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Electrochemical performance of $M_3(BTC)_2\cdot 12H_2O$ (M=Co, Ni, and Zn) for Supercapacitors

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Abstract: *A series of Metal-Organic Frameworks (MOFs) based on 1,3,5-benzenetricarboxylic (BTC) acid and M(II) acetate hydrate (M=Co, Ni, and Zn) were successfully synthesized and named as* $M_3(BTC)_2\cdot 12H_2O$*. These compounds were examined by X-ray diffraction (XRD) patterns. Electrochemical properties of the materials were characterized by cyclic voltammetry (CV) and electrochemical impedance spectroscopy (EIS) in 6 M KOH aqueous solutions. The maximum specific capacitance of* $Ni_3(BTC)_2\cdot 12H_2O$ *is found to be 429 F* g^{-1} *at 5 mV* s^{-1} *and 154 F* g^{-1} *at 200 mV* s^{-1} *scan rate.*

Keywords: Metal-Organic Frameworks, specific capacitance

1. INTRODUCTION

An electrical double-layer capacitor (EDLC) is an electricity storage media based on the physisorption of ion [1, 2]. Although the energy density of EDLCs is a little lower than that of secondary batteries, EDLCs have a much higher power density and a longer cycle life. According to the mechanism of charge storage, supercapacitor can be categorized as two types: electrical double-layer capacitor (EDLC) with activated carbon materials as electrodes, and the other is Faradic pseudo-capacitor with metal oxides or conducting polymers as electrodes [3]. Among the many types of porous solids, so-called porous coordination polymers or metal-organic frameworks (MOFs) have gathered special attention [4-7]. due to their flexibility in pore size. This flexibility arises from the unique assembly of this type of solids. Organic linkers are connected through metal centers or inorganic metal clusters to form frameworks [8]. Metal organic frameworks (MOFs) are new functional materials that combine a wide variety of properties and applications. They contain inorganic and organic networks that can be easily functionalised to get tuneable properties. They are commonly used in sensing, catalysis, ion exchange, separations or gas storage [7-13], and as electrode material for lithium ion battery [14-15]. They are also used as a template for syntheses of nanoporous carbons as electrode materials for supercapacitor [16]. In this paper, a series of Metal-Organic Frameworks (MOFs) based on 1,3,5-benzenetricarboxylic (BTC) acid and M(II) acetate hydrate (M=Co, Ni, and Zn) were successfully synthesized and named as $M_3(BTC)_2\cdot 12H_2O$. The maximum specific capacitance of $Ni_3(BTC)_2\cdot 12H_2O$ is found to be 429 F g^{-1} at 5 mV s^{-1} and 154 F g^{-1} at 200 mV s^{-1} scan rate.

2. EXPERIMENTAL SECTION

2.1. Preparation of MOFs

All chemical reagents were obtained from commercial sources and, unless otherwise noted, were used without further purification, and the method of preparation $M_3(BTC)_2\cdot 12H_2O$ (M=Co, Ni, and Zn) is according to Yaghi [17].

$Co_3(BTC)_2\cdot 12H_2O$

An aqueous mixture (15 mL) of cobalt(II) acetate tetrahydrate (0.41 g, 1.65 mmol) and the acid form of BTC ($BTCH_3$) (0.20 g, 0.95 mmol) was placed in a stainless steel vessel, which was sealed and placed in a programmable furnace. The mixture was heated to 140 °C at 5 °C/min and held at that temperature for 24 h, then cooled at 0.1 °C/min to 120 °C and held for 5 h, followed by further cooling at the same rate to 100 °C, and held for another 5 h before finally cooling to room temperature. The resulting large rod-like red crystals were filtered, washed with deionized water (3×10mL) and ethanol (3×10 mL), and then air-dried to give $Co_3(BTC)_2\cdot 12H_2O$.

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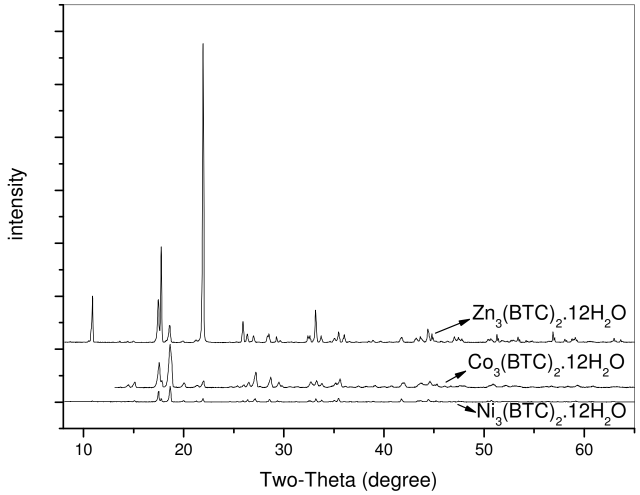

Figure 1. Typical XRD patterns of $M_3(BTC)_2\cdot 12H_2O$ (M=Co, Ni, and Zn)

$Ni_3(BTC)_2\cdot 12H_2O$

An aqueous mixture (10 mL) of nickel(II)acetate tetrahydrate (0.35 g, 1.41 mmol) and the acid form of BTC ($BTCH_3$) (0.10 g, 0.48mmol) was placed in a stainless steel vessel, which was sealed and placed in a programmable furnace. The mixture was heated to 170 °C at 5 °C/min and held at that temperature for 12 h, then cooled at 0.1 °C/min to 150 °C and held for 5 h, followed by further cooling at the same rate to 130 °C, and held for another 5 h before finally cooling to room temperature. The resulting large green crystals were filtered, washed with deionized water (3×10mL) and ethanol (3×10 mL), and then air-dried to give $Ni_3(BTC)_2\cdot 12H_2O$.

$Zn_3(BTC)_2\cdot 12H_2O$

The $Zn_3(BTC)_2\cdot 12H_2O$ was prepared as needle-like colorless crystals using an identical procedure to that described for the cobalt compound.

2.2. Electrochemical characterization

2.2.1 Preparation of electrodes and electrochemical measurement

The fabrication of working electrodes was carried out as follows. Briefly, the electroactive materials, BP2000 and poly tetrafluoroethylene (PTFE) were mixed in a mass ratio of 75:20:5 and dispersed in ethanol. Then the resulting mixture was coated onto the nickel foam substrate (1×1 cm^2) with a spatula, which was followed by drying at 100 ℃ for 2 h in a vacuum oven. Each electrode contained about 3 mg of electroactive material.

All electrochemical measurements were done in a three-electrode setup: working electrode, Pt flag and saturated calomel electrode as the counter and reference electrodes. The measurements were carried out in a 6 M KOH aqueous electrolyte at room temperature. Cyclic voltammograms (CV) and electrochemical impedance spectroscopy (EIS) were measured by a CHI660D electrochemical workstation. CV tests were done between 0 and 0.6 V (vs SCE) at different scan rates of 5, 10, 20, 50, 100, and 200 mV s^{-1}. The specific capacitance (SC) at a given scan rate, was calculated from voltammetric response using the following equation.

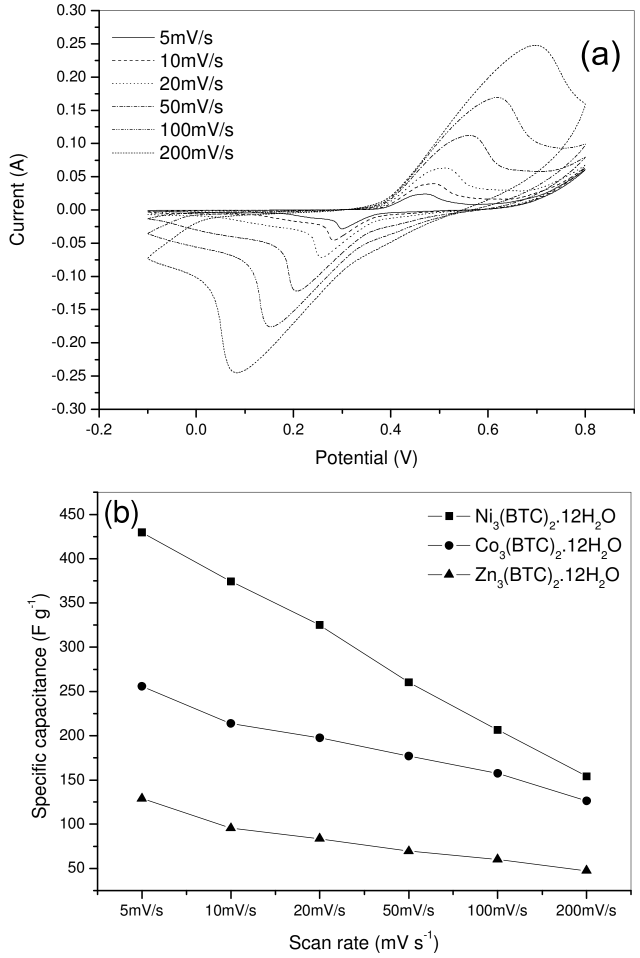

Figure 2. CV curves of $Ni_3(BTC)_2\cdot 12H_2O$ at different scan rates of 5,10,20,50,100 and 200 mV s^{-1} (a). Specific capacitance of $M_3(BTC)_2\cdot 12H_2O$ (M=Co, Ni, and Zn) composites at different scan rates (b)

$$C = \frac{1}{mv(V_f - V_i)} \int_{V_i}^{V_f} I(V)dV \tag{1}$$

Where m is the mass of the activated substance, V_f and V_i are the two integration limits of the voltammetric curve, and I(V) is the voltammetric current. C is the specific capacitance based on the mass of electroactive materials (F.g^{-1}).

3. RESULTS AND DISCUSSION

Figure 1 presents the x-ray diffraction (XRD) patterns of Metal-Organic Frameworks (MOFs) based on 1,3,5-benzenetricarboxylic (BTC) acid and M(II) acetate hydrate (M=Co, Ni, and Zn) samples, XRD studies indicate that these MOFs are $M_3(BTC)_2\cdot 12H_2O$ (M=Co, Ni, and Zn) because of these XRD patterns are very similar to the case of $M_3(BTC)_2\cdot 12H_2O$ (M=Co, Ni, and Zn) in Yaghi [17], and the method of preparation $M_3(BTC)_2\cdot 12H_2O$ (M=Co, Ni, and Zn) is according to Yaghi [17].

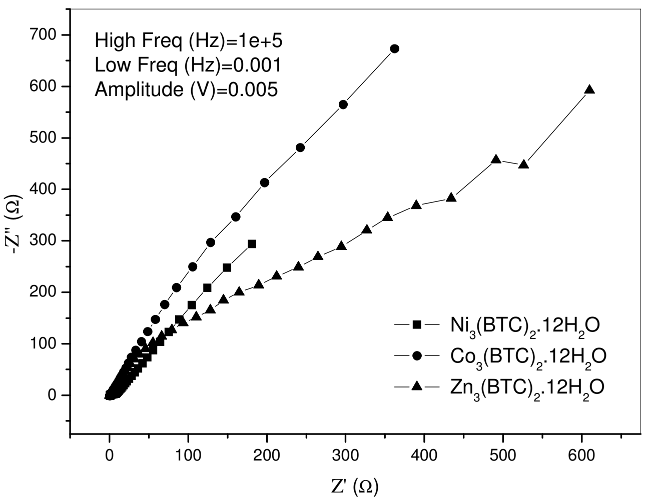

Figure 3. Nyquist plots obtained for the $M_3(BTC)_2{\cdot}12H_2O$ (M=Co, Ni, and Zn) in 6 M KOH solution

The CV curves at different scan rates from 5 to 200 mV s^{-1} in 6 M KOH within a potential window of -0.1 to 0.8 V of $Ni_3(BTC)_2{\cdot}12H_2O$ is shown in Fig 2 (a). These CV curves are relatively irregular in shape with obvious oxidation peaks and reduction peaks, but reduction peaks are more obvious than oxidation peaks, no obvious distortion in the CV curves is observed as the potential scan rate is increased to 200 mV s^{-1}. The maximum specific capacitance of $Ni_3(BTC)_2{\cdot}12H_2O$ is found to be 429 F g^{-1} at 5 mV s^{-1} and 154 F g^{-1} at 200 mV s^{-1} scan rate is shown in Fig 2 (b), and the specific capacitance of $Co_3(BTC)_2{\cdot}12H_2O$ is found to be 256 F g^{-1} at 5 mV s^{-1}, the specific capacitance of $Zn_3(BTC)_2{\cdot}12H_2O$ is found to be 129 F g^{-1} at 5 mV s^{-1}, and the specific capacitance of activated carbon-semiconducting oxide composites is 64.7 F/g at 5 mV/s have been reported[18]. The specific capacitance of $MnO_2{\cdot}xH_2O$/CRF is 226.3 F/g at 2 mV/s [19].

Fig.3 shows electrochemical impedance spectra in the form of Nyquist plots for $M_3(BTC)_2{\cdot}12H_2O$ (M=Co, Ni, and Zn) electrodes at 0.326 V where Z' and Z'' are the real and imaginary parts of the impedance, respectively. The high frequency semicircle represents the the charge transfer process at electrode/electrolyte interface, while the inclined straight line at low electrochemical processes. Therefore, the high impedance (Z') value of the system corresponds to high internal resistance as well as diffusion limitation. The impedance behavior of $M_3(BTC)_2{\cdot}12H_2O$ (M=Co, Ni, and Zn) electrodes are close to an ideal EDLC. and shows low charge transfer resistance with a vertical line shape towards lower frequency indicating DLC storage.

Fig. 4 shows the variations of specific capacitance with charge-discharge cycle number of $Ni_3(BTC)_2{\cdot}12H_2O$ electrode, As revealed in this Fig. 4. The electrode is found to exhibit excellent stability over the entire cycle numbers. The specific capacitance of the composite electrode decreases only 8.9% by repeating the CV test between -0.1 and 0.8V (vs. SCE) at a scan rate of 5mV s^{-1} for 1000 cycles.

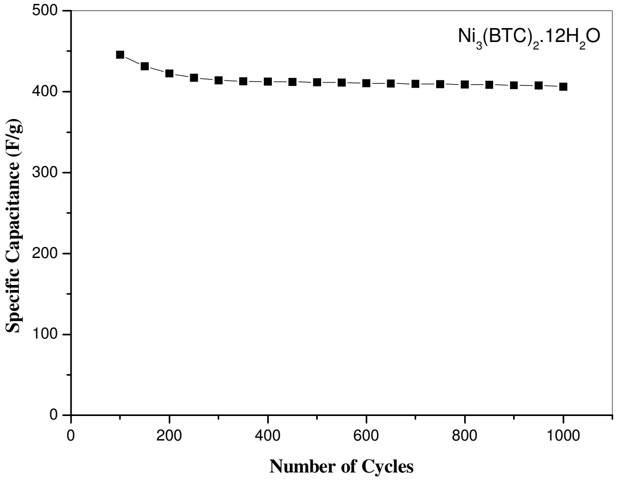

Figure 4. The variation of specific capacitance with charge-discharge cycle number of $Ni_3(BTC)_2{\cdot}12H_2O$ electrode

4. CONCLUSION

In summary, a series of Metal-Organic Frameworks (MOFs) based on 1,3,5-benzenetricarboxylic (BTC) acid and M(II) acetate hydrate (M=Co, Ni, and Zn) were successfully synthesized and used as electrode materials for supercapacitor. The maximum specific capacitance of $Ni_3(BTC)_2{\cdot}12H_2O$ is found to be 429 F g^{-1} at 5 mV s^{-1} and 154 F g^{-1} at 200 mV s^{-1}, after 500 cycles of galvanostatic charge and discharge, a higher retained specific capacitance could be obtained. These results demonstrate this MOF is a good candidate as electrode material for electrochemical capacitor. This work also offers us a novel perspective to exploit the potential application of fast growing MOF family.

5. ACKNOWLEDGEMENTS

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