Fluorine Modification over Activated Carbon Electrodes Enabling Stable 3 V Supercapacitor Operation

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Abstract: High-energy-density electrochemical supercapacitors are required by various fields in modern society. Low-temperature plasma technology is used to produce fluorine-containing functional groups on the surface of the activated carbon electrode in CF₄ gas. The passivation layer formed by the fluorine element on the electrode surface can effectively prevent the electrode material from reacting with the electrolyte, which leads to the breakdown of the electrolyte during the charging and discharging process of the supercapacitor and the destruction of the electrode material structure. After 12,000 charge-discharge cycles at 3 V, the capacitance retention rate of supercapacitors modified by fluorine for 9 minutes is 91.81%, which is 30.95% higher than that of the control group. In addition, the specific capacitance of the electrode has also increased to a certain extent.

1. Introduction
With the prosperous development of our country's economy, the market for portable electronic devices and electric vehicles has developed rapidly[1]. As an important source of energy for these devices, high-power supplies have been greatly developed[2]. Supercapacitors, also known as electrochemical capacitors, are a special type of capacitors that charge and discharge at the electrode-electrolyte interface based on materials with high specific surface areas such as porous carbon and some metal oxides. It has the advantages of fast charging speed, long service life, large operating temperature range, maintenance-free and environmental protection[3], and is very suitable for fast storage and release of energy. There are two main types of energy storage principles: electric double layer capacitors and pseudocapacitors. Electric double layer capacitors mainly store charges through the interface electric double layer. The electric double layer capacitors using porous carbon material activated carbon as symmetric electrodes are the mainstream of commercial supercapacitors[4]. Activated carbon has the advantages of wide range of raw materials, low price, large specific surface area, rich pores, etc. However, factors such as poor conductivity and poor structural stability limit the energy density of the product. The energy density of such supercapacitors is lower than that of secondary batteries, and it is difficult to meet the energy density requirements of large-scale power equipment and electric vehicles. Therefore, research on improving the energy density of supercapacitors has been widely carried out[5].

Researchers have improved the energy density of supercapacitors from the aspects of electrode materials and electrolyte. The research work on electrode materials mainly focuses on the design of the pore size of the carbon material[6] and the surface treatment of the material[7]. Since its discovery, plasma has been widely used in all aspects. The use of low-temperature plasma to modify the surface of carbon materials has received widespread attention. Low-temperature plasma technology is a chemical treatment method that uses radio frequency power to excite low-temperature plasma. Plasma is the...
fourth state of matter existing in addition to solids, liquids, and gases. It is composed of positively charged atoms or groups of atoms, negatively charged atoms or groups of atoms, electrons, excited atoms or molecules, and free radicals. These particles both have very high energy, generally higher than the bond energy of common chemical bonds. Because the ion temperature of low-temperature plasma is much lower than the electron temperature, the overall temperature is lower, and the damage to the substance in the chemical reaction process is small. According to the equation \[ E = \frac{1}{2} CV^2, \] increasing the capacitance of the supercapacitor and widening its voltage window can increase the energy density.

This article, we reported the use of low-temperature plasma to treat the surface of activated carbon electrodes in the CF$_4$ atmosphere, and the supercapacitor can have a high capacitance retention rate at a high voltage of 3 V. After 12,000 charge and discharge cycles, the remaining capacitance is 91.81%.

2. Experimental Section
Using YP-50F activated carbon powder, the authors fabricated the AC electrodes on carbon-coated Al foil with a scraper. It was vacuum dried for 12 h. CF$_4$ gas was introduced into the plasma generator, and the electrode was processed under the conditions of 80 W and 60 Pa. The treatment time was 5 min, 9 min, and 13 min, respectively.

3. Results and Discussion
The SEM images of AC electrode and fluorine-modified activated carbon electrode have no obvious difference in the surface morphology of the electrode. Because the fluorine-containing functional groups are scattered on the activated carbon surface, which is difficult to observe with SEM. The electrode surface was analysed by energy spectrum, the AC and fluorine modified 9 min activated carbon electrode 9MF@AC analysis results are shown in Figure 1. The fluorine element on the AC electrode surface comes from the binder PVDF. The fluorine element on the 9MF@AC electrode surface is evenly and densely distributed, and its distribution area is the same as that of the carbon element. Except for the fluorine element in the binder PVDF, the plasma creates new fluorine-containing functional groups on the electrode surface.

As shown in Figure 2, the AC electrode C 1s spectrum has sub-peaks at 284.60 eV, 285.65 eV and 290.60 eV, corresponding to carbon-carbon bonds(C=C/C–C), carbon-oxygen single bonds(C–O) and CF$_2$ structures, respectively. The C-O bond comes from the oxygen-containing functional groups.
(hydroxyl, ether bond) in the activated carbon. And the CF$_2$ structure comes from the binder PVDF. The C 1s spectrum of 5MF@AC electrode has four sub-peaks containing carbon-carbon bond (C=C/C-C), carbon-oxygen bond (C-O), carbon-fluorine bond (C-F) and CF$_2$ structure. Four sub-peaks’ binding energy are 284.60 eV, 285.70 eV, 288.34 eV and 290.42 eV. There are 5 sub-peaks in the C 1s spectrum of 9MF@AC electrode, which are carbon-carbon bond (284.60 eV), carbon-oxygen bond (286.63 eV), carbon-fluorine bond (289.54 eV), CF$_2$–CF$_2$ structure (291.51 eV) and CF$_3$ structure (293.29 eV). Compared with the 5MF@AC electrode, the sub-peak area representing the C–F bond increases and the binding energy shifts to the left. The increase in the content of fluorine on the electrode surface makes it more structural types with carbon, and the CF$_2$–CF$_2$ structure and the CF$_3$ structure appear.

When continue to increase the processing time of CF$_4$ plasma, the fluorine element content has a limited increase compared with the 9MF@AC electrode. And the speed of generating fluorine-containing functional groups is very slow. Since the fluorine content on the electrode surface will no longer increase greatly with the extension of the processing time, the processing time is no longer increased.

Use electrostatic force microscope to test the surface potential distribution of AC electrode and 9MF@AC electrode, as shown in Figure 3. The AC electrode potential distribution range is -4.7 V ~ 9.8 V, and the 9MF@AC electrode potential distribution range is -43.2 mV ~ 24.7 mV. The fluorine-modified activated carbon electrode has a narrower surface potential distribution range and better charge transfer ability.

As shown in Figure 4(a) and Figure 4(b), AC, 5MF@AC, 9MF@AC and 13MF@AC are measured at 3 V, a current density of 1 A·g$^{-1}$. After fluorine modification, the specific capacitance of each capacitor increased to different degrees. Among them, the first charge and discharge specific capacitance of 9MF@AC with the electrode treatment for 9 minutes was the largest, which was 89.42 F·g$^{-1}$, increased by 10.71% compared with the AC electrode. After 12000 times of charge-discharge cycles, the specific
capacitance is 82.09 F·g⁻¹. Thinking the CF₄ plasma treatment time of 9 min as the turning point, the specific capacitance first increases and then decreases with the treatment time increases. With the increase in the number of charge-discharge cycles of AC, the capacitance retention rate drops the fastest. After 12,000 times charge-discharge cycles, the capacitance retention rate is 70.11%. The capacitance retention rate of the treated capacitors first increased and then decreased with the increase of the CF₄ plasma treatment time. The 9MF@AC has the highest capacitor retention rate, which was 91.81% after 12,000 times charge-discharge cycles.

The CV curve of 9MF@AC at sweep speeds of 5 mV·s⁻¹, 10 mV·s⁻¹, 20 mV·s⁻¹, 50 mV·s⁻¹ and 100 mV·s⁻¹, the shape of the curve is approximately rectangular. It shows that the energy storage mode of the capacitor after treatment is mainly the electric double layer, as shown in Figure 4(c). Compared with AC capacitors, the charge transfer impedance \( R_{ct} \) of 9MF@AC capacitors has a small increase, and the slope of the middle and high frequency parts representing the Warburg impedance is slightly increased, indicating that the charge diffusion process on the electrode and electrolyte interface becomes slower, which caused by the deterioration of the surface wettability of the electrode, as shown in Figure 4(d). Moreover, since the fluorine element passivation layer is very thin, it will hardly affect the charge transfer process between the electrolyte ions and the electrode.

The active functional groups on the electrode are more likely to react with the electrolyte under high voltage, causing the breakdown of the electrolyte and the destruction of the electrode material structure. Therefore, the specific capacitance of AC capacitors begins to decrease rapidly after 3500 charge and discharge cycles. With the treatment time increases, the active sites such as oxygen-containing functional groups decrease and the fluorine-containing functional groups gradually increase on the electrode surface treated with CF₄ plasma. A passivation layer is formed on the electrode surface to reduce the parasitic reaction between active sites and the electrolyte and protect the structure of the
electrode from being damaged, since the electronegativity of the fluorine element is extremely large[8]. Therefore, the fluorine-modified capacitor has a high capacity retention rate.

The capacity retention rate of supercapacitors with different fluorine modification time varies. The activated carbon electrode with a shorter treatment time has fewer fluorine-containing functional groups on the surface, and the fluorine passivation layer can only cover a part of the electrode surface and cannot protect the electrode well, as shown in Figure 5(b). When the treatment time reaches 9 min, there are enough fluorine-containing functional groups on the electrode surface, and the fluorine element passivation layer can almost completely cover the surface, and the electrode protection effect is the best, as shown in Figure 5(c). The fluorine content on the surface of the 9MF@AC electrode and 13MF@AC electrode is almost the same, indicating that the surface of the 9MF@AC electrode is basically covered with fluorine. If continue to increase the processing time, the plasma cannot effectively generate new fluorine-containing functional groups on the electrode surface. High-energy particles will also damage the original structure of the electrode, resulting in a decrease in specific capacitance and capacitance retention.

Figure 5 Different surface passivation: (a) bare AC electrode (b) AC electrode with partially passivated surface (c) AC electrode with all passivated surface

4. Conclusion

In conclusion, the research shows a simple way to modify the surface of activated carbon electrode by using low-temperature plasma technology to form a fluorine-modified layer on the surface of activated carbon electrode. The fluorine element is extremely electronegative, and chemical reactions are difficult to occur. The fluorine elements form a passivation layer on the surface of the electrode. The passivation layer prevents the electrode material from reacting with the electrolyte during the charging and discharging process of the supercapacitor, which leads to the breakdown of the electrolyte and the destruction of the electrode material structure. In addition, the strong electronegativity of the fluorine element can attract more charges on the electrode surface, so that the supercapacitor has a larger voltage window and a higher specific capacitance. After 12,000 charge and discharge cycles, the 9MF@AC capacity retention rate is 91.81%, which is 30.95% larger than that of AC. High-energy density supercapacitors fill the gap between traditional capacitors and secondary batteries, and provide opportunities for wider applications in fields such as electric vehicles and mobile electronic devices.

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