Electric Double Layer Capacitor Using Polymer Hydrogel Electrolyte with 4 M H₂SO₄ Aqueous Solution

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An acidic polymer hydrogel electrolyte was successfully prepared from 4 M H₂SO₄ aqueous solution, poly(vinyl alcohol) and glutaraldehyde. The polymer hydrogel electrolyte showed higher ionic conductivity than that prepared from 1 M H₂SO₄ aqueous solution in our previous study. An electric double layer capacitor (EDLC) cell assembled using the polymer hydrogel electrolyte exhibited higher discharge capacitance in the wide range of current density than that using the hydrogel electrolyte with 1 M H₂SO₄ aqueous solution.

Key Words : Polymer Hydrogel Electrolyte, Sulfuric Acid, Ionic Conductivity, Electric Double Layer Capacitor

1 Introduction

Electric double layer capacitors (EDLCs) have attracted attention due to their high power density and long cycle life compared with batteries. Until now, various organic or inorganic solutions have been commercially used as the electrolyte, while the application of solid or gel electrolytes to EDLCs is very attractive in terms of reliability, flexibility and so on.¹⁻⁵⁾ In water-based EDLCs, alkaline solid polymer electrolytes based on poly(ethylene oxide) (PEO)-KOH-H₂O⁶⁾ and alkaline hydrogel electrolytes based on crosslinked potassium poly(acrylate) (PAAK)-KOH-H₂O⁷⁻⁹⁾ have been applied. On the other hand, there are only a few studies on acidic polymer hydrogel electrolytes. Although Choudhury *et al.* reported a hydrogel electrolyte based on poly(vinyl alcohol) (PVA) and perchloric acid,¹⁰⁾ the ionic conductivity (10⁻³–10⁻² S cm⁻¹ at room temperature) is quite low probably due to the low acid concentration, compared with concentrated sulfuric acid solutions (*e.g.* 30–50 wt.%) used in practical EDLCs.

We have proposed an acidic polymer hydrogel electrolyte composed of PVA crosslinked by glutaraldehyde (GA) and 1 M (M = mol dm⁻³) H₂SO₄ aqueous solution.^{11,12)} The obtained transparent hydrogel electrolyte showed high ionic conductivity and good electrochemical characteristics in EDLC cell as well as 1 M H₂SO₄ aqueous solution. In addition, self-discharge of the cell was fairly suppressed by using the polymer hydrogel electrolyte. From the viewpoint of ionic conductivity, it is more desirable to use sulfuric acid with higher concentration. However, in the previous study, when H₂SO₄ aqueous solutions with higher concentration than 1 M were used, the crosslinking reaction occurred rapidly and partially due to the high acid concentration even with stirring, and transparent homogeneous hydrogel could not be obtained. In this study, a homogeneous acidic polymer hydrogel electrolyte with 4 M H₂SO₄ aqueous solution which shows higher ionic conductivity than the previous

one was successfully prepared by decreasing the rate of the crosslinking reaction. The resulting polymer hydrogel electrolyte was applied to the EDLC cell, and its electrochemical characteristics were investigated.

2 Experimental

Basically, the acidic polymer hydrogel electrolyte with 4 M H₂SO₄ aqueous solution was prepared according to the previous procedures.^{11,12)} In the present study, the concentrations of PVA and GA and temperature for crosslinking reaction were lowered, compared with the previous condition in order to restrain the rapid crosslinking reaction. 0.70 g of PVA (Aldrich, #163-03045) was dissolved in 9 ml of 4.4 M H₂SO₄ aqueous solution at 40 °C. After that, the solution was cooled to -14 °C. Then, while stirring the solution, 1 ml of 1.4 wt.% GA aqueous solution (Wako, #073-00536) was added as the crosslinking agent. The crosslinking reaction gradually proceeded, and a transparent homogeneous polymer hydrogel electrolyte was successfully obtained. This electrolyte can be also obtained as a self-standing membrane.

The conductivity of the polymer hydrogel electrolyte was measured by ac impedance spectroscopy between 10 Hz and 10 kHz with the amplitude of 10 mV in the temperature range from -20 to 60 °C. Preparation of activated carbon electrodes and fabrication of the EDLC cell were performed in almost the same manner as described in our previous paper¹²⁾ except that glassy carbon plates were used as current collectors. Cyclic voltammetry of the cell was performed in the voltage range of 0.2–0.8 V at a scan rate of 1 mV s⁻¹, and charge-discharge tests were done at a current density of 1 mA cm⁻². Moreover, high-rate dischargeability was measured changing the discharge current density. These electrochemical measurements were carried out at 30 °C. To comparison, another EDLC cell was also assembled using the polymer hydrogel electrolyte with 1 M H₂SO₄ aqueous solution and characterized. In what follows, the

polymer hydrogel electrolytes with 1 M and 4 M H_2SO_4 aqueous solutions are denoted by hydrogel (1 M) and hydrogel (4 M), respectively.

3 Results and Discussion

Figure 1 shows Arrhenius plots of the ionic conductivity for the polymer hydrogel electrolytes and a 4 M H_2SO_4 aqueous solution. As expected, ionic conductivity of the polymer hydrogel electrolyte was markedly increased in the wide temperature range by using sulfuric acid with higher concentration. For example, conductivities at 30 °C were *ca.* 0.26 and 0.60 S cm^{-1} for the hydrogel (1 M) and hydrogel (4 M), respectively. The latter is a very high value similar to that of a 4 M H_2SO_4 aqueous solution (0.77 S cm^{-1} at 30 °C). Moreover, both hydrogels showed approximately linear relationship in the wide temperature range of Arrhenius plots. The activation energy (evaluated in the range of 10–60 °C) is 8.9 kJ mol^{-1} for the hydrogel (4 M), which is very close to that of the 4 M H_2SO_4 aqueous solution, 8.8 kJ mol^{-1} . This result may suggest that the ionic conduction mechanisms of the two electrolytes are very similar.

Cyclic voltammograms of EDLC cells with the polymer hydrogel electrolytes are shown in Fig. 2. In both cases, the voltammograms similar to the ideal rectangular shape were observed, indicating that the cells were reversibly charged and discharged by adsorption and desorption of ions at the electrolyte/electrode interface. Additionally, no visible current peaks in the voltammograms suggest that the hydrogel electrolytes are electrochemically stable without decomposition in the applied voltage range. The higher the concentration of sulfuric acid was, the larger the observed current was. Capacitances calculated from the voltammograms were *ca.* 0.55 and 0.68 F for the EDLC cells with hydrogel (1 M) and hydrogel (4 M), respectively.

Figure 3 shows typical charge-discharge curves (tenth cycle) for the polymer hydrogel electrolytes. Almost linear charge and discharge curves were obtained for both the electrolytes, indicating that the EDLC cells worked successfully. In each case, ohmic voltage drop was very small under the present charge-discharge condition, and

it is inferred that good contact of the polymer hydrogel electrolyte with the activated carbon electrode is accomplished. From the slope of each discharge curve, capacitances for the EDLC cells with hydrogel (1 M) and hydrogel (4 M) can be estimated to be *ca.* 0.54 and 0.68 F, respectively. These values are almost equivalent to those calculated from the cyclic voltammograms. Capacitances based on the total weight of activated carbon in each cell were *ca.* 33 and 42 F g^{-1} for the EDLC cells with hydrogel (1 M) and hydrogel (4 M), respectively. It is indicated that the higher ionic conductivity of hydrogel (4 M) is responsible for the higher capacitance of the activated carbon electrode. High ionic conductivity down the pores may increase chargeable surface area of the activated carbon electrode, consequently leading to high capacitance of the electrode.¹³⁾

High-rate dischargeability was also investigated for the two polymer hydrogel electrolytes. As can be seen from Fig. 4, discharge capacitance for the EDLC cell with hydrogel (4 M) was higher than that for the EDLC cell with hydrogel (1 M) over the whole current density. We can say that use of sulfuric acid with higher concentration is effective in increasing the discharge capacitance in the wide range of current density. In conclusion, it was clarified that the concentration of sulfuric acid in the polymer hydrogel electrolyte was a very important factor to improve the characteristics of the EDLC cell as well as the case of usual aqueous solution.

Fig. 2 Cyclic voltammograms for EDLC cells with hydrogel (1 M) and hydrogel (4 M).

Fig. 1 Arrhenius plots of the conductivity for hydrogel (1 M), hydrogel (4 M) and a 4 M H_2SO_4 aqueous solution.

Fig. 3 Charge-discharge curves for EDLC cells with hydrogel (1 M) and hydrogel (4 M).

Fig. 4 High-rate dischargeabilities for EDLC cells with hydrogel (1 M) and hydrogel (4 M).

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