A bendable solid-state supercapacitor based on alkaline polyvinyl alcohol

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Abstract. Flexible electrochemical double layer capacitors (EDLCs) based on polyvinyl alcohol (PVA) electrolytes are fabricated. During the process, electrode materials are mixed into a film and pressed on the current collector instead of the traditional coating method. In order to explore the electrochemical performance of this kind of supercapacitors, a series of testing method including cyclic voltammetry, Galvano static charge discharge testing and electrochemical impedance spectroscopy. It is revealed that the electrochemical capacitor based on PVA exhibits excellent electrochemical performance and long cycle life. The specific capacitance for the EDLC based on PVA reaches 187F/g at the current density of 1A/g, and the specific capacitance decreased with the increasing of the scanning rate. The results indicate that the supercapacitor cell capacitance keeps more than 70% after 10000 charging and discharging cycles.

1. Introduction

In recent years, supercapacitors serving as a novel energy storage element ignite the worldwide research and analysis. [1, 2] In the future, wearable electronic devices propose requirement of bendable and flexible energy storage system. From this perspective, supercapacitors are expected to be flexible and foldable with high power density and long cycle life. [3] Nowadays, basic principles including pseudo capacitors and Electric Double-Layer Capacitors (EDLCs) are thoroughly researched, meanwhile, excellent-performing electrode [4] and electrolyte [5] materials are synthesized. Compared with supercapacitors based on traditional aqueous electrolytes, solid electrolyte supercapacitors have the advantages of easy encapsulation and molding, flexible folding, and no risk of electrolyte leakage and encapsulation bursting due to internal gas release [5]. Furthermore, it’s also not as flammable as organic electrolytes. Therefore, solid-state flexible supercapacitors has broad application prospect in many special electronic products, such as microelectronics, biomedical engineering and printable electronic products. Yang et al. [6] applied PVA/KOH gel to supercapacitors for the first time, coating activated carbon slurry as electrode materials and PVA/KOH gel as the electrolyte to assemble the supercapacitor and obtain the specific capacitance of 123.1F/g. Singh et al. [7] used graphene nanosheets prepared by vapor deposition method as electrodes, which were ground and coated on the collector surface. In addition, six gels, including PVA/KNO₃, PVA/LiCl, PVA/KNO₃, PVA/KCl, PVA/KOH and PVA/NaOH, were prepared as electrolytes and assembled as supercapacitors. The results of cyclic voltammetry showed that the specific capacitance of PVA/KOH and PVA/NaOH hydrogels was higher than 50 uF/cm². Due to PVA’s stable structure, low price and excellent electrochemical performance,
and good biological compatibility, it has fascinated wide attention. [8] All-solid-state flexible supercapacitors are involved in materials science, chemistry, electrical engineering, nanotechnology and other disciplines. In a large sense, at present, there are still some deficiencies in the existing all-solid-state flexible supercapacitors, so it is a meaningful work to further explore the current flexible supercapacitors.

2. Experimental

2.1. Preparation

2.1.1. Preparation of PVA gel electrolytes. A gel polymer electrolyte is prepared in solution-casting method by modifying the procedure described in the previous literature. [9] Polyvinyl alcohol (PVA, molar mass 75,000-80,000, Sigma-Aldrich) and KOH (Aladdin) are used as received without additional processing. 1g of PVA is taken in a beider, and 40mL of deionized water is added into the beider. The mixture is heated and stirred for 2h at 80°C in a water bath pot. Take 1g of KOH (Aladdin) and dissolve it in proper amount of deionized water. Add KOH into the solution and continue to stir for 4h. To avoid excessive evaporation of solution from the beider, it is advisable to seal the beaker with a cover with holes or plastic wrap with a few holes. After that, the solution is poured into a clean petri dish and dried overnight at room temperature to produce a gel electrolyte.

2.1.2. Preparation of electrode. Distinguished from traditional slurry coating method, here we introduce another way to synthesis electrode. [10] Take a clean mortar and add anhydrous ethanol (Aladdin) to moisten the bottom slightly. Take 80mg of activated carbon (Aladdin) in a mortar, then 10mg of graphite (Aladdin) in a mortar. Add a little anhydrous ethanol to completely wetting mixture, mix evenly, fully grind for 30 minutes. In the process, when the anhydrous ethanol is dried, anhydrous ethanol is added again until the mixture is completely immersed and the grinding continues. Polytetrafluoroethylene emulsion (PTFE, Aladdin) with a mass fraction of 60% is taken. 60uL PTFE is removed with a pipegun and added to the mixture. Add anhydrous ethanol again, change the nozzle of the pipette, and remove 50 uL PTFE with the pipette again, continue grinding until the mixture becomes a film. The obtained film is wetted with anhydrous ethanol and rolled repeatedly on a roller press to obtain the active material film. Take two pieces of weighing paper, clamp the active material film, and use a punch to make a small round sheet. After that, the sheet is pressed on the current collector with the pressure of 10MPa.

2.1.3. Supercapacitor assembly. Take two electrodes and appropriately cut PVA/KOH gel electrolytes and superposition them into a sandwich shape and wrap the outside with tape. The nickel foils on both sides are connected to the electrochemical workstation as electrodes for electrochemical test. Before electrochemical testing, bending test is conducted. It can be seen that the supercapacitor cell can be bended freely.

2.2. Characterization

Electrochemical testing including Cyclic voltammetry(CV), Galvano static charge-discharge test(GCD) and the ac impedance spectroscopy(EIS) are used to examine the electrochemical performance of the solid-state EDLC on the electrochemical workstation(CHI760E,China). The electrochemical window of cyclic voltammetry is selected from -1 to 0V, and the scanning rates are 5mV/s, 10mV/s, 20mV/s, 50mV/s and 100mV/s, respectively. The electrochemical window of Galvano static charge-discharge test is set as -1 to 0V, and the current density is set as 1A/g, 2A/g, 5A/g and 10A/g, respectively. In the electrochemical impedance spectroscopy test, the frequency ranges from 0.01Hz to 10^5Hz and the amplitude is 0.005V.
3. Results and discussion

Figure 2 shows the test results of PVA/KOH supercapacitor cell at the electrochemical window of 1V and scanning rate between 5-100mV/s at 25°C. The results clearly shows the high capacitance values of all solid state double layer capacitors at high scanning rate. On the one hand, the cyclic voltammetry test results are close to rectangle, and there is no obvious redox peak between -1V and 0V. This indicates that the desorption and adsorption of ions on the electrode active material are highly reversible, and indicated that this flexible capacitor will have ideal cycling performance. The charging and discharging capacitance can be estimated using (1) and (2). Specific capacitance calculated by cyclic voltammetry at different scanning rates is shown in Figure 2(b). This indicates that the specific capacitance of the cell decreased with the increase of scanning rate, but generally at a relatively high level.

\[
C_{cell} (F) = \frac{dQ}{dE} = \frac{I}{dE} = \frac{I}{dE/dt} \Rightarrow \frac{I}{v}
\]

(1)

\[
C_{spec} (\frac{F}{g}) = \frac{2C_{cell}}{m}
\]

(2)

Where \(C_{cell}, I, Q, v\) and \(E\) are the capacitance (F), the charging/discharging current (A), the total charge (Che scan rate (V s\(^{-1}\)) and the cell potential difference (V), respectively. \(C_{spec}\) and \(m\) are tance of the EDLC (F g\(^{-1}\))
Figure 2 Electrochemical performance of the flexible alkaline PVA supercapacitor (a) CV curves collected at different scan rates (b) capacitance calculated from CV curves

Figure 3 shows the test results of Galvano static charge-discharge test of flexible capacitors at different current densities when the potential window is between -1V and 0V. The electrochemical performance can be calculated by (3) and (4).

\[
C_{eq}(F) = \frac{Q}{\Delta E} = \frac{(I \times t)}{\Delta E} \tag{3}
\]

\[
ESR = iR_{drop} / (2 \times I) \tag{4}
\]

Due to its highly symmetrical charge-discharge performance, the flexible capacitor shows very good double-layer capacitance characteristics, which indicates that the capacitor has good cycle performance. The capacitor i\(R_{drop}\) can be obtained from the voltage knee point, and the equivalent series resistance (ESR) of the capacitor can be obtained by further approximation. It can be qualitatively analyzed from the graph that the supercapacitor’s ESR is small, and its quantitative calculation will be calculated by the next part of electrochemical impedance spectrum. According to the image, under the current density of 1A/g, the charging and discharging period of the capacitor exceeds 370s, and the discharging time is as long as 187s, which shows its large capacitance and power density.

Figure 3. Galvano static charge-discharge test curve of the flexible alkaline PVA supercapacitor
As shown in Figure 4, the electrochemical impedance spectroscopy (EIS) of the flexible supercapacitor is tested. The results of electrochemical impedance spectroscopy are described by Nyquist curve, from which the resistance can be quantitatively calculated and the capacitance observed qualitatively. For supercapacitors, the high-frequency region will be semi-circular and the low-frequency region linear. At high frequencies, the spectral lines show a finite diffusion process and at low frequencies represent pure capacitance characteristics. The Nyquist curve shows a vertical real axis characteristic in the low frequency region of the flexible supercapacitor tested, which means its pure capacitive performance. The internal resistance is 6.89 Ω via computation, the resistance is not significant.

Figure 4. EIS curves of the flexible alkaline PVA supercapacitor.

Figure 5 shows the specific capacitance of the flexible supercapacitor after 10,000 cycles at a high current of 10A/g. It can be observed that in the first 1000 cycles, the attenuation of capacitance is more serious, while in the subsequent charging and discharging process, the attenuation ratio is very low. After the final charge and discharge of 10,000 times, there is still a specific capacitance of more than 130F/g. The capacitance retention rate reaches 71%, and has excellent cycle performance.

Figure 5. Cyclic testing result of the flexible alkaline PVA supercapacitor
4. Conclusion
In summary, we have successfully fabricated a flexible free-standing solid state supercapacitor based on alkaline PVA. While synthesizing electrode, we have innovated traditional electrode synthesizing process. The electrochemical capacitance has been evaluated by means of cyclic voltammetry, Galvano static charge-discharge test and electrochemical impedance spectroscopy. The experimental data indicates that the capacitance of the all-solid capacitor reached 187F/g at 1A/g. Meanwhile, after 10000 charging and discharging cycles, the capacitance remains over 70% of the initial condition. It can be concluded that, comparing with tradition coating method, pressing thin carbon film directly on the current collector seems achieving better effect. Accordingly, the all solid state supercapacitor based on alkaline PVA electrolyte might be a promising option for use in EDLCs.

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