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Short communication

# A new class of alkaline polymer gel electrolyte for carbon aerogel supercapacitors

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#### Abstract

A carbon aerogel supercapacitor has been fabricated with an alkaline polymer gel electrolyte. The electrolyte, which also acts as a separator, has a thickness of 3 mm and a conductivity of around  $10^{-2}$  S cm<sup>-1</sup> at room temperature. The capacitor is characterized by means of cyclic voltammetry, impedance spectroscopy, and galvanostatic cycling. A specific capacitance of 9 F g<sup>-1</sup> is shown by cyclic voltammetry. © 2005 Elsevier B.V. All rights reserved.

Keywords: Supercapacitor; Carbon aerogel; Polymer gel electrolyte; Polyethylene oxide; Conductivity; Specific capacitance

## 1. Introduction

Electric double-layer capacitors, or supercapacitors, are complementary devices to secondary batteries and are attractive as rechargeable pulse-power sources for electronic portable devices, electric vehicles, and memory back-up systems [1–5]. The operational mechanism of a supercapacitor is based on charge separation at the electrode|electrolyte interface.

To date, aqueous electrolyte or organic electrolyte solutions have been used in electric double-layer capacitors. Replacing liquid electrolytes with solid electrolytes will enhance the reliability of the capacitor, as it will prevent leakage of the liquid, corrosion, etc. [6]. Use of solid polymer electrolyte is advantageous as parameters such as low conductivity, poor contact, high internal resistance and low mechanical strength can be minimized. Gel electrolytes have properties that are superior to those of solid polymers for use in supercapacitors that operate at room temperature.

To serve as electrodes in supercapacitors carbon aerogels are required to have high surface area, low electrical resistance, good polarizability, high capacity  $(100-200 \,\mathrm{F g^{-1}})$ ,

and no participation in faradaic reactions at the applied voltage. Unlike activated carbon, carbon aerogel gives a large capacitance as it combines high surface area with a high bulk density [7–9].

This study reports the characteristics of electrochemical capacitors that are fabricated with an alkaline polymer gel electrolyte in a nickel foam current-collector. To our knowledge, this is the first communicated investigation of alkaline (KOH)-based gel polymer electrolyte for use in a carbon aerogel supercapacitor. For comparative purposes, a carbon aerogel capacitor with a liquid electrolyte is also assembled and tested.

# 2. Experimental

# 2.1. Preparation of gel electrolyte and fabrication of symmetric capacitor

The required quantity of polymer blends; polyvinyl alcohol and polyethylene oxide (molecular weight  $\sim$  1,000,000) were added to 20 wt.% KOH solution. The solution was stirred well until the mixture yielded a homogeneous solution. The resulting viscous solution was cast on to a glass plate and allowed to cool to room temperature. The thickness of

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the gel electrolyte was 3 mm. The electrodes were prepared by mixing 80% of carbon aerogel with 20% of Kynar flex using *n*-methyl pyrrolidine as binder. The slurry was pasted on to nickel foam of  $1 \text{ cm}^2$  geometric area. The capacitor was fabricated by sandwiching the electrolyte between the two symmetrical carbon aerogel electrodes.

The performance of the capacitor was characterized by cyclic voltammetry (CV), impedance spectroscopy, and galvanostatic charge–discharge measurements. The CV measurements were conducted at various scan rates. The specific capacitance for various scan rates was calculated by:

$$C = \frac{It}{Vm} \tag{1}$$

where *I* is the current in amperes, *t* the time in seconds, *V* the voltage in volts and *m* the mass of active material in grams.

Conductivity measurements were obtained by means of an electrochemical impedance analyzer (Model 63101 EG &G, Princeton Applied Research) in the frequency range of 100 KHz to 10 mHz at a signal level of 5 mV. The charge–discharge performance of the capacitor was galvanostatically measured for various cycles with a Won-A-Tech Automatic Battery Cycler.

The internal resistance of the cell was calculated from the charge–discharge curve, i.e.,

internal resistance = 
$$\frac{\text{initial step voltage}(V)}{\text{constant current}(I)}$$
. (2)

## 3. Results and discussions

#### 3.1. Electrical conductivity of gel-polymer electrolyte

The ac impedance spectra of the polymer gel electrolyte and the KOH aqueous liquid electrolyte at 25 °C are shown in Fig. 1. The KOH-based gel electrolyte exhibits high conductivity of the order of  $10^{-2}$  S cm<sup>-1</sup> at room temperature.



Fig. 1. ac impedance plot for capacitors with (a) liquid electrolyte and (b) polymer gel electrolyte.



Fig. 2. Cyclic voltammogram for (a) a capacitor based on 6 M KOH aqueous solution and (b) a polymer gel electrolyte at room temperature and a scan rate of  $20 \text{ mV s}^{-1}$ .

A clear semicircle is obtained in the complex plane for the gel electrolyte at room temperature. The conductivity of the gel electrolyte is high and almost comparable with that of the liquid electrolyte. The polarization resistance diameter is less for the gel electrolyte than for the liquid electrolyte.

# 3.2. Electrochemical characteristics of carbon aerogel supercapacitor

The electrochemical behaviour of a capacitor with the polymer gel electrolyte or with 6 M KOH aqueous solution, as examined by cyclic voltammetry at 20 mV s<sup>-1</sup> and room temperature, is shown in Fig. 2. The high capacitance of the capacitor with the gel polymer electrolyte indicates the diffusion of ions into a carbon aerogel with a high surface area. The specific capacitance values for the cells based on both electrolytes calculated from the cyclic voltammograms are given in Fig. 3. The specific capacitance is  $4 \text{ F g}^{-1}$  for the capaci-



Fig. 3. Specific capacitance, calculated from cyclic voltammograms, for cells based on (a) polymer gel electrolyte and (b) liquid electrolyte.

(4)

tor with liquid electrolyte, but is  $9 \text{ F g}^{-1}$  for the cell based on polymer gel. In both cases, the specific capacitance decreases with increasing scan rate. Since the polymer gel electrolyte has a high conductivity and a wide potential window, it is a candidate electrolyte for carbon aerogel supercapacitors.

The benefit of replacing an aqueous electrolyte with a solid electrolyte in a capacitor lies mainly in a possible enhancement in specific energy. The energy stored in a capacitor is equal to  $1/2CV^2$ , where *C* is the capacitance and *V* is the applied potential.

Thus, the electric energy stored in the carbon aerogel capacitor with a liquid KOH electrolyte can be calculated as:

$$\frac{1}{2}CV^2 = \frac{1}{2} \times 4 \times 0.5^2 = 0.5 \,\mathrm{W}\,\mathrm{g}^{-1}.$$
(3)

whereas, for the polymer gel electrolyte based capacitor, the energy is

 $\frac{1}{2}CV^2 = \frac{1}{2} \times 9 \times 0.5^2 = 1.125 \,\mathrm{W \, g^{-1}}.$ 



Fig. 4. Galvanostatic charge–discharge curves at current density of  $5 \text{ mA cm}^{-2}$ : (a) with liquid electrolyte and (b) with gel polymer electrolyte.

The increase in specific energy may be due to the high ionic conductivity and the lower electronic resistance of the polymer gel electrolyte.

#### 3.3. Charge–discharge characteristics

Galvanostatic charge-discharge curves conducted at a current density of 5 mA cm<sup>-2</sup> are presented in Fig. 4. The supercapacitor with the polymer gel electrolyte displays excellent cycleability that is similar to that obtained with a 6 M KOH aqueous solution. This is due to the strong adhesive force between the polymer electrolyte and the electrode material. Hence, contact discontinuity between the electrode and the gel electrolyte does not occur during charging and discharging. The polymer electrolyte might also hold sufficient water for the progress of charge-discharge reactions at the electrode electrolyte interface. It is found that the internal resistance (IR) is low  $(100 \Omega)$  for the gel electrolyte capacitor, but is of the order of  $160 \Omega$  for the liquid electrolyte capacitor due to the presence of the separator. The cyclelife of the supercapacitor with a liquid electrolyte is 6000 cycles while that of the gel polymer version is more than 8000 cycles.

It is seen from the discharge curve that the capacitance of the liquid electrolyte cell is less than that of the polymer gel electrolyte cell. This may be due to the effects of ion diffusion and the IR drop. The high internal resistance of the liquid electrolyte cell is due to the solution resistance.

## 4. Conclusion

The results of the present study suggests that an alkaline (KOH)-based gel polymer electrolyte is a prospective improved electrolyte for carbon aerogel supercapacitors.

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