

A metal-organic framework of Co(II): synthesis and supercapacitive properties

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A metal-organic framework based on pytpy and H4abtc as secondary ligands, namely Co₂(pytpy)(abtc)₂ was solvothermally synthesized and structurally characterized. The supercapacitive behavior of MOFs was determined. There are reduction and oxidation peaks when cyclic voltammetry is performed at different scan rates, which shows typical faradic redox characteristics. The specific capacitances slowly decrease along with the increase in scan rates, which signifies that the material has a good high-rate capability. The results show that the loss of specific capacitance of Co-MOF is not remarkable and it has an excellent cycle life after 1000 cycles test.

Keywords: Metal-organic framework; Supercapacitive properties; Co(II)

INTRODUCTION

At present, there are a lot of materials based on carbon and transition metal oxides which are mainly used as supercapacitor materials. MOF material is prospectful to be applied in a supercapacitor, because its porosity provides a larger number of active sites, which is beneficial to the penetration of the electrolyte and the ion transport [1,2]. Recently, some MOFs of cobalt and nickel have been reported as supercapacitor electrode materials [3-8], and there are several teams which have investigated on this topic in our country [9-13], but the specific capacitance values of overall MOF materials as supercapacitor electrode materials need to be improved. In addition, due to the low stability and poor electrical conductivity of MOF materials, direct reports on using MOF materials in supercapacitor electrode materials are very limited. In this paper, we used pytpy and H4abtc ligands to synthesize a new MOF under solvothermal conditions, and analyzed the structure of the compound, which determines the supercapacitor properties of the compound.

EXPERIMENTAL

Materials and Methods

All starting materials were of analytical grade and were used as received without further purification. Powder X-ray diffraction (PXRD) data were recorded on a Rigaku D/M-2200T automated diffractometer. Electrochemical properties were determined in a CHI 760D electrochemical workstation.

Co₂(pytpy)(abtc)₂ (1): A mixture of HNO₃/DMA was prepared by mixing 2.2 mL of HNO₃ and 10 mL of DMA in a 20 mL vial, and was ultrasonicated for 5 min. Compound 1 was prepared by solvothermal reaction of Co(NO₃)₂·6H₂O (11.6 mg, 0.04 mmol), pytpy (12.4 mg, 0.04 mmol), H₄abtc (14.3 mg, 0.04 mmol), DMA (0.5 mL), ethanol (0.5 mL), H₂O (0.5 mL), HNO₃/DMA (0.2 mL) at 100°C for 3 days. The mixture was sealed with tin foil paper in a 20 mL vial. After gradually being cooled to room temperature colorless crystals of 1 were obtained.

X-ray Crystallography

Single-crystal XRD data for compound 1 were recorded on a Bruker Apex II diffractometer with graphite monochromatized Mo K α radiation ($\lambda = 0.71073 \text{ \AA}$) at 285(2) K. Absorption corrections were applied by using multiscan technique. All structures were solved by the direct method of SHELXS-97 and refined by the full-matrix least-squares technique using the SHELXL-97 program within WINGX. No-hydrogen atoms were refined with anisotropic temperature parameters. The hydrogen atoms of the organic ligands were refined as rigid groups. The detailed crystal data and structure refinement parameters for the compound 1 are summarized in Table 1.

RESULTS AND DISCUSSION

Structure of [Ca₂(BTEC)(DMF)(H₂O)₃] (1)

Compound 1 crystallizes in triclinic crystal system of *P*-1. In the asymmetric unit there are two crystallographically unique Co(II) atoms, two pytpy

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anions and a H₄abtc ligand (Fig. 1). In the asymmetric unit, the two metal centers Co1 and Co2 are not in the same environment. Coordination mode of H₄abtc ligand is different. Some oxygen atoms in the carboxyl have monofunctional coordination. Some oxygen atoms in the carboxyl have chelated coordination. Some oxygen atoms in the carboxyl are in the form of O, O. The Co1 atom is coordinated by four oxygen atoms from two H₄abtc ligands, two nitrogen atoms from two different H₄abtc ligands and two nitrogen atoms from two different pytpy ligands. The Co2 atom is the same as the Co1 atom, but the direction of the pyridine ring which connects nitrogen atom is opposite. Both Co1 and Co2 anions are connected by H₄abtc ligands in the *ab* plane extended into a 2D layer structure (Fig. 2). Each 2D layer structure is connected by a pytpy ligand extended into a 3D framework (Fig. 3), which shows the 3D framework in the *x* plane for 1 (Fig. 4).

PXRD Analysis

Fig. 5 shows the simulated and experimental PXRD patterns of compound 1. The experimental peak positions match well to the simulation of the single crystal data, and the results indicate that the synthesized compound is of good phase purity.

Table 1. Crystal data and structure refinement for the compound 1

Compound	1
Empirical formula	C ₅₆ H ₃₄ Co ₂ N ₁₀ O ₈
Formula weight (g/mol)	1092.79
Temperature (K)	296(2) K
Crystal system	Triclinic
Space group	P-1
a (Å)	13.646(3)
b (Å)	16.705(3)
c (Å)	16.783(3)
α (°)	100.01(3)
β (°)	103.30(3)
γ (°)	108.23(3)
V (Å ³)	3409.0
Z	2
Calculated density (g/cm ³)	1.065
Absorption coefficient (mm ⁻¹)	1.408
Theta range for data collection (°)	3.17-27.43
	-7<=h<=8
Limiting indices	-27<=k<=27
	-17<=l<=17
F(000)	1116
Reflections collected	24245
Completeness	99.1 %
Data/restraints/parameters	4167/0/266
Goodness-of-fit on F ²	1.054
R1a/wR2b [I>2σ(I)]	0.0768/0.2492
R1/wR2 (all data)	0.1127/0.2829
Largest diff. peak and hole (e ⁻ ·Å ⁻³)	0.796/-0.443

$${}^a R_1 = \frac{\sum ||F_o| - |F_c||}{\sum |F_o|} \quad {}^b wR_2 = \frac{\sum [w(F_o^2 - F_c^2)^2]}{\sum [w(F_o^2)]^{1/2}}$$

$$F_c^2]/\sum [w(F_o^2)]^{1/2}$$

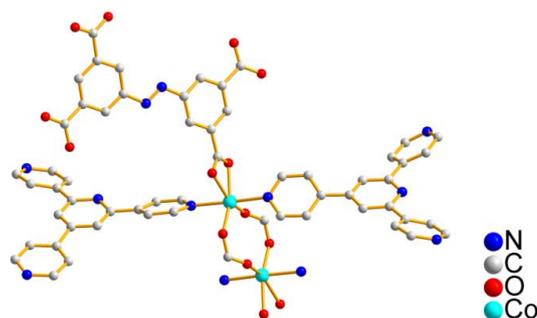


Fig. 1. Coordination environment of Co(II) atom in 1

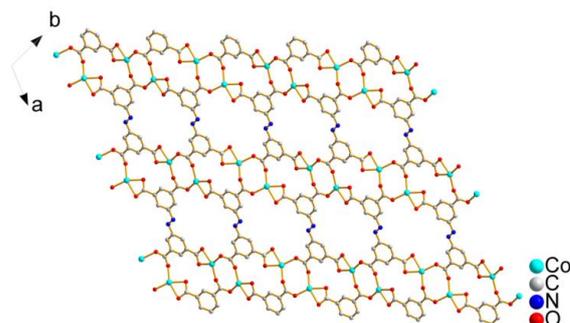


Fig. 2. View of 2D planar layer in the *ab* plane

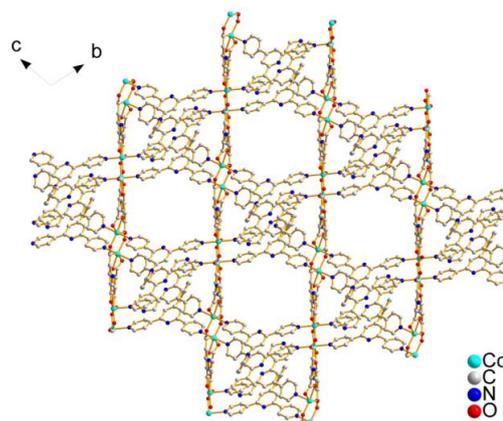


Fig. 3. Perspective view of the 3D framework for 1

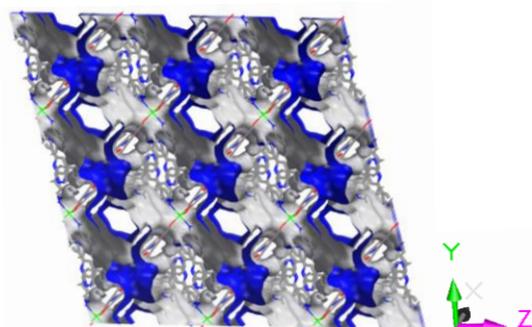


Fig. 4. View of the 3D framework in the *x* plane for 1

All electrochemical experiments were performed according to the standard three-electrode system at room temperature. The saturated calomel

electrode was the reference electrode and the platinum electrode – the auxiliary electrode. For working electrode, a mixture containing 80% of active substance, 10% of acetylene black and 10% of polyvinylidene fluoride was mixed well, and a suspension made from N-methyl-2-pyrrolidone (Aldrich) was smeared on the nickel foam current collector (1 cm × 1 cm), and dried at 100 °C for 10 h. Cyclic voltammetry (CV) and galvanostatic charge-discharge (GC) were performed on an electrochemical workstation (CHI 760D).

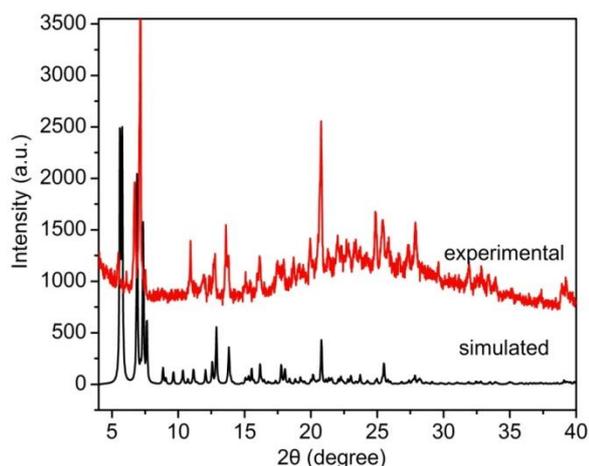


Fig. 5. Simulated and experimental XRPD patterns for 1

Fig. 6 shows the cyclic voltammetry (CV) curves of the Co-MOF electrode at various scan rates (5~50 mVs⁻¹). As depicted in Fig. 6, it clearly exhibits a couple of redox peaks at +0.33V (oxidation) and +0.23V (reduction) at a low scan rate of 5 mV s⁻¹, indicating that the pseudocapacitive behavior resulted from the surface faradic redox reactions. Electrochemical capacitor properties of Co₂(pytpy)(abtc)₂ may be due to Faraday redox reaction of Co(II) ion in the framework (Co²⁺/Co³⁺), and OH⁻ of alkaline electrolyte may be mediated. Similar to most of the capacitor electrode materials, the symmetry of the scan curve of the cyclic voltammetry is good between positive and negative, which indicates that the electrode material has reversibility and good capacitance characteristics. With the increase in scan rate, the potential of the anodic peak gradually increases and the cathodic peak gradually decreases, which shows that the electrode material has good rate capability. The galvanostatic charge-discharge curves at different current density are shown in Fig. 7. As can be seen, the curve shape of charge and discharge is very similar, and there are potential platforms. It shows the typical pseudocapacitor characteristic, which is consistent with the cyclic voltammetry curve. According to Fig. 7 we can calculate the specific capacitance at different current densities. The specific capacitance of the activated crystalline electrode is 101.65, 94.19, 88.19, 79.52, 74.55 and 72.06 F g⁻¹ when the

current density is 0.5, 1, 2, 4, 6 and 8 A g⁻¹, respectively.

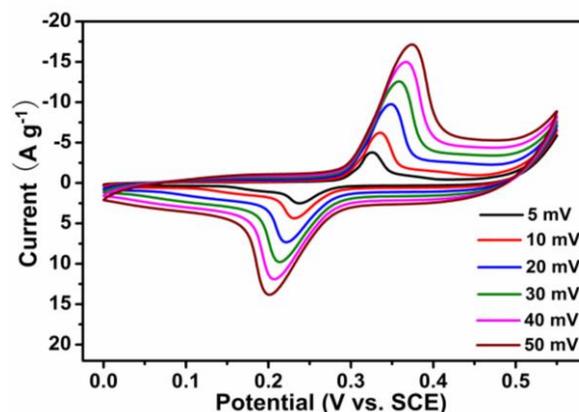


Fig. 6. Cyclic voltammetry curves at different scan rates

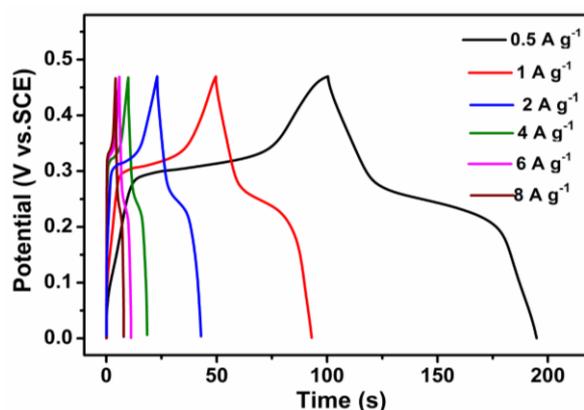


Fig. 7. Galvanostatic charge-discharge curves at different current densities

We obtained the curve of the specific capacitance of electrode as a function of the change in current density (Fig. 8). It can be seen from the figure that the specific capacitance slowly descends with current density decrease, the electrode materials have good rate capability. In addition, its value is similar to some typical supercapacitors of cobalt oxide, such as CoMoO₄ nanorods (62.8 F g⁻¹/1 A g⁻¹), MnMoO₄ nanorods (9.7 F g⁻¹/1 A g⁻¹) [11], but not as good as the supercapacitor of NiO@ CoMoO₄ nanomaterials [12] and the electrode of CoMoO₄-3D graphene hybrid (NSCGH) [13]. It is the key factor that cycle life of supercapacitor applies to practice. It was found that the capacitance retention was kept at 78% of its highest value after 1000 cycles, indicating that this kind of Co-based MOF material not only has large specific capacitance and good rate capability but also has excellent cycling stability (Fig. 9). This might be attributed to the fact that the charge transfer resistance slightly increased after long cycles. The results showed that the compound 1 has a good application prospect as a supercapacitor electrode material.

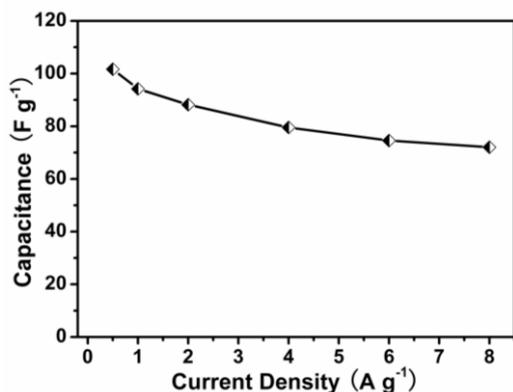


Fig. 8. Curve of specific capacitance change along with the current density

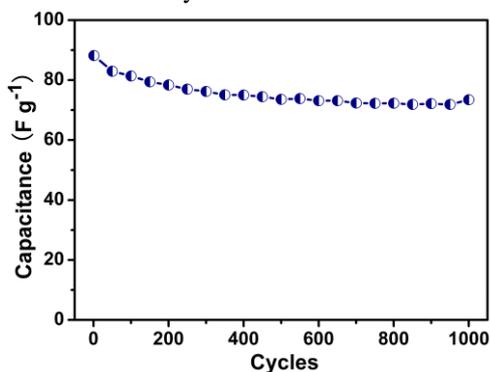


Fig. 9. Curve of cycling stability in 2 A g⁻¹

CONCLUSION

We used pytpy and H₄abtc ligand to synthesize a new MOF under solvothermal conditions. The structure and supercapacitive behavior were characterized.

Reduction and oxidation peaks are observed when cyclic voltammetry is performed at different scan rates, which show typical faradic redox characteristics. The specific capacitance slowly decreases along with the increase in scan rate, which means that the material has a good high-rate capability. The results show that the loss of specific

capacitance (Co-MOF) is not remarkable and the sample has excellent cycle life after 1000 cycles test.

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МЕТАЛ-ОРГАНИЧНА МРЕЖА НА Co(II): СИНТЕЗ И СУПЕРКАПАЦИТИВНИ СВОЙСТВА

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(Резюме)

Метал-органична мрежа Co₂(pytpy)(abtc), основаваща се на pytpy и H₄abtc₂ като вторични лиганди, е синтезирана солвотермично, охарактеризирана е структурно и са определени суперкапацитивните свойства на MOF. При циклична волтаперометрия с различни скорости на сканиране се наблюдава редукционен и окислителен пик, които са с типични фарадееви редокс характеристики. Специфичният капацитет бавно намалява с нарастването на скоростта на сканиране, което свидетелства за добрите отнасяния на материала при високи скорости. Установено е, че загубата на специфичен капацитет на Co-MOF не е съществена и материалът има отлични показатели след 1000 цикъла.