

Metal-organic frameworks-derived porous carbon polyhedrons for highly efficient capacitive deionization

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Experimental

Fabrication

Polyvinyl alcohol (PVA), zinc nitrate and 2-methylimidazole (Hmim) were purchased from Sinopharm Chemical Reagent Co., Ltd. All the reagents were used without further purification.

The zeolitic imidazolate framework-8 (ZIF-8) crystals was prepared in a typical procedure.¹ Briefly, zinc nitrate (2.58 g) and Hmim (2.63 g) were dissolved in methanol (200 ml) to generate clear solutions, respectively. Then, they were mixed together and aged at 25 °C for 24 h. After that, the white powders were centrifuged and washed very carefully with methanol, then dried in a vacuum oven at 80 °C for 24 h. The as-synthesised ZIF-8 crystals were subsequently thermally treated in nitrogen for 5 h with a heating rate of 2 °C/min. Finally, the obtained powders were washed extensively by HCl to remove residual Zn²⁺.

Characterization

The surface morphology and structure of the as-synthesized porous carbon polyhedrons (PCPs) were examined by field emission scanning electron microscopy (FESEM, JEOL JSM-LV5610), transmission electron microscopy (TEM, CM200), selected area electron diffraction (SAED) patterns, X-ray diffraction (XRD, Holland Panalytical PRO PW3040/60, with Cu-K α radiation (V=30kV, I = 25 mA)), Raman spectroscopy (Renishaw inVia) and X-ray photoelectron spectroscopy (XPS). Nitrogen adsorption-desorption isotherms were measured at 77 K with an ASAP 2020 Accelerated Surface Area and

Porosimetry System (Micrometitics, Norcross, GA).

To explore the electrochemical and electrosorption performances, the as-synthesized PCPs and PVA, with a weight ratio of 90:10, were homogenously mixed in deionized water at 80 °C to get carbon slurries. Then, the carbon slurries were uniformly coated on graphite substrates through casting method. Finally, the electrodes were dried at 80 °C in vacuum for 2 h. The potential sweep cyclic voltammetry (CV) and electrochemical impedance spectroscopy (EIS) measurements were carried out in 1 M NaCl solution by using Autolab PGSTAT 302N electrochemical workstation in a three-electrode mode, including a standard calomel electrode as reference electrode and a platinum foil as counter electrode. In EIS measurement, a frequency range of 0.1 Hz to 100 kHz and an AC amplitude of 5 mV were applied. The specific capacitance (C_{sp} in F g⁻¹) can be obtained from the CV process according to the equation:

$$C_{sp} = \frac{\bar{i} \times \Delta t}{\nu \times m} \quad (1)$$

where \bar{i} (A) is the average current, ν (V s⁻¹) is the scan rate and m (g) is the total mass of electrodes.

Electrosorption experiments

The electrodes for the electrosorption experiments were fabricated in a typical procedure: the as-synthesized PCPs and PVA, with a weight ratio of 90:10, were homogenously mixed in deionized water at 80 °C to get carbon slurries. Then, the carbon slurries were uniformly coated on graphite substrates through casting method. Finally, the electrodes were dried at 80 °C in vacuum for 2 h. The size, mass and thickness of all electrodes were

8 cm × 8 cm, ~300 mg and ~200 μm, respectively. Electrosorption experiments were conducted in a continuously recycling system including a unit cell, as described in our previous work.² In each experiment, the analytical pure sodium chloride (NaCl) solution was continuously pumped from a peristaltic pump into the cell and the effluent returned to the unit cell with a flow rate around 50 ml min⁻¹. The volume and temperature of the solution were maintained at 50 ml and 298 K, respectively. Meanwhile, the variation of NaCl concentration was monitored and measured at the outlet of the unit cell by using a conductivity meter (DDS-308, Precision & Scientific Instrument). The relationship between conductivity and concentration was obtained according to a calibration table made prior to the experiment, which has been described in our previous work.³

In our experiment, the electrosorption capacity is defined as follows:

$$\text{electrosorption capacity (mg g}^{-1}\text{)} = \frac{(\rho_0 - \rho_e) \times V}{m} \quad (2)$$

where ρ_0 (mg l⁻¹) and ρ_e (mg l⁻¹) are initial and final NaCl concentrations, respectively. V (l) is the solution volume, and m (g) is the total mass of the electrodes.

Results and discussion

Table 3 Comparison of electrosorption capacities among various carbon electrode materials from the literatures.

Electrode material	Applied voltage (V)	Initial NaCl concentration (mg l ⁻¹)	Electrosorption capacity (mg g ⁻¹)
CAs ⁴	1.2	~500	2.90
AC ⁵	1.2	500	9.72
	1.2	1000	10.80
	1.2	1500	11.00
	1.2	2000	11.76
CNTs ⁶	1.2	3000	1.70
CNTs ⁷	1.2	500	2.57
	1.2	1000	3.71
	1.2	1500	4.76
	1.2	2000	5.24
AC/graphene ²	1.2	~2230	2.94
CNTs/graphene ⁸	1.2	~500	1.40
Graphene sponge ⁹	1.2	500	14.90
Graphene aerogel ¹⁰	1.2	500	9.90
Carbon spheres ¹¹	1.2	500	5.81
Carbon nanorods ¹²	1.2	500	15.12
PCP1200 (This work)	1.2	500	13.86

Obviously, the electrosorption capacity of our PCP1200 electrode is among the highest

values of the existing carbon materials measured in the similar experimental conditions. Unlike most conventional carbon materials that suffer from either high electrical resistance (AC, etc.) or low specific surface area (graphene, CNTs, etc.), the MOFs-derived PCPs enjoy both high specific surface area and low electrical resistance, which are both crucial factors for the electrosorption process. Nevertheless, their electrosorption capacity still needs to be further improved when compared with other water desalination technique.¹³ However, this is the first attempt to apply MOFs-derived PCPs in CDI field and there is still a room to improve their performance by chemical or physical treatment, such as activation or heteroatom doping.

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