A Three Dimensional Conductive Matrix of Activated Carbon Coated Copper-Cobalt Prussian Blue Material for Sodium Ion Supercapacitors

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Abstract. In this work, a three dimensional (3D) conductive material of activated carbon coating Copper-Cobalt Prussian Blue (PB) is synthesized and applied on sodium ion supercapacitors. The activated carbon is proved able to enhance the conductivity, prevent structural collapse during sodium ion deintercalation, reduce interstitial water in PB crystals as well as special hindrance, and improve electrochemical performance of super capacitors dramatically. It is demonstrated that a specific capacity of 90.4 F g⁻¹ and power density of 4.3 kW kg⁻¹ as well as energy density of 65.1 Wh kg⁻¹ are achieved for CuCoHCF@AC//AC device. In addition, 90% % starting value are retained for the specific capacity after 2000 cycles operation.

1. Introduction
As a result of their unique crystal structures which favor intercalation and deintercalation of large radius alkali ions, Prussian blue analogues are widely researched as cathode material for alkali ion batteries and supercapacitors. The diffusion process of sodium ion (Na⁺) is key step of the deintercalation process [1-3]. During discharging process, Na⁺ diffuse from outer layer to core of cathode material, the inadequacy of diffusing channels for large amount of Na⁺ deintercalation result in transporting blockage and increased resistivity [4]. The material structure may also suffer from collapse during ion intercalation and deintercalation, which will jeopardize electrochemical performance. Efforts are devoted to improving the material conductivity and stability, and iron ion replacement with other metal ions has proved to be a valid method [5].

The electrochemical properties of PB materials can be manipulated by doping of metal elements. Moritomo et al. [6] found that only Co doping to Na₉₆Mn[Fe(CN)₆]₀.₉ would improve device capacity but make the cycling performance poor, while Ni doping would decrease device capacity but improve material stability. Therefore, the disadvantages of individual element may be conquered by synthesizing Prussian blue analogues with two or more transitional metals [7-14].

Carbon materials are popular in battery and supercapacitor studies to improve cathode conductivity as well as device performance. Moritomo et al. used glucose as carbon source for carbon coating, and applied it on the Na⁺ energy storage device [15]. Yang et al. used graphene oxide (GO) coating to synthesized micro-cubic Prussian blue (PB) without coordinated water, which delivered high electrochemical performances [16]. Prabakar et al. reported the synthesis of highly crystalline PB

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embedded in GO layers, which demonstrated superior electrochemical properties [17]. Therefore, carbon coating promotes the ionic conductivity and stabilized the crystalline structure of PB materials.

In this work, activated carbon coated PBA material with two metal substitution (CuCoHCF@AC) was prepared by one-step method. The activated carbon coating improved the electronic and ionic conductance of the material, protected the crystal structure from damage, and reduced the intergranular water content of the material. The specific capacity and energy density of CuCoHCF@AC//AC device were significantly improved compared with the uncoated CuCoHCF//AC device.

2. Experimental

2.1. Synthesis

Activated carbon and chemical agents including Cu(NO3)2 (AR), K3Fe(CN)6 (AR), and Co(NO3)2 (AR) were all purchased from Aladdin. CuCoHCF and CuCoHCF@AC was synthesized by chemical co-precipitated method. Cu(NO3)2 and Co(NO3)2 was added into K3Fe(CN)6 solution, and stirred at high speed to form CuCoHCF. Additionally, activated carbon was dropped into the above-mentioned solution to form CuCoHCF@AC precipitates. In the end, these two precipitates (CuCoHCF and CuCoHCF@AC) were filtered, washed with water, and dried in vacuum at 60 °C.

2.2. Characterization

X-ray powder diffraction (XRD) patterns and X-Ray photoelectron spectra (XPS) of CuCoHCF and CuCoHCF@AC precipitates were carried out by using the DX-2700B X-ray diffractometer in CuKα radiation with a wavelength of 1.54 Å and the ESCALAB 250Xi X-ray photoelectron spectrometer at room temperature in ambient air, respectively. IR spectra for CuCoHCF and CuCoHCF@AC sample were collected by using a Fourier Transform Infrared Spectrometer (FT-IR, Vertex80 spectrometer). Raman spectroscopy of the CuCoHCF and CuCoHCF@AC samples was characterized using inver-Reflex equipped with a 532 nm excitation laser. Working electrodes were prepared by coating active materials onto Nickel foam, the active materials were composed of carbon black and PVDF (polyvinylidene fluoride) with a mass ratio of 8: 1: 1 compared to Nickel. Typical loadings were about 1 mg/cm² for the active materials. Electrochemical activities were evaluated using a three-electrode cells measurement, using 0.4 M NaNO3 aqueous solution as the electrolyte, saturated calomel electrode (SCE) as the reference electrode and a graphite rod as the counter electrode, respectively. Asymmetric supercapacitor was assembled to perform the electrochemical tests by integrating CuCoHCF@AC on nickel foam as the cathode and AC on nickel foam as the anode, respectively. Supercapacitor performance were evaluated using a CHI 760 electrochemical workstation through galvanostatic charge-discharge (GCD) cycle, cyclic voltammetry (CV) and electrochemical impedance spectroscopy (EIS) tests. EIS measurements were carried out from 100 kHz to 1Hz with a potential amplitude of 5 mV.

3. Results and Discussion

3.1. Preparation and Characterization of CuCoHCF@AC

Raman and XRD demonstrated that the activated carbon was successfully coated on CuCoHCF. Figure 1a is the Raman spectrum of CuCoHCF@AC, giving direct evidence for the presence of activated carbon. Raman spectra showed two distinct characteristic peaks located at 1360 cm⁻¹ and 1594 cm⁻¹, corresponding to the D (disordered carbon) band and G (graphite) band. The wide D band and the high ID/IG ratio indicated that the carbon in CuCoHCF@AC was mainly amorphous. Figure 1b shows the XRD patterns of CuCoHCF@AC and CuCoHCF materials. Only face-centered cubic structure related peaks were found with no other impurity peaks, indicating high purity and good crystallinity of the material. The sharper diffraction peak of CuCoHCF coated with AC manifested that the coating of AC protects the crystal structure of the material, which could improve stability of the material.
XPS was performed to determine the composition of CuCoHCF and CuCoHCF@AC. The peak positions of Cu, Co, Fe elements in XPS spectrum of CuCoHCF sample were almost the same as those in CuCoHCF@AC one. Figure 2a exhibited the high-resolution XPS spectra of C 1s spin-orbit, the carbon peaks were totally different for the two samples. For CuCoHCF samples, three typical peaks at 284.8 eV, 286 eV and 288.6 eV were detected, which is identified as C≡N bond, C-O-H bond and C=O bond, respectively. However, for CuCoHCF@AC sample, C-O bond decreased dramatically, and C-O-H disappeared. Figure 2b exhibited the IR spectra for the CuCoHCF and CuCoHCF@AC samples, for CuCoHCF, the OH bending vibration band at 1670 cm⁻¹ disappeared after AC coating, and the OH stretching vibration band was also diminished after AC coating [18], the results indicated that the trace interstitial water in CuCoHCF, has been remarkably reduced after AC coating.

3.2. Electrochemical Performance of CuCoHCF@AC Hybrid Supercapacitors

Figure 3 exhibited the CV curves of CuCoHCF and CuCoHCF@AC from 0 to 1V at scan rate of 5, 10, 20, 50 and 100 mV s⁻¹, with increasing the scanning speed, the curves shaped similarly indicating good rate capability. It was also observed from the CV curves that a pair of obvious redox peaks appeared at 0.7 V and 0.45 V in each cycle respectively, corresponding to the redox reaction of Co³⁺/Co²⁺ pair. The redox peak intensity increased with a slight deviation with increased scanning rate, indicating good cyclic stability of the material. The potential difference between the oxidation peak and reduction peak of CuCoHCF@AC was closer than that of CuCoHCF, indicating that the electrode reaction reversibility of CuCoHCF material was significantly improved by AC coating. During discharge, the active substance CuCoHCF was embedded into Na⁺ to form NaCuCoHCF.

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\text{CuCoHCF@AC} + \text{Na}^+ + e^{-} \xrightarrow{\text{discharge}} \text{NaCuCoHCF}
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Figures 3c and 3d present the GCD curves of CuCoHCF and CuCoHCF@AC. The symmetrical charge-discharge curves indicated high electrochemical reversibility. Both materials exhibit significant discharge voltage platforms, indicating capacitive and battery-type behavior of the electrodes had.
capacitive and battery-type behavior. According to figures 3c and 3d, CuCoHCF@AC exhibited much longer discharge time, indicating a higher specific capacity. The specific capacitance within 0-1 V potential window at current density of 0.4, 0.5, 1, 2 A g⁻¹ were plotted in figure 4e. The specific capacitance of CuCoHCF were 127, 118.8, 90.7 and 85.1 F g⁻¹ at current density of 0.4, 0.5, 1 and 2 A g⁻¹ respectively. While the specific capacitance of CuCoHCF@AC were 156.8, 124.1, 114, 99.2 F g⁻¹, whose capacity promotes a lot. That could be explained that the coating improved the electrical conductivity, reduced the collapse of the frame, and ensured the stability of the structure.

Figure 3. Electrochemical properties of CuCoHCF and CuCoHCF@AC: (a) CV curves at different scan rates of CuCoHCF; (b) CV curves at different scan rates of CuCoHCF@AC; (c) galvanostatic discharge curves at different current densities of CuCoHCF; (d) galvanostatic discharge curves at different current densities of CuCoHCF@AC; (e) the corresponding specific capacitance as a function of current density.

Supercapacitor were assembled for CuCoHCF@AC sample to evaluate the electrochemical performance. As shown in figures 4a and 4b, the specific capacitance of hybrid supercapacitor for CuCoHCF@AC//AC were 90.4, 83.7, 69.1, 45.1 F g⁻¹ at current density of 0.4, 0.5, 1 and 2 A g⁻¹, which has been effectively increased after AC coating, compared to 51.4, 50.2, 31.1 and 22.3 F g⁻¹ for CuCoHCF//AC. As the current density increased from 0.4 A g⁻¹ to 2 A g⁻¹, the capacitance retention was achieved up to 49% suggesting excellent stability.

Electrochemical impedance spectroscopy were measured and shown in figure 4d to study the dynamics of reaction process. On one hand, the AC conductive skeleton affiliated the electron transfer between CuCoHCF particles, reduced electrochemical polarization, and promoted the electrochemical reaction. On the other hand, the three-dimensional frame structure offered sufficient diffusion channels for Na⁺ insertion and extrication. It was observed that the EIS curves were fitted with a semicircle in the high frequency and a line with 45° in the low frequency, which corresponded to electron transfer and Warburg diffusion process, respectively. CuCoHCF@AC//AC had the Rs (1.33 ohm) and Rct (0.99 ohm), far lower than the Rs (2.1 ohm) and Rct (1.77 ohm), indicating that CuCoHCF@AC has more ideal capacitance characteristics.

The power densities of CuCoHCF@AC//AC hybrid supercapacitor were plotted as a function of energy densities (Ragone plots) in figure 4e. The energy densities as well as power densities were
calculated from GCD curves. The upper power densities limit were both around 4.3 kW kg\(^{-1}\) at current density of 2 A g\(^{-1}\) for the CuCoHCF//AC and CuCoHCF@AC//AC hybrid supercapacitors, however, for CuCoHCF@AC//AC hybrid supercapacitor, the energy density of was 65.3 Wh kg\(^{-1}\) at current density of 0.4 A g\(^{-1}\), which was 30% higher than that of CuCoHCF//AC.

Since AC coating process has effectively reduced the interstitial water in PBAs and improved the conductivity. The long-term cyclic charge/discharge curve in 0-1.2 V in figure 4f for CuCoHCF@AC//AC and CuCoHCF//AC samples exhibited that after 2000 cycles operation, CuCoHCF@AC//AC maintained a capacitance retention as much as 90.0% even, much higher than that of CuCoHCF//AC.

Figure 4. Electrochemical performance of CuCoHCF and CuCoHCF@AC hybrid capacitors: Charge/discharge curves at different current densities of (a) CuCoHCF; and (b) CuCoHCF@AC; (c) the corresponding specific capacitance as a function of current density; (d) Nyquist plots; (e) Ragone plots, and (f) Cycle performance of CuCoHCF and CuCoHCF@AC hybrid capacitors.

4. Conclusions
Activated carbon CuCoHCF was prepared by co-precipitation and applied in sodium supercapacitors. Activated carbon coating not only increased the energy density of the device, but also greatly improved the stability of the device. The content of crystal water in the material was studied by XPS and IR characterization. The diffusion resistance and electrochemical resistance of the material were studied by EIS test. It has been proved that AC coating is a viable method to improve the electrochemical properties of Prussian blue material.

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