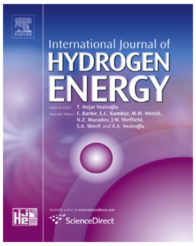
Available online at www.sciencedirect.com
ScienceDirect
journal homepage: www.elsevier.com/locate/he



Improving the energy density of quasi-solid-state supercapacitors by assembling two redox-active gel electrolytes

Le-Qing Fan[*], *Ji Zhong*, *Can-Yang Zhang*, *Ji-Huai Wu*[**], *Yue-Lin Wei*

Engineering Research Center of Environment-Friendly Functional Materials, Ministry of Education, College of Materials Science and Engineering, Huaqiao University, Xiamen, Fujian 361021, China

ARTICLE INFO

Article history:
Received 20 December 2015
Received in revised form
18 February 2016
Accepted 18 February 2016
Available online 12 March 2016

Keywords:
Supercapacitor
Gel polymer electrolyte
Redox additive
$VOSO_4$
Na_2MoO_4

ABSTRACT

Redox additives of $VOSO_4$ and Na_2MoO_4 were respectively added into two polyvinyl alcohol (PVA)–H_2SO_4 gels to form two gel polymer electrolytes (GPEs). These two redox-active GPEs were separated by a Nafion 117 membrane and assembled with a pair of activated carbon electrodes to construct quasi-solid-state supercapacitors, in which PVA–H_2SO_4–$VOSO_4$ and PVA–H_2SO_4–Na_2MoO_4 GPEs worked on the sides of the negative and positive electrodes of the supercapacitor, respectively. Cyclic voltammetry, galvanostatic charge–discharge and electrochemical impedance spectroscopy techniques were used to evaluate the electrochemical performances of the supercapacitor with optimized PVA–H_2SO_4–$VOSO_4$ and PVA–H_2SO_4–Na_2MoO_4 GPEs. After the introduction of $VOSO_4$ and Na_2MoO_4, the specific capacitance and energy density of the supercapacitor with PVA–H_2SO_4–$VOSO_4$|PVA–H_2SO_4–Na_2MoO_4 GPEs can reach 543.4 F g^{-1} and 17.9 Wh kg^{-1}, respectively, which are about four times those of the supercapacitor with a PVA–H_2SO_4 GPE. The enhanced energy storage is attributed to the reversible Faradaic reactions related to $VOSO_4$ and Na_2MoO_4 in the corresponding gel polymer electrolytes. In addition, the supercapacitor shows good cyclic durability.

Introduction

Carbon-based supercapacitors mainly depend on the reversible electrostatic accumulation of electrolyte ions on the electrode surfaces to store electrical energy. Such energy storage mechanism affords that carbon-based supercapacitors have higher power density, longer cycle life, shorter charging time than traditional batteries and can be widely used in various electronic devices and instruments [1–6]. At present the main issue for carbon-based supercapacitors is the low energy density. To improve the energy density of carbon-based supercapacitors without sacrificing their power density, activated carbon with a large surface area are employed as electrodes, because high surface area is beneficial to form high specific capacitance; on the other hand, the aqueous electrolytes are chosen due to their high ionic conductivity and low cost [7,8]. However, liquid

---

[*] *Corresponding author*. Fax: +86 5926162221.

[**] *Corresponding author*. Fax: +86 5926162221.

E-mail addresses: leqingfan@163.com (L.-Q. Fan), jhwu@hqu.edu.cn (J.-H. Wu).

http://dx.doi.org/10.1016/j.ijhydene.2016.02.052

electrolytes have their own shortcomings such as leakage, poor safety and inflexible geometry. Therefore gel polymer electrolytes (GPEs) were proposed to overcome the drawbacks of liquid electrolytes for their appropriate ionic conductivity and high stability [9–11].

In order to enhance the specific capacitance and energy density of supercapacitors, single redox additive such as $VOSO_4$ [12], Na_2MoO_4 [13], KI [14–16], hydroquione [17–19], *p*-phenylenediamine [20,21], *m*-phenylenediamine [22], methylene blue [23] and indigo carmine [24] was introduced into the liquid electrolyte or GPE, where the additional pseudocapacitance can be formed due to the electron transfer redox reaction of the redox additive. And it was observed that the redox reactions related to cationic and anionic redox additives occurred at negative and positive electrodes, respectively [14,15,23,25]. For example, the iodine-based system offers very good pseudocapacitance on the positive electrode rather than on the negative electrode [14,15]. If both cationic and anionic redox additives simultaneously are incorporated into the GPE, the energy storage of quasi-solid-state supercapacitors will be remarkably improved. Therefore the development of such a GPE containing cationic and anionic redox additives used in quasi-solid-state supercapacitors is greatly significant.

In this work, two redox additives of $VOSO_4$ and Na_2MoO_4 were added into polyvinyl (PVA)–H_2SO_4 gels to form redox-active PVA–H_2SO_4–$VOSO_4$ and PVA–H_2SO_4–Na_2MoO_4 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 negative and positive electrodes of a quasi-solid-state supercapacitor based on activated carbon electrodes, respectively, because cationic VO^{2+} and anionic MoO_4^{2-} can produce pseudocapacitance on the corresponding electrodes. Due to the reversible Faradaic reactions related to $VOSO_4$ and Na_2MoO_4 in the relevant GPEs, the energy density is greatly improved without the loss of power density. And the quasi-solid-state supercapacitor shows excellent cyclic durability.

Experimental section

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), $VOSO_4$ (Shanghai Aladdin Reagent, China), Na_2MoO_4 (Shanghai Aladdin Reagent, China) were in analytical grade and without further treatment. Nafion 117 membrane was purchased from Shanghai Hesen Co. Ltd, China.

Synthesis of gel polymer electrolytes

To synthesize PVA–H_2SO_4–$VOSO_4$ GPE [26], 1.5 g of PVA was firstly dissolved in 20 mL of sulfuric acid solution (1 M) with stirring at 60 °C for 5 h. Then a certain amount of $VOSO_4$ was added into the above transparent viscous solution. Subsequently, after the appearance of homogeneous colloidal substance, the mixture was put into a refrigerator at −27 °C for 12 h. At last, after thawing, PVA–H_2SO_4–$VOSO_4$ GPE was formed.

PVA–H_2SO_4–Na_2MoO_4 GPE was prepared by the similar method mentioned above. 1.5 g of PVA was added into 20 mL of sulfuric acid solution (1 M) and stirred at 60 °C for 5 h to dissolve PVA. After that, appropriate quantity of Na_2MoO_4 was added into the above solution and stirred until the formation of homogeneous colloidal substance. Then the resultant mixture was placed into a refrigerator at −27 °C for 12 h. Finally, after thawing, PVA–H_2SO_4–Na_2MoO_4 GPE was obtained. For comparison, PVA–H_2SO_4 GPE without $VOSO_4$ or Na_2MoO_4 was also synthesized using the same method.

Preparation of activated carbon electrode and assemble of supercapacitors

At room temperature an appropriate amount of ethanol was added into a mixture of AC, acetylene black and PTFE with the mass ratio of 90:5:5 and then stirred continuously to get homogeneous slurry. Subsequently the slurry was pressed to form a thin sheet using the Decal method. The thin sheet with a mass of 2.5 mg and a fixed surface area of 0.5 cm^2 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–$VOSO_4$ and PVA–H_2SO_4–Na_2MoO_4 GPEs, and Nafion 117 membrane were assembled to give rise to a two-electrode supercapacitor in a sandwich configuration, in which the Nafion 117 membrane was used to separate these two GPEs. For comparison, supercapacitor with PVA–H_2SO_4 GPE and optimized PVA–H_2SO_4–$VOSO_4$ and PVA–H_2SO_4–Na_2MoO_4 GPEs were also constructed. In all two-electrode supercapacitors, the distances between the two AC electrodes are 4 mm.

Characterizations

All electrochemical tests of two-electrode supercapacitors were conducted on an electrochemistry workstation (CHI660E, Shanghai Chenhua Co. Ltd, China). Cyclic voltammetry (CV) measurements were performed in the potential range of 0–1.0 V at various scan rates of 5–25 mV s^{-1}. Galvanostatic charge–discharge (GCD) behaviors were measured in the potential range of 0–1.0 V at different current densities. Electrochemical impedance spectroscopy (EIS) tests were carried out at frequencies being from 10 mHz to 100 kHz and the data

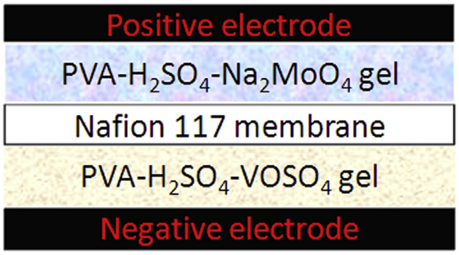


Fig. 1 – The schemactic representation of supercapacitor with PVA–H_2SO_4–$VOSO_4$|PVA–H_2SO_4–Na_2MoO_4 GPEs.