Development of a flexible poly(ether ether ketone) supercapacitor as electrolyte and separator.

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Abstract. The urgent demand for portable electronics has promoted the development of high-efficient energy sources. A typical portable device requires a low power input that can be supplied by a supercapacitor (SC), which are high-power energy-storage devices enabled by reversible ion adsorption at electrolyte/electrode interface with superior properties such as long cycling life and high-power. However, current SCs using aqueous electrolytes possess the safety hazard of liquid leakage meanwhile solid polymer electrolytes can address this issue, and offers advantages such as simple assembly, low cost and flexible packages, and possible high-voltage operation. In this paper we report a flexible SPEEK supercapacitor used simultaneously as solid-state electrolyte, and ion-conducting surfactant.

1. Introduction

Nowadays, one of the greatest challenges is the development of new and efficient storage and conversion energy devices; capacitors have ignited significant investigation due their advantages including large specific capacitance, rapid charging/discharging rates and high-power performance. Super capacitors (SC) or Electrical Double Layer Capacitors (EDLC) store the charge electrostatically using reversible adsorption of ions of the electrolyte onto active materials that are electrochemically stable. They can complement or replace batteries in electrical energy storage and harvesting applications. SC has emerged as one of the more promising and efficient space-saving energy storage for portable and wearable electronics. The key to reaching high capacitance by charging the double layer is using high specific surface area (SSA) blocking and electronically conducting electrodes. Activated carbons are the most widely used materials today, because of their high SSA and moderate cost [1].

Electrolyte plays a critical role in SCs, the ionic conductivity and potential range of the electrolyte can influence its performance. Liquid electrolytes possess high ionic conductivity but low potential range (limited to ~ 1V), and importantly disadvantageous problems as in the liquid electrolytes, such as leakage, corrosion and explosions [2].

Therefore, solid electrolytes have several advantages over liquid ones that includes easy handling without spillage of hazardous liquid and thus making it environmentally safe, low internal corrosion,
simple construction and flexibility in packaging. Due to the relatively high electric breakdown field, low loss, light weight, fast speed and low cost, polymers are primary choice. Dielectric capacitors with high energy density can significantly reduce the volume and weight of SCs. Among them, sulfonated poly(ether ether ketone) (SPEEK) has been widely used as proton-conducting polymer membrane in fuel cell systems, and consist of aromatic groups in the main chain and are expected to have higher dielectric constant through the contribution if delocalized \( \pi \)-electrons in aromatic groups. Furthermore, the overall polarizability can be increased by modifying these polymers through the incorporation of polar side groups, resulting in an additional ionic contribution to the overall polarization.

2. Methodology

2.1 Dielectric synthesis and electrode preparation

The synthesis of SPEEK was carried out with the procedure reported previously [3]. The synthesized polymer was prepared from 5 g of PEEK (Victrex 450P, MW: 38300) with 100 mL of \( \text{H}_2\text{SO}_4 \) (Aldrich, 98%). The solution was stirred vigorously with a magnetic stirrer at \( T=50^\circ\text{C} \) during \( t=4\text{ hr} \). The reaction is stopped by precipitating the polymer in cold ultrapure water (\( T=4^\circ\text{C} \)). Then, the excess acid was removed by washing with ultrapure water. The sulfonation degree (SD) was determinate by titration (60% SD).

The carbon electrodes were prepared by an ink with 2 mg of carbon black in 10 mL of ethanol. Subsequently, it was deposited by airbrush on 4 cm\(^2\) of carbon paper, to increase the surface area.

2.2 Capacitor assembly

The SC was manufactured by packaging the polymer between a pair of carbon electrodes with an area of 0.25cm\(^2\). All electrochemical measurements of the SC were conducted using a two-electrode system under ambient conditions.

2.3 Electrochemical characterization

The electrochemical test consisted of cyclic voltammetry (CV) performed using a potentiostat/galvanostat (BioLogic SAS Science Instrument VSP-300). All measurements were performed in ambient conditions and in a two-electrode system. Cyclic voltammetry (CV) is a well know technique to stablish the capacitor performance. CV for the SPEEK-SC at scan rate from \( \nu=20\text{ mV/s} \) to 100 mV/s, with 20 mV/s steps, in the potential range \( E=0.5\text{ to }0.5\text{ V} \) were carried out in order to perceive the electrical double layer behavior. Whit the aim to find the real potential interval, CV were carried out at scan rate of \( \nu=20\text{ mV/s} \) in a potential from -0.5– 0.5 V to -1– 1V with 0.1V steps. Galvanostatic charge discharge (GCD) curves at different current densities 50, 100, 150 and 200 \( \mu\text{A} \) in a potential difference of \( \Delta E = 0.5\text{ V} \) were carried out for capacitance calculations.

3. Results and Discussion

The supercapacitor characteristics were calculated by processing the charge-discharge data:

\[
C = \frac{\text{IM}}{\Delta E A}
\]

where \( I \) is the applied charge/discharge current, \( \Delta t \) is the charge/discharge duration, \( \Delta E \) is the voltage difference between the initial and final potential either on charging or discharging process and \( A \) is the contact electrode area. The calculated capacitance is 0.05 F/cm\(^2\). As the charge and discharge were performed at the same current rate, the coulombic efficiency is equal

\[
\%\text{Efficiency} = \frac{\Delta t_{\text{disch}}}{\Delta t_{\text{ch}}} \times 100
\]

where \( \Delta t_{\text{disch}} \) and \( \Delta t_{\text{ch}} \) are the discharge and charge time and is showed in figure 4.
As seen in figure 1, SPEEK-SC shows a fusiform which indicates that the supercapacitor possess a typical electrical double-layer capacitance due its ionic conductivity, not redox peak is observed at different scan rate, that confirms that the electrolyte is not reacting with the electrode. In the other hand, figure 2 shows a high potential range stability in which a rectangular shape remains between -1 and 1 V, meaning that no reaction is taking place under this potential range.

Figure 1. CV at scan rates from 20 mV/s to 100 mV/s shows a typical behavior of non-faradaic currents.

Figure 2. CV range potential from 1V to 2V.

Figure 3. GCD from 50 μA to 200 μA.

Figure 4. Efficiency at different currents.
The galvanostatic charge/discharge (GCD) is a reliable method to evaluate the electrochemical capacitance of materials. GCD curves in figure 3, shows the charging/discharging curves for the supercapacitor, a linear behavior is related to a no significative IR drop, that would be directly translated into energy and power losses [4]. The GCD curves shows an excellent capacitance performance which are related to a good conductivity of the carbon electrode and the movement of charge carriers (ions) in the electrolyte across the separator to the electrodes and into their porous structure.

In general, the efficiency of the supercapacitors is associated with the electrical double layer feature and the reversible faradic reaction. Figure 4 shows an efficiency increment as cycles increase; this could be attached to a gradual increase in the number of some electrically floating inactive grains forming a better conducting path at and initial cycling number.

4. Conclusions
We report a supercapacitor with a commercial and well-know material, few reports for this application. The present supercapacitor does not require a metallic current collector and acts like a polymer separator and electron interchanger. The potential range of the SPEEK SC reported (2 V), is greater in comparison to capacitors reported previously (1 V) [5], facile package and low cost materials. Besides, it has been reported that the addition of a blinder or/and an electron collector increased the SC performance [6], so the addition of any of them can improve its characteristics considerably.

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