Rapid microwave etching of carbon cloth to form porous flexible zinc-ion hybrid supercapacitor electrodes

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Abstract. It has been a research hotspot to develop flexible cathode for zinc-ion hybrid supercapacitors. Here, a simple and fast way of surface modification of carbon cloth (CC) is proposed. The surface-modified carbon cloth (MCC) was obtained by a few minutes of simple treatment using a microwave oven. The MCC had a porous structure and was assembled with zinc sheets to form ZHSCs with an excellent surface capacity of 0.82 mAh cm-2 and outstanding rate performance. Moreover, a capacity retention of 90.15% was demonstrated by the ZHSCs following 15,000 cycles at a current density of 20 mA cm-2. This outcome offers a straightforward and cost-effective approach for the fabrication of flexible electrodes.

Keywords: zinc-ion hybrid supercapacitors, surface modification, carbon cloth, microwave oven, flexible electrodes.

1. Introduction

The increasing demand for energy with the rapid development of modern societies, the continuous exploitation of fossil fuels and the growing environmental degradation are forcing people to develop more environmentally friendly and sustainable energy sources and energy storage devices [1,2]. The reliable energy storage systems such as batteries and supercapacitors (SCs) are the critical factors to realise these evolutions in the energy structure. Among them, commercialised lithium-ion batteries are often limited in their development due to safety and scarcity of resources. Besides, SCs have been considered as an alternative energy storage device to lithium-ion batteries due to their high power density, good cycling stability and high safety. However, the energy density of SCs falls far short of requirements for medium- and large-scale energy storage systems [3,4]. By combining the advantages of battery-type electrodes and capacitor-type electrodes, constructing hybrid supercapacitors has become an effective method to improve the energy density of supercapacitors in order to solve this problem. Zinc-ion hybrid supercapacitors (ZHSCs), as a new type of energy storage device, have received widespread attention because they integrate the advantages of high energy density of zinc-ion batteries and high power density and long cycle life of supercapacitors [5].

The operating principle of zinc-ion hybrid supercapacitors is primarily based on the charge storage mechanism of the two electrodes: the positive electrode is an electric double layer capacitor formed based on the adsorption/desorption of ions on the electrode surfaces, and the negative electrode is a pseudocapacitor based on the fast and reversible surface redox reaction of zinc ions [6]. This hybrid energy storage mechanism enables ZHSCs to achieve high energy density while maintaining high power density. In terms of positive electrode materials, researchers are working to develop a variety of carbon-based materials, including porous carbon, graphene, carbon nanotubes and biomass carbon [7,8].

As a common carbon material with the advantages of good flexibility, good electrical conductivity and low cost, carbon cloth (CC) has become a research hotspot for wearable flexible devices in recent years. However, the performance of unmodified carbon cloth often fails to meet practical requirements in some specific electrochemical applications. At this point, the development of nanotechnology and surface science provides new ideas and methods for the surface modification of carbon cloth. By modifying the surface of carbon cloth, specific functional groups,

nanostructures or other active substances can be introduced to significantly improve its electrochemical performance [9,10].

In some recent researches, Han et al. designed a novel redox etching strategy to synthesise carbon cloth electrodes with 3D interconnected pore structures [11]. Zheng et al. showed that modified nitrogen-doped carbon fibre cloth containing oxygen groups could be obtained by annealing pre-oxidised polyacrylonitrile cloth followed by an oxidation process using a mixture of concentrated sulphuric acid and concentrated nitric acid [12]. Wang et al. significantly enhanced the hydrophilicity and specific surface area of the modified carbon cloth using a high-temperature annealing process, thereby improving its electrochemical properties by three orders of magnitude [13]. As we can see, all of these surface modification methods significantly enhance the electrochemical performance of the carbon cloth by increasing the specific surface area and active sites on its surface [14]. However, there are some drawbacks to these studies, such as the complexity of their processing steps, some of which require multiple steps and take dozens of hours at each step.

In this work, we have presented a simple microwave oven treatment method. Surface-modified carbon cloth (MCC) was obtained by using a household microwave oven in which CC was directly placed for microwave treatment for 0.5 to 4 min.The surface of MCC had significantly increased nanoporosity and oxygen content. We used it as a positive electrode for ZHSCs and obtained an area capacitance enhancement to 0.82 mAh cm-2. This research provides an easy path for the development of flexible ZHSCs.

2. Experimental section

2.1 Preparation of MCC

The commercial carbon cloth (CC) was directly placed in a domestic microwave oven and microwaved for 0.5, 1.0, 2.0, 3.0 and 4.0 min, respectively, washed and dried to produce MCC.

2.2 Material Characterization

A scanning electron microscope (SEM) was used to view the micro-morphologies. To obtain N2 adsorption-desorption isotherms, a surface area analyzer was utilized. The Brunauer-Emmett-Teller (BET) equation was used to determine the specific surface area (SSA).. Utilizing X-ray diffraction (XRD), the samples' surface chemical states and crystal structure were examined.

2.3 Electrochemical Measurements

Zn foil was used as the anode, CC and MCC (1×1 cm2) as the cathode, and 2 M ZnSO4 solution as the electrolyte to assess the electrochemical performance of a two-electrode system.

3. Results and discussion

The MCC electrodes were synthesised by a simple microwave oven treatment method and the duration of the treatment was only a few minutes. We used SEM to observe the morphological changes before and after CC treatment. As shown in Figure 1a, the untreated CC has a smooth and flat surface with hydrophobic properties. The microwave oven-treated MCC, as shown in Figure 1b, had abundant nanopores, which provided more space for the storage of ions [15,16]. In addition, the nitrogen isothermal adsorption-desorption test was also a test capable of demonstrating changes in the surface porosity of CC. As shown in Figure 1c, the BET specific surface area (SSA) results calculated from the nitrogen adsorption-desorption curves showed that the SSA of the common CC was only 1.49 m2 g-1. It proved that there were almost no pores on the surface, which provided very little space for the storage of ions, and this is the main reason for its extremely low electric capacity [17]. However, after a simple microwave oven treatment, the SSA of MCC was enhanced to 21.75 m2 g-1, which is a qualitative improvement. The increase in SSA is due to the high

temperature condition during the treatment process, which resulted in the increase of carbon framework defects [18]. Notably, the resulting pores facilitated the rapid transport and diffusion of electrolyte ions, providing more surface area for charge storage [19]. As shown in Figure 1d, there was almost no difference between the XRD curves of CC and MCC. They both showed two noticeable peaks at 24° and 44°, belonging to the graphitic carbon lattice (002) and (100) planes, respectively, indicating that the treatment did not change the composition and structure of the MCC, and they were both predominantly amorphous [20].

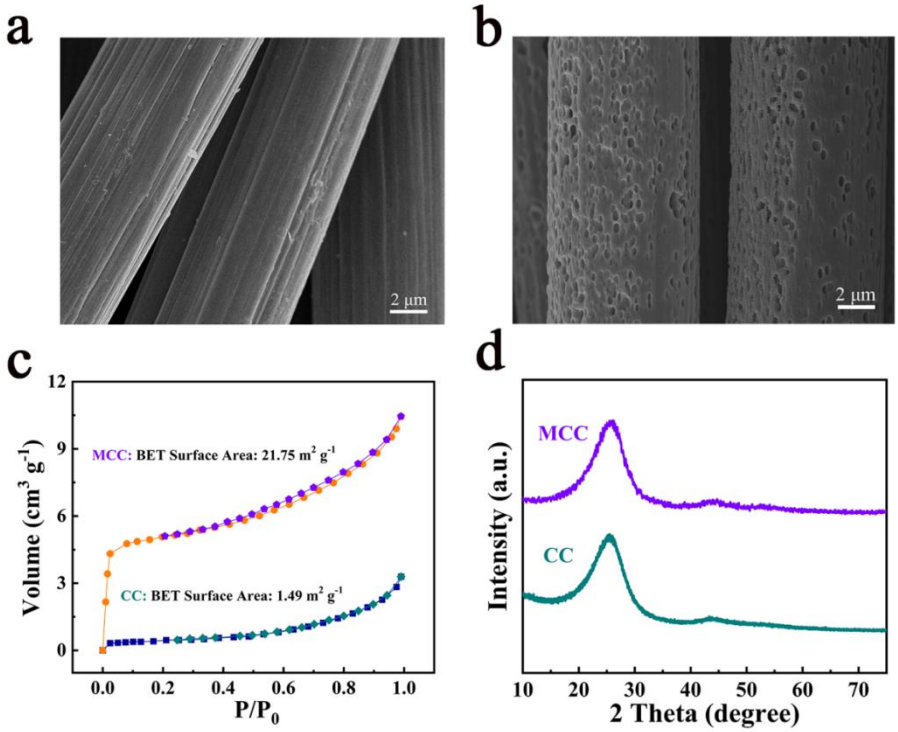

Fig. 1. SEM images of (a) CC and (b) MCC. (c) Nitrogen adsorption-desorption isotherms, (d) XRD patterns of CC and MCC.

We assembled ZHSCs devices based on CC and MCC electrodes to investigate their electrochemical performance. Figure 2a showed the GCD plots comparing CC and MCC at a current density of 1 mA cm-2, and it can be seen that the discharge duration of MCC electrode was improved by two orders of magnitude after a simple and quick treatment. Combined with the CV curve in Figure 2b at a scan rate of 1 mV s-1, the MCC electrode possessed a larger rectangular area. Both of these data demonstrate a qualitative improvement in the electrochemical performance of the MCC electrode. In addition, we compared the MCCs based on different microwave processing times. As shown in Figure. 2c, the treatment durations were 0.5, 1.0, 2.0, 3.0 and 4.0 min. Based on the GCD results, it can be seen that the surface capacity of the MCC increased with the increase of the treatment duration and reached the optimum at 3.0 min. With further increase in treatment duration, the surface capacity instead decreased, which was attributed to the excessive destruction of the surface structure of MCC by further treatment. Figure 2d illustrated the GCD curves of MCC-based ZHSCs at different current densities. The corresponding area capacities were 0.82, 0.61, 0.50, 0.38, 0.29, 0.17 mAh cm-2 at current densities of 0.5, 1, 2, 5, 10, 20 mA cm-2. And it can be seen from Figure 2e that they also have excellent rate performance, maintaining the initial facet capacitance after a series of cycles. Specifically, at a current density of 20 mA cm-2, it was able to possess a capacity retention of 90.15% after 15,000 cycles.

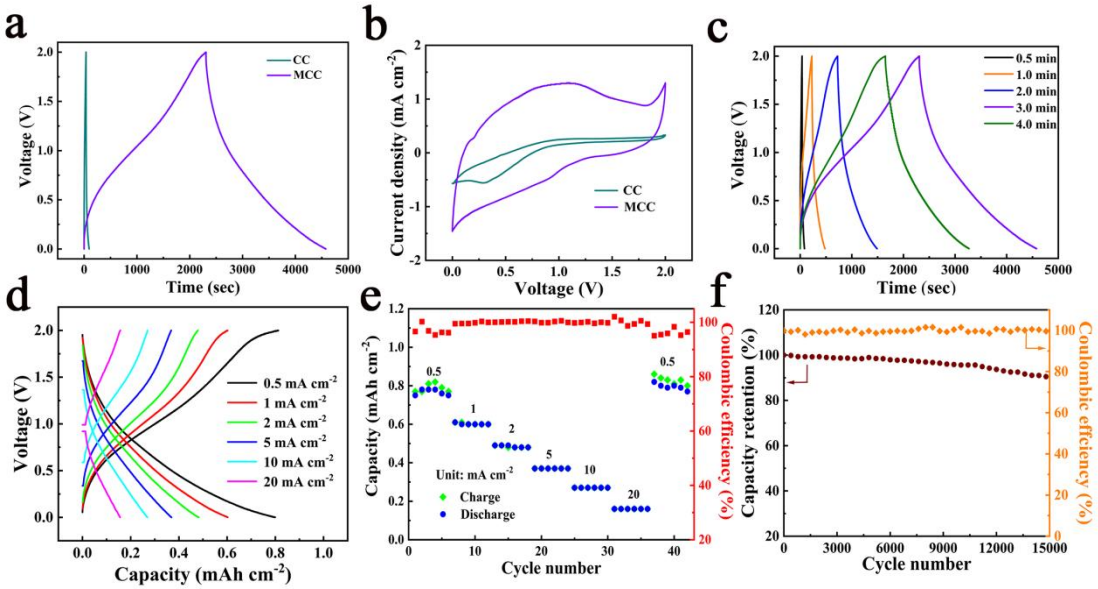

Fig. 2. Electrochemical performance of ZHSCs based on CC and MCC. (a) GCD plots at 1 mA cm^{-2}, (b) CV plots at 1 mV s^{-1}. (c) GCD plots at 1 mA cm^{-2} for different treatment durations. MCC-based ZHSCs at various current densities for (d) GCD graphs, (e) Rate capacities. (f) Cycling graphs of 20 mA cm^{-2}.

4. Conclusions

In this work, we performed successful surface modification of commercial CC using a domestic microwave oven. The modification method is simple and fast, and it takes only a few minutes to significantly improve the electrochemical properties of CC. The modified MCC is rich in nanopores, and when used as a cathode for ZHSCs, it is able to exhibit an admirable surface capacity of 0.82 mAh cm-2, and also has excellent cycling stability. This work provides a fast method for synthesising low-cost, high-performance flexible electrodes.

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