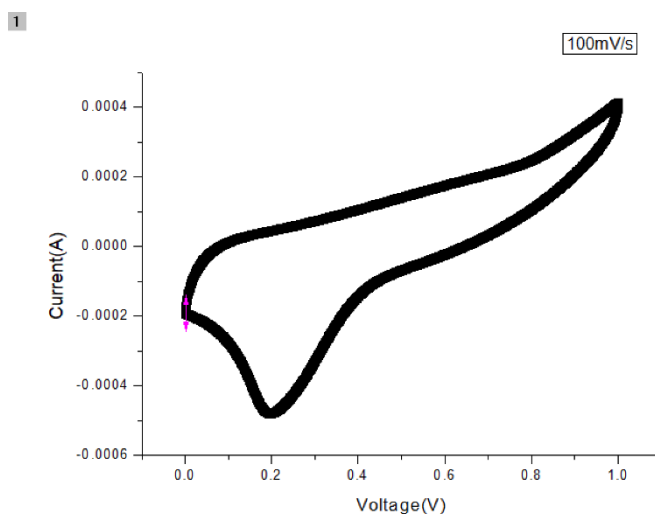


Fig.6 Cyclic voltammetry curve of MOF-5 electrode material at a sweep rate of $100 \text{ mV} \cdot \text{s}^{-1}$

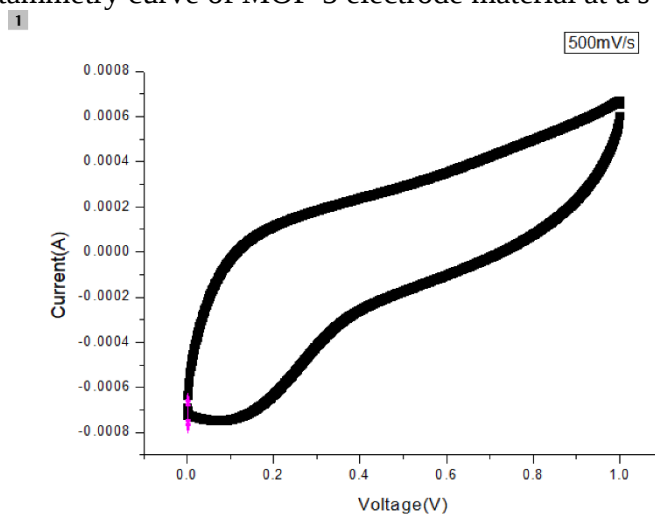


Fig.7 Cyclic voltammetry curve of MOF-5 electrode material at a sweep rate of $500 \text{ mV} \cdot \text{s}^{-1}$

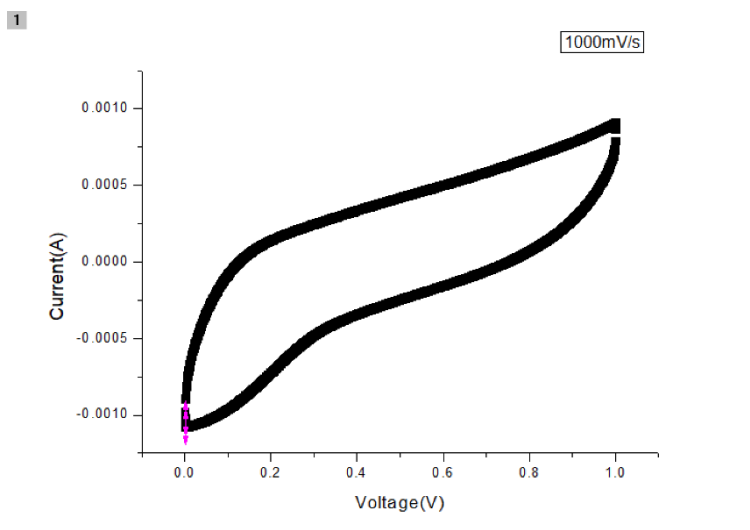


Fig.8 Cyclic voltammetry curve of MOF-5 electrode material at a sweep rate of $1000 \text{ mV} \cdot \text{s}^{-1}$

In order to better compare the properties and variations of the figures under different sweep rates, so as to facilitate corresponding conclusions, Origin software was used in this experiment to superimpose the curves of various sweep rates in the same figure.

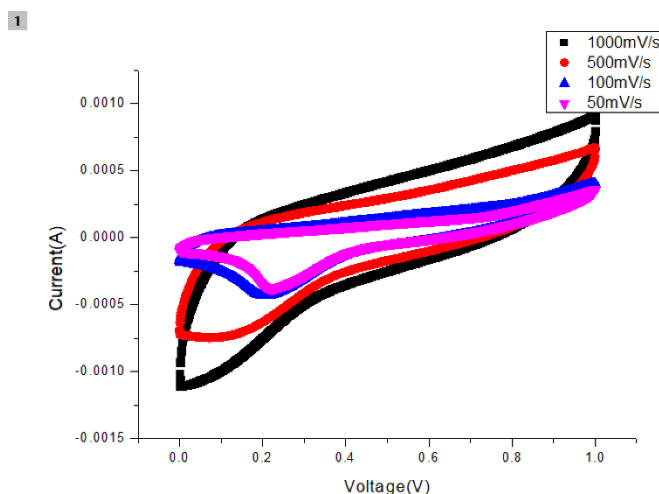


Fig.9 Cyclic voltammetry curve of MOF-5 electrode material at various sweep rates

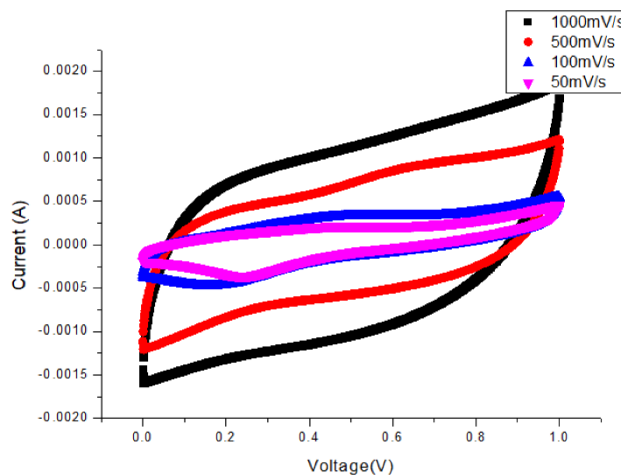


Fig.10 Cyclic voltammetry curve of Ni-MOF-5 electrode material at various sweep rates

Through the analysis of the figure above, it is clear that an obvious redox peak in each CV curve of MOF-5 and Ni-MOF-5 can be observed, which is because of the OH⁻ extraction and insertion in the whole process, and which also indicates that the Faraday reaction typical of pseudocapacitors occurred in the process. Besides, with the increasing of sweep rate, the CV curves of MOF-5 and Ni-MOF-5 expand, and the potential difference between the redox peaks of Ni-MOF-5 is larger than that of MOF-5, which is caused by a greater polarization degree of Ni-MOF-5. The results indicated that MOF-5 performance was improved by Ni doping, and the expected effects were achieved. Under the same current density, the area of CV curve of Ni-MOF-5 is obviously larger than that of MOF-5, which means a higher specific capacitance value. The main reason for this result may be that Ni-MOF-5 has larger specific surface area and open channels which can speed the diffusion of electrolyte ions and increase the conductivity of the electrode. Verification of this explanation is to be carried out in the future through characterizing with nitrogen absorption-desorption isotherm test, X-ray diffraction and scanning electron microscopy (SEM) on the material structure and the morphology. Through the CV analysis above, the conclusion can be made that the performance of MOF-5 material was improved after Ni doping.

3.2 Analysis of the specific capacitance

In order to verify the feasibility of the innovation point of the experiment (preparing composite materials using metal Ni and MOF materials) scientifically, multiple cycle voltammetry tests were carried out in this experiment, and numerous cyclic voltammetry data were obtained under the four sweep rates of 50 mV · s⁻¹, 100 mV · s⁻¹, 500 mV · s⁻¹ and 1000 mV · s⁻¹ (in order to exclude the influence of sweep rates on experimental results).

The specific capacitance can be calculated with the following formula using the integral area obtained in Origin:

$$C = \frac{1}{s \cdot m \cdot \Delta V} \int_{V_0}^{V_0 + \Delta V} i dV$$

Where s is the sweep rate; m is the effective mass of the electrode; ΔV is the potential difference; i is the current; $\int_{V_0}^{V_0 + \Delta V} i dV$ is the integral area

The data of the specific capacitance of the two supercapacitors were calculated and listed in the table below

Table 2. Specific capacitances of MOF-5 and Ni-MOF-5 supercapacitors at different sweep rates

specific capacitance (F/g)	materials	MOF-5	Ni-MOF-5
Scanning speed (mV/s)			
50		63	105
100		44	78
500		23	44
1000		18	35

4. Conclusions

From the analysis of data in this experiment, scientific and rigorous conclusions are derived. In this paper, MOF-5 material was prepared with the hydrothermal method in conjugation with Ni doping. After that, Ni-MOF-5 electrode and MOF-5 electrode were fabricated using the binding method, and finally supercapacitors were obtained by means of compaction. Cyclic voltammetry of the two supercapacitors were carried out and the data were processed with Origin to get the integral area of the corresponding cyclic voltammetry figure so as to calculate the specific capacitance of the corresponding supercapacitor. By comparing the supercapacitors with MOF-5 and Ni-MOF-5 electrode, it can be found that different electrode materials have a significant impact on the performance. The specific capacities of Ni-MOF-5 supercapacitor under sweep rates of $50\text{mV} \cdot \text{s}^{-1}$, $100\text{mV} \cdot \text{s}^{-1}$, $500\text{mV} \cdot \text{s}^{-1}$ and $1000\text{mV} \cdot \text{s}^{-1}$ were $105\text{F} \cdot \text{g}^{-1}$, $78\text{F} \cdot \text{g}^{-1}$, $44\text{F} \cdot \text{g}^{-1}$ and $35\text{F} \cdot \text{g}^{-1}$ respectively, while that of MOF-5 supercapacitor under sweep rates of $50\text{mV} \cdot \text{s}^{-1}$, $100\text{mV} \cdot \text{s}^{-1}$, $500\text{mV} \cdot \text{s}^{-1}$ and $1000\text{mV} \cdot \text{s}^{-1}$ were $63\text{F} \cdot \text{g}^{-1}$, $44\text{F} \cdot \text{g}^{-1}$, $23\text{F} \cdot \text{g}^{-1}$ and $18\text{F} \cdot \text{g}^{-1}$ respectively.

By comparison, it can be found that the specific capacitance of the Ni-doped supercapacitor is larger than that of the not doped one at each different sweep rate. This indicates that Ni-doped electrode has more favorable properties and better cycle performance, which makes it a conductive material of great application potential.

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