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Improved energy density of quasi-solid-state supercapacitors using sandwich-type redox-active gel polymer electrolytes

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ABSTRACT

Quasi-solid-state supercapacitors were assembled using a pair of activated carbon electrodes and two polyvinyl alcohol (PVA)-H_2SO_4 gel polymer electrolytes (GPEs) containing respectively redox additives of hydroquinone (HQ) and methylene blue (MB), which were separated by a Nafion 117 membrane in a sandwich-type configuration. PVA-H_2SO_4-HQ and PVA-H_2SO_4-MB GPEs worked on the sides of the positive and negative electrodes of the supercapacitor, respectively. The electrochemical performances of the supercapacitor with optimized PVA-H_2SO_4-HQ and PVA-H_2SO_4-MB GPEs were evaluated by cyclic voltammetry, galvanostatic charge-discharge and electrochemical impedance spectroscopy techniques. After the introduction of HQ and MB, the supercapacitor with PVA-H_2SO_4-HQ|PVA-H_2SO_4-MB GPEs can exhibit high specific capacitance of 563.7 F g^{-1} and energy density of 18.7 Wh Kg^{-1}, increasing by about fourfold in comparison with a supercapacitor with a PVA-H_2SO_4 GPE. The improved energy storage is ascribed to the reversible Faradaic reactions related to HQ and MB in the corresponding gel polymer electrolytes. Additionally, the supercapacitor shows excellent cyclic durability with 90.0% capacitance retention after 3000 cycles.

1. Introduction

Electric double-layer capacitors (EDLCs), exhibiting higher power density, shorter time needed for full charging, high coulombic efficiency and longer cycle life than traditional batteries, are widely used in various electronic devices and instruments [1–5]. The electric double-layer capacitance comes from pure electrostatic attraction between ions in an electrolyte and the charged surface of an electrode, such as carbon materials, which are not electrochemically active [6–9]. As a result, high power density can be obtained, but energy density is relatively low, which limits the practical application of EDLCs. An approach to increase the energy density of EDLCs is to assemble pseudocapacitors, in which the electrode materials can be made by adding electrochemically active materials to carbon-based electrodes or completely replacing the carbon materials with electrochemically active materials, for example, transition metal oxides/hydroxides, metal chalcogenides and conducting polymers [1,10–18]. The production of pseudocapacitance is ascribed to fast and reversible redox reaction, electrochemical doping/dedoping and adsorption/desorption processes on the electrochemically active electrode materials. Pseudocapacitors typically present higher capacitance and energy density than EDLCs, but suffer from low power density and lack of stability because the electrode materials take on low electrical conductivity and emerge framework swelling during cycle, similar to batteries [5,18,19]. Most researches therefore are focused on the design and synthesis of high-performance materials to improve the energy density of supercapacitors without sacrificing their power density.

Electrolyte acts as an ionic medium in the charge/discharge process in supercapacitors. So, in addition to electrode, electrolyte also plays an important role in supercapacitors. At present, aqueous solutions (acidic, alkali and neutral solutions) are mostly used as electrolyte due to their high ionic conductivity and low price, but low operating potential (the water decomposition potential of 1.23 V) restricts the acquisition of high energy density [3,20]. Moreover, liquid electrolytes are associated with the problems of leakage, poor safety and inflexible geometry. The concept of gel polymer electrolytes (GPEs) was put forward to overcome the drawbacks of liquid electrolytes because of their appropriate ionic conductivity and high stability [21,22].

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Glossary

EDLC	electric double-layer capacitor
PVA	polyvinyl alcohol
HQ	hydroquinone
MB	methylene blue
GPE	gel polymer electrolyte
AC	activated carbon
CV	cyclic voltammetry
GCD	galvanostatic charge-discharge
EIS	electrochemical impedance spectroscopy
C_T	specific capacitance of supercapacitor
C_s	specific capacitance of single electrode
Δt	discharge time
m_{ac}	total mass of active materials in supercapacitor
ΔV	voltage change during the discharge process excluding potential drop
E	energy density
P	power density
σ	ionic conductivity
l	distance between the two stainless steel sheets
R_b	bulk resistance
A	contact area of the GPE film with the steel sheets
T_d	discharge time
T_c	charge time
R_s	internal resistance
R_p	polarization resistance
C_{dl}	electric double-layer capacitance
C_L	limit capacitance
W	Warburg element
A_w	Warburg coefficient

An innovative approach to supercapacitors has recently been developed by the introduction of a single redox additive such as hydroquione [23–25], methylene blue [26],*p*-phenylenediamin [27,28], *m*-phenylenediamine [29], indigo carmine [30], KI [31–33], Na_2MO_4 [34] or $VOSO_4$ [35] into the liquid electrolyte or GPE. The specific capacitance and energy density of the supercapacitor are greatly increased as a result of the additional pseudocapacitance deriving from the electron transfer redox reaction of the redox additive. And it was found that the redox reactions related to cationic and anionic redox additives occurred at negative and positive electrodes, respectively [26,31,32,36]. For example, the iodine-based system offers very good pseudocapacitance on the positive electrode rather than on the negative electrode [31,32]. If both cationic and anionic redox additives simultaneously are incorporated in the GPE, the energy storage of quasi-solid-state supercapacitors will be remarkably increased. Therefore it is significant to develop such a GPE containing cationic and anionic redox additives used in quasi-solid-state supercapacitors.

In this work, two redox additives of hydroquinone (HQ) and methylene blue (MB) were added into polyvinyl alcohol (PVA)-H_2SO_4 gels to form redox-active PVA-H_2SO_4-HQ and PVA-H_2SO_4-MB gels. These two gels were separated by a Nafion 117 membrane in a sandwich-type configuration and acted as electrolytes on the sides of the positive and negative electrodes of a quasi-solid-state supercapacitor based on activated carbon electrodes, respectively. Due to the reversible Faradaic reactions related to HQ and MB in the corresponding GPEs, the energy density is greatly improved without the loss of power density. And the quasi-solid-state supercapacitor shows excellent cyclic durability.

2. Experimental section

2.1. Materials

Activated carbon (AC, Fuzhou Yihuan Co. Ltd, China, specific surface area of 2167 $m^2 g^{-1}$), acetylene black (Alfa Aesar), polytetrafluoroethylene (PTFE) aqueous solution (60 wt%, Guangzhou Xingshengjie Co. Ltd, China), polyvinyl alcohol (PVA, Shanghai Aladdin Reagent, China), methylene blue (MB, Sinopharm Chemical Reagent Co. Ltd, China), hydroquinone (HQ, Shanghai Aladdin Reagent, China) were purchased in analytical grade and without further treatments. Nafion 117 membrane was from Shanghai Hesen Co. Ltd, China.

2.2. Preparation of gel polymer electrolytes

PVA-H_2SO_4-HQ GPE was prepared as follows [37]: Firstly, 1.5 g of PVA was dissolved in 20 mL sulfuric acid solution (1 M) and stirred at 60 °C for 5 h. Secondly, a certain amount of HQ was added into the above transparent viscous solution. Thirdly, after a homogeneous colloidal substance appeared, the mixture was put into a refrigerator at −27 °C for 12 h. Finally, after thawing, PVA-H_2SO_4-HQ GPE was formed.

The synthesis of PVA-H_2SO_4-MB GPE was similar as that above mentioned. Typically, 1.5 g of PVA was dissolved in 20 mL sulfuric acid solution (1 M) with stirring at 60 °C for 5 h. Then appropriate quantity of MB was added into the above solution and stirred until the formation of dark blue gel-like solution. Subsequently, the resultant mixture was put into a refrigerator at −27 °C for 12 h. Finally, after thawing, PVA-H_2SO_4-MB GPE was obtained. For comparison, PVA-H_2SO_4 GPE without HQ and MB was also prepared using the same method.

2.3. Preparation of activated carbon electrode and assemble of supercapacitors

AC, acetylene black and PTFE with the mass ratio of 90:5:5 were dispersed in appropriate amount of ethanol at room temperature and stirred continuously to form homogeneous slurry. After that, the slurry was pressed to give rise to a thin sheet using the Decal method. The thin sheet with a fixed surface area of 0.5 cm^2 and a mass of 2.5 mg was painted onto a stainless-steel net under a pressure of 10 MPa. After drying at 100 °C for 24 h under vacuum, an AC electrode was attained.

As shown in Fig. 1, a pair of AC electrodes, optimized PVA-H_2SO_4-HQ GPE, PVA-H_2SO_4-MB GPE and Nafion 117 membrane were assembled to form a two-electrode supercapacitor in a sandwich configuration, where the Nafion 117 membrane separated these two GPEs. For comparison, supercapacitors with PVA-

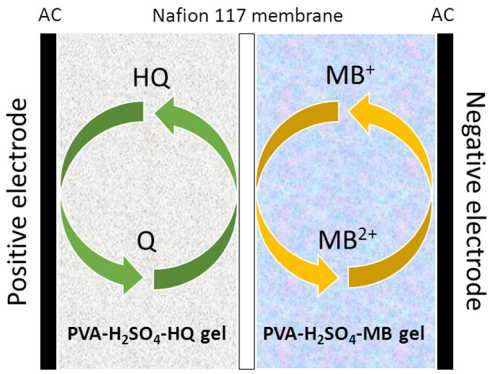

Fig. 1. The schematic representation of supercapacitor with PVA-H_2SO_4-HQ|PVA-H_2SO_4-MB GPEs.