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The effects of electrolyte on the supercapacitive performance of activated calcium carbide-derived carbon

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HIGHLIGHTS

- ► Comparable electrochemical behaviors of samples in various aqueous electrolytes.
- ► Comparisons of ions in various aqueous electrolytes are carried out.
- ► Sample in 6 M KOH has better capacitive behaviors and higher capacitance.

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ABSTRACT

Porous calcium carbide-derived carbon (CCDC) has been prepared by one-step route from CaC_2 in a freshly prepared chlorine environment at lower temperature, and following activated by $ZnCl_2$ to get activated CCDC. The performances of the supercapacitors based on activated CCDC as electrode active material in aqueous KOH, K_2SO_4, KCl and KNO_3 electrolytes are studied by cyclic voltammetry, constant current charged/discharged, cyclic life and electrochemical impedance spectroscopy. It has been found that the supercapacitor using 6 M KOH as electrolyte shows an energy density of 8.3 Wh kg^{-1} and a power density of 1992 W kg^{-1} based on the total weight of the electrode active materials with a voltage range 0 V–1 V. Meanwhile, the specific capacitance of the supercapacitor in 6 M KOH electrolyte is 68 F g^{-1} at the scan rate of 1 mV s^{-1} in the voltage range of 0 V–1 V, the charge-transfer resistance is extremely low and the relaxation time is the least of all. The supercapacitor also exhibits a good cycling performance and keeps 95% of initial capacity over 5000 cycles.

1. Introduction

As we have seen, the most common electrical energy storage devices are batteries and capacitors. Rechargeable batteries generally provide a high specific energy and a rather low specific power. Usually, capacitors can supply high specific powers, but the amount of energy stored is very low. Supercapacitors (often called electrochemical capacitors or ultra-capacitors) are charge-storage devices that possess excellent reversibility, exhibit ideal high power density and fairly long cycle life [1]. They are applied to various electronic devices, such as power electronics, as well as in hybrid electric vehicles and space flight technology [2]. Recently, many researches on the electrochemical capacitors aim to increase power and energy density as well as lower fabrication costs while using environmental friendly materials, which can be realized by using the larger capacitance materials and/or increasing the cell voltages [3].

The electrochemical behaviors of the supercapacitors are decided not only by the exposed surface area of the carbon electrode, but also by the matching degree between the size of solvated ions in the electrolytes and the pore size distribution of carbon electrode [4,5,6]. A lot of efforts have been done on the compatibility of electrodes with electrolytes. In the literature, [7] electrolyte concentration showed a strong effect on supercapacitor capacitance. For example, if electrolyte concentration is high, ion transport within the electrode layer will be easier, leading to an effective building-up for electric double layer. However, if the electrolyte concentration is too high, the viscosity of solution will increase due to less water hydration, resulting in decreases of ion mobility. The properties of solvents in electrolytes also have great impact on the migration speed and size of the solvated ions. For instance, the radius of solvated ions in aqueous solvents is mostly less than that in organic electrolyte. For this reason, a carbon electrode with a larger number of macropores is preferable in organic solvents [8]. However, despite the remarkable performance of these organic-based nonaqueous electrolytes, they suffer from severe safety hazards. The fabrication costs of capacitors using such electrolytes

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are also high due to the use of a water-free environment needed to manipulate and assemble. For this reason, many researches have focused on choosing proper positive and negative electrode materials to form a hybrid system in aqueous electrolyte. Therefore, finding an eco-friendly and efficient aqueous electrolyte will be highly significant. Indeed recent studies [9,10,11,12] have shown that symmetrical type carbon/carbon capacitor and asymmetric carbon/MnO_2 electrochemical capacitors (based on various porous carbon materials) with different aqueous electrolytes of K_2SO_4, KCl, KNO_3 and KOH possess excellent electrochemical performance, especially with KOH. However, there have been few reports about the effects of electrolyte on the supercapacitive performance of the activated CCDC.

CCDC produced by halogenation of carbides exhibits a narrow pore size distribution, a tunable pore and microstructure by choosing the appropriate carbide precursor and chlorination temperature. Yushin et al. [13] studied the effect of pore size on hydrogen uptake and heat of adsorption about carbide-derived carbons. The results showed how smaller pores increase both the heat of adsorption and the total volume of adsorbed H_2. It has been demonstrated that increasing the average heat of H_2 adsorption above 6.6 kJ mol^{-1} substantially enhances H_2 uptake at 1 atm (1 atm = 101,325 Pa) and −196 °C. The heats of adsorption up to 11 kJ mol^{-1} exceed values reported for metal–organic framework compounds and carbon nanotubes. Schmirler et al. [14] developed an in-situ thermal activation in CO_2 parallel to the carbides chlorination for the preparation of carbide-derived carbons. For this in-situ activation and chlorination of carbides the influence of the processing, the concentration of CO_2 and activation time on the pore structure of CDC were studied.

In previous work, our group has carried out a lot of works on CCDC and their supercapacitive behaviors. Dai et al. [15] developed a type of one-step preparation technique for CCDC, which was synthesized from CaC_2 in a freshly prepared chlorine environment in the temperature range of 100 °C–600 °C. Zheng et al. [16] prepared CCDC/polyaniline (PANI) composite materials by in-situ chemical oxidation polymerization of an aniline solution containing well-dispersed CCDC, the specific capacitance of CCDC/PANI composite electrode showed as high as 713.4 F g^{-1} measured by cyclic voltammetry at 1 mV s^{-1}, but the capacitance retention of coin supercapacitor just remained 80% after 1000 cycles. The activation technology will usually influence specific surface area, microstructure and supercapacitive behaviors of porous carbon material. In order to study the effect of activation technology on the electrochemical performances of supercapacitors using CCDC as electrode active material, we have used H_3PO_4, $ZnCl_2$ and KOH as activation agent to activate CCDC and found that $ZnCl_2$ was the best activation agent [17]. In this paper we will investigate further the electrochemical performance of activated CCDC in the different aqueous electrolytes, e.g., 0.5 M K_2SO_4, 2 M KCl, 1 M KNO_3 and 6 M KOH [9,10,11,12].

2. Experimental

2.1. Synthesis of activated CCDC

All chemicals were of analytical grade and used without any further purification. The CCDC were prepared as follows: CaC_2 powders were placed in a quartz tube furnace then the tube was Ar purged for 30 min and heated to 400 °C. Fresh prepared chlorine gas was directly passed through the tube furnace once reached the desired reaction temperature. After chlorination for 2 h, the furnace was naturally cooled down to room temperature under Ar purge. The resultant product was soaked in HCl solution (3 mol L^{-1}) and washed with distilled water to remove further remainder. Acidic product was washed into neutral condition and then dried in desiccators at 80 °C for 12 h to obtain CCDC.

The resultant CCDC sample was soaked in $ZnCl_2$ solution (0.37 mol L^{-1}) and stirred in 80 °C for 7 h, then filtrated and dried at 80 °C for 12 h. The filtered product was placed in a quartz tube furnace, and the tube was Ar purged for 30 min, then heated to 600 °C. The product was soaked in diluted hydrochloric acid, heated to 90 °C and stirred for 30 min, then washed with distilled water until the pH of filtrate water became neutral. The filtered product was dried at 80 °C for 12 h [18,19].

2.2. Preparation of electrode and button cell supercapacitor assembly

The mass ratio of activated CCDC/acetylene black was 8:1. The powder mixture was mixed with 10 wt% of polyvinylidene fluoride (PVDF) aqueous suspension as a binder to obtain a paste. The paste was then pressed into the steel mesh substrate using a spatula. After drying in vacuum at 110 °C for 12 h, the electrode of steel mesh was pressed at 15 M Pa for 1 min to assure a good electronic contact and form a circular tablet. The geometric surface area of the electrodes was kept to be 1.0 cm^2; the electrodes typically had a thickness of about 0.1 mm. Symmetrical button cell supercapacitors were constructed with various electrolytes (0.5 M K_2SO_4, 2 M KCl, 1 M KNO_3 and 6 M KOH), in which two activated CCDC electrodes were separated by a separator of electrode/separator/electrode order. Then the supercapacitors were sealed with a packing machine.

2.3. Characterization of the material

The activated CCDC was characterized by physical N_2 adsorption/desorption at 77 K (using an AUTOSORB-1 instrument from Quantachrome). The specific surfaces (SBET) were derived from N_2 adsorption isotherms by means of the BET equation. The pore size distributions and medium pore diameter were determined using the BJH. The micropore volume (V_{micro}) was obtained by Dubinin–Raduskevich equation and the total volume of porous (V_{total}) by Gurvitsch rule at $P/P_0 \approx 0.985$.

2.4. Electrochemical measurements

The electrochemical performances of the as-prepared electrode materials were characterized by cyclic voltammetry (CV) between −1 V and 0 V with the different scan rates of 1 mV s^{-1}–20 mV s^{-1}, galvanostatic charge/discharge tests at various constant current densities with cutoff voltage of 0 V–1 V and electrochemical impedance spectroscopy (EIS) in the frequency range from 10^5 Hz to 10^{-2} Hz with amplitude of 5 mV. The CV, the galvanostatic charge/discharge and EIS measurements were performed by means of electrochemical analyzer systems, CHI660 (CH Instruments, USA). The experiments were carried out using button cell supercapacitors. The cycle life was measured by potentiostat/galvanostat (BTS 6.0, Neware, Guangdong, China) on button cell supercapacitors.

3. Results and discussion

Cyclic voltammetries are performed to estimate the electrochemical properties of the symmetric supercapacitors with activated CCDC as electrode active materials at the scan rate range of 1 mV s^{-1}–20 mV s^{-1} with the voltage range of 0 V–1 V in various aqueous electrolyte solutions. Fig. 1 shows cyclic voltammograms of activated CCDC supercapacitors in the aqueous electrolytes of 6 M KOH, 1 M KNO_3, 0.5 M K_2SO_4 and 2 M KCl. It can be found from