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Effects of Various Binders on Supercapacitor Performances

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Supercapacitor performances are influenced by binder types and contents in the electrodes. The electrochemical performances of activated carbon (AC) with Nafion, poly(tetrafluoroethylene) (PTFE) and poly(vinylidenedifluoride) (PVDF) and different contents of each binder were investigated by cyclic voltammetry (CV), galvanostatic charge discharge (GCD) and electrochemical impedance spectroscopy (EIS). The optimal content of binder in the electrode is 10 wt% for Nafion and PTFE, but only 5 wt% for PVDF. The specific capacitances of the AC electrodes with optimal content of Nafion, PTFE and PVDF are respectively 131.3, 156.6 and 160.6 F g^{-1}; their corresponding specific capacitances retain 87%, 91% and 79.6% after 2000 CV cycles with a scan rate of 200 mV s^{-1}. Therefore, PTFE is the best suitable binder for supercapacitors and its optimal content is 10 wt%.

Keywords: supercapacitor; activated carbon; Nafion; PTFE; PVDF; binder

1. INTRODUCTION

With the rapid economic development and the leap of population, people have higher requests to energy. Fossil fuel depletion, air pollution and global warming issues urgently require people to look for clean and efficient energy. Therefore, the new energy has become a hot research. Electrical double layer capacitors (EDLCs) use carbon material as a main electrode material, which can provide a high power in a short time and have an excellent cycle life as a new energy storage device.[1-3] Therefore, the supercapacitor is widely used in backup power, portable electronics and a variety of vehicles starting power micro devices which need high power density and long cycle life. In order to achieve the application of these devices, we need to give priority to the cost, environment-friendly and the feasibility of industrial production. Electrodes are usually fabricated by brushing or printing electrode paste or slurry on a substrate such as nickel foam (NF), electrode paste or slurry is prepared by ultrasonically stirring a mixture of active materials, conductive agents and binders. Binders play roles of binding active material and conductive agent together and also cohering with electrode material substrates, to avoid active materials falling off during the electrode working. The role of the binder should provide enough strengthen during the electrode formation and appropriate pore sizes. However, cohesive agents or binders inevitably cover some surface areas or pores of active materials. Thus, the properties of binders and their contents in the electrodes will directly influence electrochemical performances of supercapacitors. How to choose a suitable binder is important.

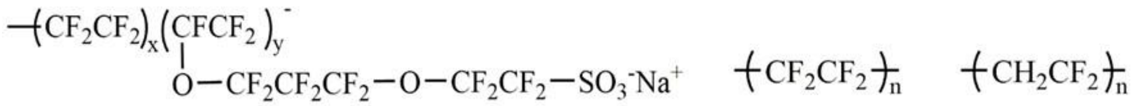


Figure 1. Chemical structures of Nafion (Left), PTFE (Middle) and PVDF (Right).

Various binders have different properties. Poly(tetrafluoroethylene) (PTFE) only has a CF_2-CF_2 unit as shown in Figure 1 (Middle), which demonstrates excellent chemical stability. However, it has properties of hydrophobicity and insulation, which are unfavorable for electrodes to get wetted by electrolytes and lead to an increase of internal resistances.[4-6] Perfluorosulfonic acid-PTFE copolymer (Nafion) has been widely applied in proton exchange membrane fuel cells, and it was firstly used as a binder in supercapacitors.[7] The chemical structure of Nafion is shown in Figure 1(Left). It is divided into two parts: a hydrophobic PTFE skeleton and a hydrophilic ion exchange group (sulfonic acid group) branches, which makes Nafion with good chemical stability and excellent hydrophilicity.[8-9] However, Nafion is much more expensive than PTFE. Poly(vinylidenedifluoride) (PVDF) consists of a CH_2-CF_2 unit, as shown in Figure 1 (Right).The polymer has a typical stability of fluoropolymers but interactive groups will produce a unique polarity, thus results in its good chemical and oxidative resistances, poor hydrophilicity and significant swelling property in the electrolyte.[10-11] Dong J *et al* in order to effectively fabricate and use MnO_2 in supercapacitors, a graphene/PVDF composite binder has been designed and fabricated, which shows high specific capacitance and excellent cycling stability.[12]

Laforgue *et al* investigated carboxymethylcellulose (CMC), PVDF and PTFE. PVDF and PTFE conferred good mechanical properties but isolate the active materials from the current collector. CMC maintained the electrochemical properties of the polymers but the mechanical property was quite poor and could not be used above 40 °C with any water and oxygen.[13] So CMC/PTFE was used and exhibited a lower resistivity and an improved mechanical properties.[14]

A polyvinylidene chloride (PVDC) was also used as a binder. The electrode consists of a composition of 70 wt% SWNTs and 30 wt% PVDC binder. The performance of PVDC binder is better than that of polyvinyl alcohol with an optimized composition.[15]

Sulfonated polyetheretherketone (SPEEK) was synthesized by sulphonation and used as solid-state electrolyte, binder and surfactant for supercapacitors. Reduced graphene dispersed by SPEEK (RGDS) was used as a conducting additive. The activated carbon//RGDS unit supercapacitor was tested from 1 to 8 A g^{-1} and its capacitance retention was 93%, no capacitance fading was observed after cycled over 5000 times at 5 A g^{-1} .[16]

Mixtures of polyvinylpyrrolidone/polyvinyl butyral (PVP/PVB) are good binders for the carbon electrodes in aqueous electrolyte supercapacitors. The AC electrodes with a mass ratio of 1.5:6 for AC/PVP/PVB are mechanically stable and water resistant. Compared to PVDF, the specific surface area of the assembled electrodes was 10% higher.[17]

This work aims at comparing the performance of AC electrode material based on Nafion, PTFE or PVDF binders. It has been observed that the PTFE based electrode performance better than the other two, also found that the optimal ratio of the three binder in the electrode material.

2. EXPERIMENTAL PART

2.1. Electrode fabrication

Nickel foam (NF, ∼320 g m^{-2} in area density, ∼1.6 mm in thickness, Changsha Liyuan New Material Company) was used as the electrode substrate after subsequently washed with acetone, alcohol, and deionized water for 5 minutes in an ultrasonic bath. Activated carbon (AC) and carbon nanotubes (CNTs) were used as active material and conductive agent, respectively. 5 wt% Nafion solution (DuPont), 60 wt% PTFE (Sigma-Aldrich) and PVDF (Arkema) emulsion were respectively applied as a binder. The AC electrodes fabricated with different binders are denoted as AC-PTFE, AC-Nafion, and AC-PVDF. To fabricate an electrode, a typical procedure is as follows: a certain mass ratio of AC, CNTs and binder was ultrasonically mixed in ethanol, and then the homogeneous slurry was dropped onto the NF, repeated several times until a certain areal mass density was obtained. Then the electrode was placed in a vacuum at 60 °C for 2 hours to ensure binder completely cured. Later, the electrode was hot-pressed under 10 ton cm^{-2} at 130 °C for 90 s before electrochemical tests. When optimize the binder content in the electrode, a fixed content of conductive agent is adopted, and only vary the proportion of AC and the binder.

2.2. Electrochemical measurements

All electrochemical tests were conducted on a PG302N Autolab Potentiostat in 6 M KOH aqueous solution with a three-electrode configuration. The above electrode was used as the working electrode, a Pt coil and a saturated calomel electrode (SCE) were applied as a reference and a counter electrode, respectively. Cyclic voltammetry (CV) and galvanostatic charge–discharge (GCD) were performed to measure capacitive performances. The specific capacitance was calculated from the CV curves and discharging curves of GCD using the following equations:

$$C_s = \frac{\int IdV}{m\upsilon\Delta V} \qquad (1)$$

Where C_s represents the specific capacitance (F g^{-1}), I is the current (A), V is the potential (V), ν is the potential scan rate (V s^{-1}), ΔV is the potential window (V), and m is the mass of the electroactive materials in the electrodes (g).

$$C_s = \frac{I\Delta t}{m\Delta V} \qquad (2)$$

Where C_s represents the specific capacitance (F g^{-1}), I is the discharge current (A), t is the discharge time (s), ΔV is the potential window (V), and m is the mass of the electroactive materials in the electrodes (g).

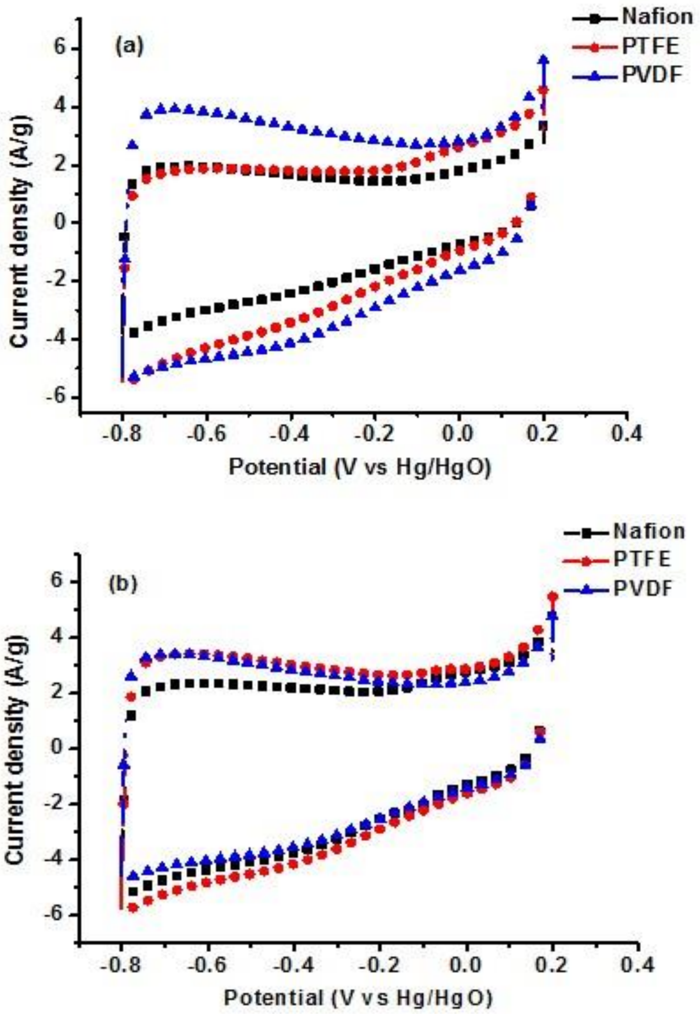
A life time test of the electrode was experienced for 2000 cycles with a CV scan rate of 200 mV s^{-1}. Electrochemical impedance spectroscopy (EIS) was recorded in the frequency range of 1 mHz to100 kHz at the open circuit potential.

3. RESULTS AND DISCUSSION

Cyclic voltammetry (CV) is considered to be a suitable technique to characterize the capacitive behavior of any material. Figure 2 presents the CV curves of AC electrodes fabricated with the three binders in 6 mol L^{-1} KOH solution. In Figure 2(a), a common binder proportion of 5 wt% is used. We can see that a rectangular shape is displayed, which is typical for an electrical double-layer material. This is because AC stores charges by a mechanism of adsorption-desorption,[18-20] the electrochemical surface area and conductivity will decide the capacitive performances of the electrode. Under identical conditions, larger CV area means bigger specific capacitance, thus for the AC electrodes with different binders, the sequence of specific capacitance is AC-PVDF> AC-PTFE > AC-Nafion. According equation (2), the corresponding specific capacitances are 160.6 F g^{-1}, 121.4 F g^{-1} and 93.3 F g^{-1} for the three electrodes, respectively. The AC-PVDF electrode demonstrates biggest area of CV and maximum specific capacitance, which indicates that PVDF is a suitable binder under this condition with respect to specific capacitance. With increments of binder contents to 10 wt% and 20 wt% in the electrodes, the changes in the specific capacitances are shown in Figure 2(b) and Figure 2(c). The CV curves demonstrate similar shapes as those of 5 wt% binders. As the binder content is 10 wt%, the specific capacitances are 131.3 F g^{-1}, 156.6 F g^{-1}, and 142.9 F g^{-1} for the electrode with binder of Nafion, PTFE, and PVDF, respectively. AC-PTFE electrode has maximum specific capacitance. When assembling the supercapacitors, most scientific researchers prefer to use PTFE as a binder, but they do not optimize its proportion, so the capacitance of electrode material often cannot reach the expected results.[21-22] In this research, optimal binder content will be investigated. As the binder content increases to 20 wt%, the specific capacitances of the electrodes with different binders decrease. All data of the electrodes with different contents for three binders are listed in Table 1. For each binder, the specific capacitances of both AC-Nafion and AC-PTFE electrodes firstly increase with content of binder, and then decrease with further increment, 10 wt% of addition is the optimal content. However, for the AC-PVDF electrode, the specific capacitance decreases with increase of binder content. So a less addition of PVDF is necessary to be investigated. 2 wt% PVDF is considered and the specific capacitance decreases to 105.5 F g^{-1}. Thus for PVDF, the optimal content is 5 wt%. The AC content in the electrode can be increased up to 90 or even 93%, but the mechanical properties of the electrodes decrease.[23]

Table 1. Specific capacitances of AC electrodes with various contents of three binders at scan rate of 20 mV s^{-1}.

Content / Specific capacitance	2 wt%	5 wt%	10 wt%	20 wt%
Nafion	90.4	93.3	131.3	89.0
PTFE	103.5	121.4	156.6	107.7
PVDF	105.5	160.6	142.9	125.0



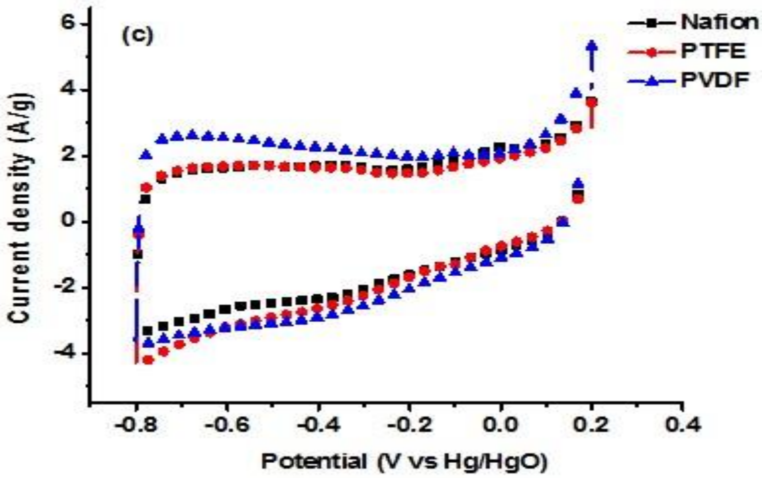


Figure 2. CV curves of AC electrodes with 5 wt% (a) 10 wt% (b) 20 wt% (c) of three binders at scan rate of 20 mV s^{-1} in 6 mol L^{-1} KOH solution.

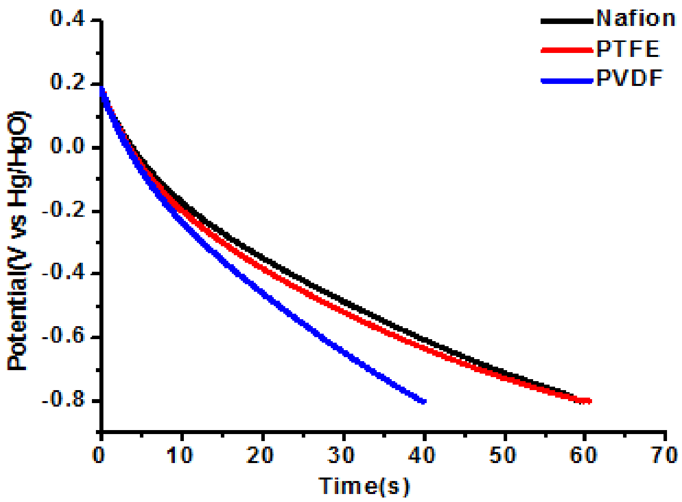


Figure 3. Discharge curves of AC electrodes with different binders at 2 A g^{-1}. (10 wt% for Nafion and PTFE, 5 wt% for PVDF)

However, an excellent binder is required not only providing high specific capacitance, but also good adhesive property, excellent thermal, chemical and electrochemical stability for extraordinarily long cycles. Then the AC electrode with optimal ratio for each binder (10 wt% for Nafion and PTFE, 5 wt% for PVDF) is chosen to carry out galvanostatic charge–discharge test and life test. The GCD curves are displayed in Figure 3. The specific capacitances of the three electrodes with different binders are 116 F g^{-1} for Nafion, 124 F g^{-1} for PTFE and 80 F g^{-1} for PVDF at discharge current of 2 A g^{-1}. AC-PVDF electrode exhibits the smallest specific capacitance might be due to less stability of PVDF than Nafion and PTFE after CV tests. Commonly Nafion is used in fuel cells, PVDF is used in lithium ion batteries, and PTFE is used in supercapacitors. Three of them have good adhesive properties.

Judge from their structures, we can predict that chemical and electrochemical stabilities of PTFE are more excellent that those of Nafion and PVDF, because Nafion has branch chain and PVDF is not completely fluoridated. Figure 4 illustrates the cycling stability of AC electrodes with three binders. At a rapid scan rate of 200 mV s^{-1}, the specific capacitances of AC electrodes with different binders are 71.9 F g^{-1}, 98.5 F g^{-1} and 98.2 F g^{-1} for AC-Nafion, AC-PTFE and AC-PVDF, respectively. After 2000 cycles, AC-PTFE electrode still remains a high value of 89.4 F g^{-1}, the capacitance retention is 90.8%, showing superior cycle stability. AC-PVDF electrode has better initial capacitive performance than AC-Nafion, but after 2000 cycles, the capacitance decreases to 78.2 F g^{-1}, the capacitance retention is 79.7% as compared to 87.0% of AC-Nafion. Therefore, we can regard that for an AC electrode, PTFE is the best suitable binder. This is in agreement with that the use of PTFE binder could improve the performances of the electrodes, as compared to the use of PVDF and Nafion.[24-25] Later, only AC-PTFE electrode will be focused on further investigation.

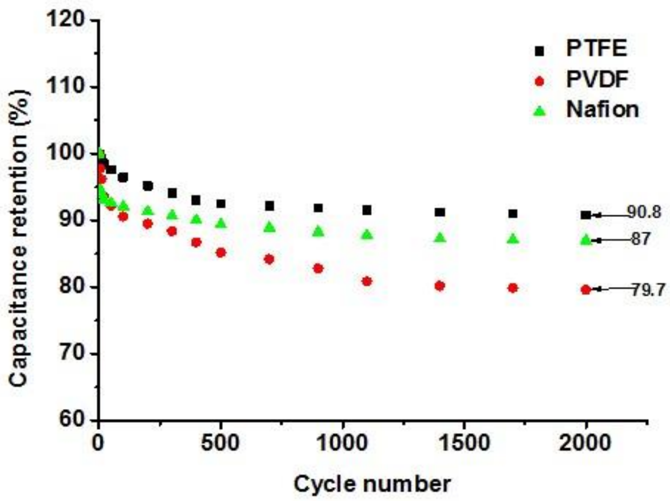


Figure 4. Cycle stabilities of the electrode with three binders at scan rate of 200 mV s^{-1}.

The AC-PTFE electrode before and after life test was then further examined by electrochemical impedance spectroscopy with frequency ranging from 0.01 Hz to 100 Hz at open circuit potential, as shown in Figure 5. It is accepted that a smaller semicircle means a lower charge-transfer resistance and a higher slope means a bigger diffusion rate. [14] From Figure 5 and the inset, we can see that the AC-PTFE electrode demonstrates a very small semicircle and very high slope. This result indicates that the AC-PTFE electrode has low charge transfer and diffusion resistances, because AC is a carbon material and it stores charges via double-layer mechanism. The equivalent series resistance (ESR) obtained from the x-intercept of the plot is 0.38 Ω, and after 2000 CV cycles at scan rate of 200 mV s^{-1}, the Rs increases a little to 0.40 Ω. However, the diffusion resistance does not be observed a significantly change at all. These tiny ESR value and minor changes in Rs and diffusion resistance further indicate that the PTFE is a suitable binder for the supercapacitors.

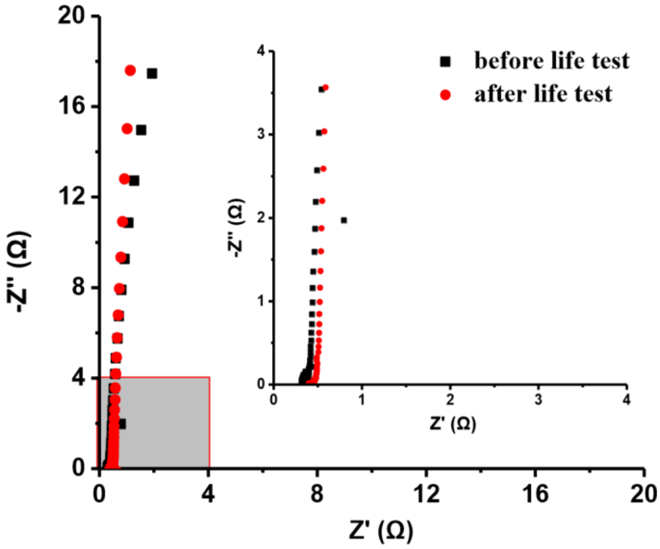


Figure 5. Nyquist plots of AC-PTFE (10 wt%) electrode.

Table 2. Rate capability of the AC-PTFE (10 wt%) electrode.

Scan rate (mV s^{-1})	20	50	100	200
Specific capacitance (F g^{-1})	156.6	156.3	148.4	133.5
Rate capability	100%	99.2%	93.4%	83.8%

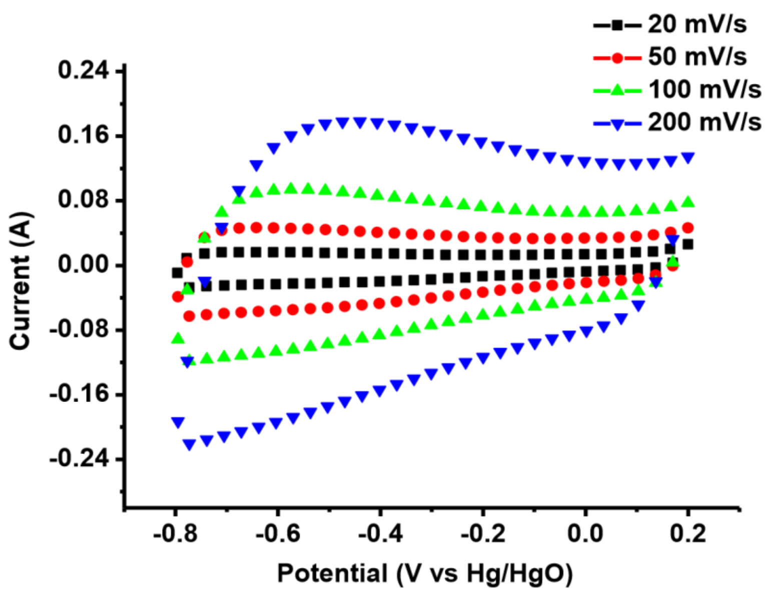


Figure 6. CV curves of the AC-PTFE (10 wt%) electrode at different scan rates.

Eventually, the rate capability of the AC-PTFE (10 wt%) electrode will be studied by CV, the CV curves are shown in Figure 6. When the scan rate increases from 20 mV s^{-1} to 200 mV s^{-1}, CV curves display a rectangular shape which is typical for an electrical double-layer capacitor, and the shape is almost close to an ideal rectangular and does not change much with increase of scan rate, which means the Rs is quite small.[26] This is in consistent with the EIS result, that Rs is 0.38 Ω. The specific capacitance decreases from 156.6 F g^{-1} to 156.3 F g^{-1}, 148.4 F g^{-1} and 133.5 F g^{-1} as the scan rate increases from 20 mV s^{-1} to 50 mV s^{-1}, 100 mV s^{-1} and 200 mV s^{-1}, respectively. Accordingly, the rate capability decreases to 99.2%, 93.4%, and 83.8% with increase of the scan rate. The detailed results are listed in Table 2. This reveals the AC-PTFE electrode possesses an excellent rate performance.

4. CONCLUSIONS

Three binders such as Nafion, PTFE and PVDF were investigated in this paper. Less content of PVDF is required in the electrode but its stability is not satisfied. Nafion and PTFE have the similar tendency with the content change. PTFE is the best suitable binder judged from the comprehensive electrochemical performances such as specific capacitance, stability and rate capability. The specific capacitance of AC-PTFE electrode reaches 156.6 F g^{-1} at scan rate of 20 mV s^{-1} with PTFE content of 10wt%, and the rate capability can keep 99.2% when scan rate increases to 50 mV s^{-1}, 93.4% at 100 mV s^{-1}, and 83.8% at 200 mV s^{-1}. Therefore, PTFE is the best suitable binder for supercapacitors and the optimal content is 10 wt% to achieve the best electrochemical performances.

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