

Electrochemical characteristics of new electric double layer capacitor with acidic polymer hydrogel electrolyte

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Abstract

The acidic polymer hydrogel electrolyte was prepared from 1 M H₂SO₄ aqueous solution, poly(vinyl alcohol) (PVA) and glutaraldehyde (GA). A new electric double layer capacitor (EDLC) with the polymer hydrogel electrolyte was assembled, and its electrochemical characteristics were investigated. As a result, the EDLC cell with the polymer hydrogel electrolyte exhibited almost the same discharge capacitance and high-rate dischargeability as that with a 1 M H₂SO₄ aqueous solution as an electrolyte. It was also found that the self-discharge was remarkably suppressed by using the polymer hydrogel electrolyte.

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1. Introduction

Electric double-layer capacitors (EDLCs) are known to have characteristics such as high power density and long cycle life, in which H₂SO₄ aqueous solution has been generally used as an aqueous electrolyte. Replacement of the electrolyte by a solid or gel electrolyte would be very attractive in terms of reliability, flexibility and so on. EDLCs with alkaline polymer solid or gel electrolytes based on poly(ethylene oxide) (PEO)–KOH–H₂O [1,2] and crosslinked potassium poly(acrylate) (PAAK)–KOH–H₂O [3,4] have been investigated. Nevertheless, the acidic gel electrolyte has been scarcely reported.

Poly(vinyl alcohol) (PVA) aqueous solution can be easily changed into the gel, and the hydrogel prepared by several methods have been reported [5–8]. One of the gelation methods is to use the crosslinking agent [7,8]. The crosslinking reaction as shown in Fig. 1 occurs in the presence of protons. The hydrogel prepared in this manner recently have attracted attention in the field of biomedical technology, electrochemistry and so on. The

preparation of the acidic polymer hydrogel electrolyte would lead to application to the EDLCs. Previously, we successfully prepared an electrochemically stable acidic polymer hydrogel electrolyte from 1 M H₂SO₄ aqueous solution, PVA and glutaraldehyde (GA) solution [9]. The obtained polymer hydrogel electrolyte has a good mechanical strength, so it is expected that the polymer hydrogel electrolyte can be used as the self-standing membrane in EDLCs. In addition, the ionic conductivity of the polymer hydrogel electrolyte was close to that of a 1 M H₂SO₄ aqueous solution in the wide temperature range. In this study, an EDLC cell was assembled using the acidic polymer hydrogel electrolyte, and its charge–discharge and self-discharge characteristics were evaluated and discussed.

2. Experimental

The acidic polymer hydrogel electrolyte was prepared according to the following steps. PVA (Aldrich, #163-03045) (1.5 g) was added to 0.01 dm³ of 1 M H₂SO₄ aqueous solution, and dissolved with stirring in a beaker at 80 °C. After the PVA was completely dissolved and the solution was cooled to room temperature, 25 wt.% GA solution (Wako, #073-00536) (50 μl) was added as a crosslinking agent. The crosslinking reaction

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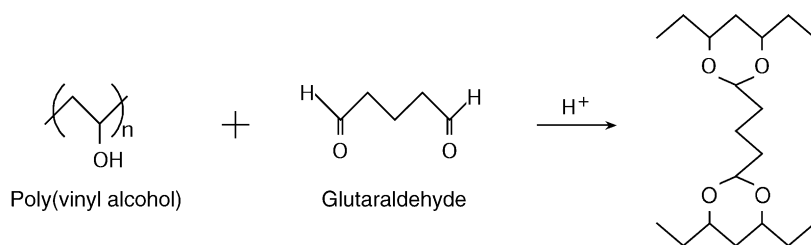


Fig. 1. Schematic representation of the crosslinking reaction of poly(vinyl alcohol) (PVA) with glutaraldehyde (GA) in the presence of protons.

started to occur soon and homogeneous polymer hydrogel was then obtained within 20 s. The resulting hydrogel was fairly stable at room temperature and separation of phases was not observed even after storage in a sealed vessel for some months. When H_2SO_4 aqueous solutions of higher concentration than 1 M were used, the crosslinking reaction occurred too rapidly to obtain the homogeneous hydrogel in the present condition.

Activated carbon fiber cloths (Kuraray Co. Ltd., specific surface area: ca. $2000 \text{ m}^2 \text{ g}^{-1}$) were used as electrode material of EDLC cells. The carbon cloths ($10 \text{ mm} \times 10 \text{ mm}$) were dried at 120°C for 24 h in order to remove impurities such as adsorbed organic compounds. A 1 M H_2SO_4 aqueous solution was impregnated into the cloths in a beaker under a vacuum. Then, the carbon cloths were put out the beaker and stuck on stainless steel sheets with the carbon paste to prepare activated carbon (AC) electrodes. Before the solution containing PVA, H_2SO_4 and GA as described above was gelled, it was poured onto the AC electrode with acrylic spacer (thickness: 1 mm), and the electrode with the solution was combined with another AC electrode impregnated with a 1 M H_2SO_4 . Fig. 2 shows the experimental cell assembly for the polymer hydrogel electrolyte-based EDLC. For comparison, the similar type cell with a 1 M H_2SO_4 aqueous solution instead of the polymer hydrogel electrolyte was also assembled. Charge–discharge cycling tests were performed between cell voltages of 0.2 and 0.8 V at a current density of 1 mA cm^{-2} . Moreover, high-rate dischargeabilities were measured changing the discharge current density. Their capacitances were calculated based on the mass of only carbon material. Self-discharge characteristics were investigated as follows. After 10 charge–discharge cycles, the experimental cells

were charged to 0.8 V, and the time courses of cell voltage were then measured on open circuit. Leakage currents were also measured at a constant cell voltage of 0.8 V after charging to 0.8 V.

3. Results and discussion

Fig. 3 shows the galvanostatic charge–discharge curves for the EDLC cells with the polymer hydrogel electrolyte and a 1 M H_2SO_4 aqueous solution. Each curve exhibited the typical behavior of EDLC. It is indicated that good electrode/electrolyte interface was formed in each experimental cell and that the experimental cell successfully worked as an EDLC even if the polymer hydrogel electrolyte was used. Moreover, the curves for both the electrolytes were very similar, probably due to the high ionic conductivity [9] and good contact with the electrode of the polymer hydrogel electrolyte as well as the H_2SO_4 aqueous solution. The IR drop due to the internal resistance of the cell was slightly observed at the beginning of discharge in each case. The discharge capacitance was calculated from the discharge curve observed after the IR drop. The discharge capacitances of the electrodes were evaluated to be 110 and 115 F g^{-1} for the polymer hydrogel electrolyte and the 1 M H_2SO_4 aqueous solution, respectively. The capacitance for the polymer hydrogel electrolyte was nearly comparable to that for the 1 M H_2SO_4 aqueous solution.

High-rate dischargeability of the cell with the polymer hydrogel electrolyte was measured compared to that with the 1 M H_2SO_4 aqueous solution. As shown in Fig. 4, it was found that the cell even with the polymer hydrogel electrolyte had high-rate

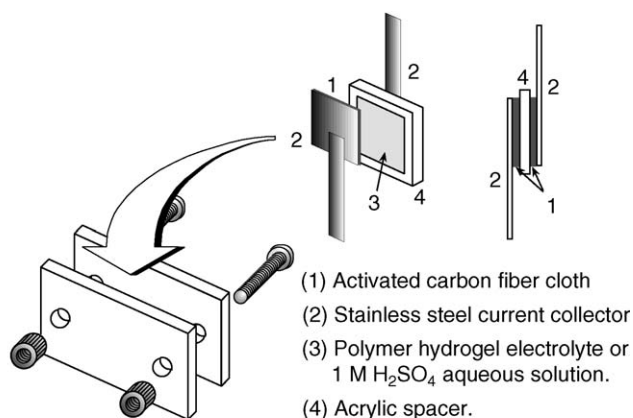


Fig. 2. Schematic representation of the experimental cell assembly.

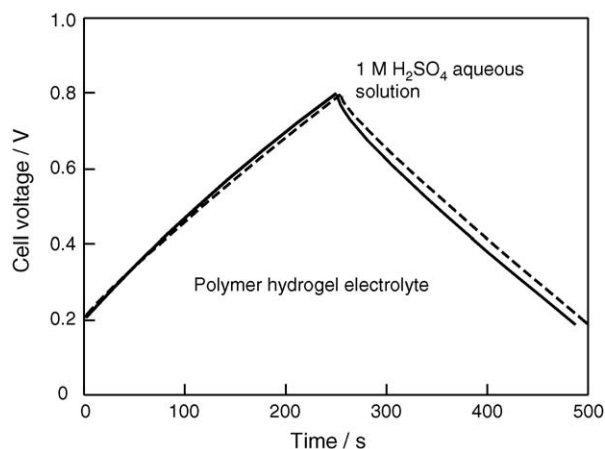


Fig. 3. Charge–discharge curves for the EDLC cells with the polymer hydrogel electrolyte and a 1 M H_2SO_4 aqueous solution.

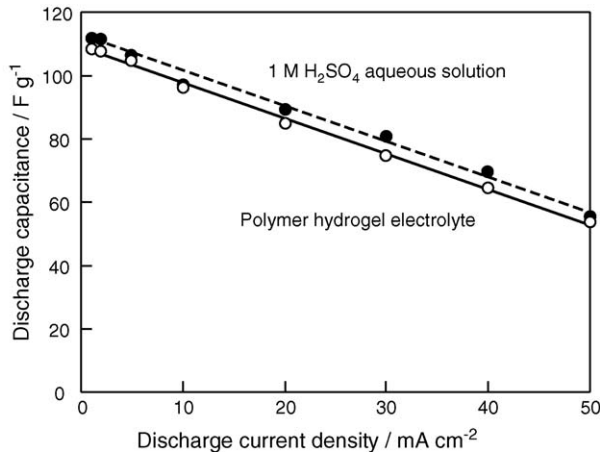


Fig. 4. High-rate dischargeabilities for the EDLC cells with the polymer hydrogel electrolyte and a 1 M H₂SO₄ aqueous solution.

dischargeability compared to that with the 1 M H₂SO₄ aqueous solution under the present experimental condition. This can be mainly ascribed to high ionic conductivity of the polymer hydrogel electrolyte.

Fig. 5 shows the time courses of the open-circuit voltage for the cells with the polymer hydrogel electrolyte and a 1 M H₂SO₄ aqueous solution after charging. It is clear that the voltage decay for the cell with the polymer hydrogel electrolyte is lower than that with the 1 M H₂SO₄ aqueous solution. This implies that the self-discharge is suppressed by using the polymer hydrogel electrolyte.

Leakage currents of the cells are shown in Fig. 6. In each case, the leakage current significantly decreased in the beginning, and then the current gradually became smaller and more stable. This current is ascribed to the self-discharge in the cell. As can be seen from this figure, the leakage current was largely decreased by using the polymer hydrogel electrolyte. Generally, the causes of self-discharge reported in the literature [10] are mainly as follows: (i) the shuttle reaction caused by the impurities in carbon material; (ii) the micro-short circuit of carbon fiber through the separator, and so on. Iron of ca. 20 ppm is

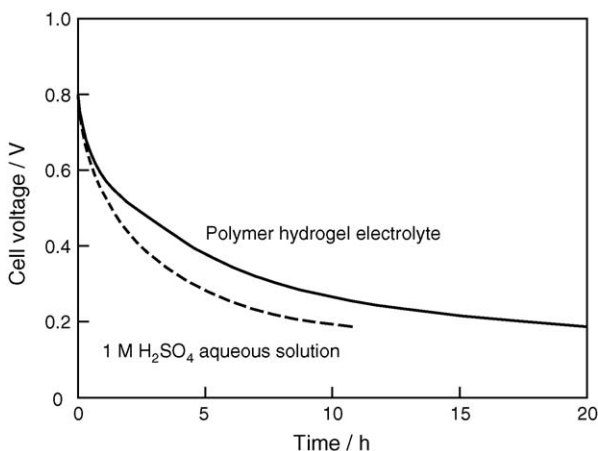


Fig. 5. Time courses of the cell voltages on open circuit for the EDLC cells with the polymer hydrogel electrolyte and a 1 M H₂SO₄ aqueous solution.

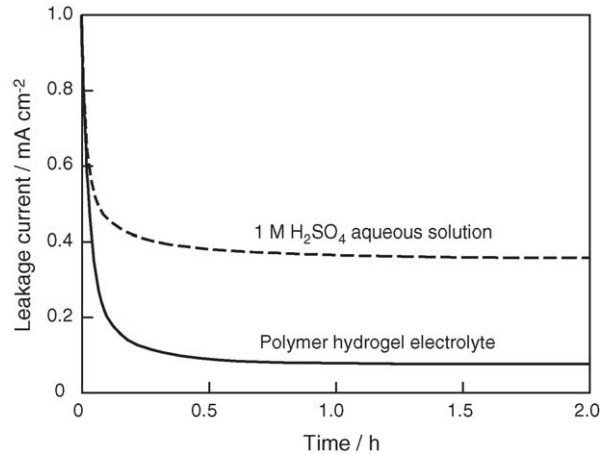


Fig. 6. Time courses of leakage currents at the cell voltage of 0.8 V for the EDLC cells with the polymer hydrogel electrolyte and a 1 M H₂SO₄ aqueous solution.

included as one of impurities in the carbon electrode used in this work. It is thought that the metal impurities dissolve into the electrolyte and shuttle between the two electrodes changing their valence. Previously, it was reported that the polymer hydrogel electrolyte based on PAAK, KOH and H₂O restrained diffusion of metal species dissolved from the electrode in Ni/MH batteries, leading to a marked improvement in the capacity retention characteristics [11,12]. It is possible that the acidic polymer hydrogel electrolyte used in this study also restrains diffusion of the impurities such as iron and suppresses the shuttle reaction. Moreover, the mechanical strength of the polymer hydrogel electrolyte may inhibit the micro-short circuit of carbon fibers.

As mentioned above, the acidic polymer hydrogel electrolyte exhibited charge–discharge characteristics similar to the 1 M H₂SO₄ aqueous solution and markedly suppressed the self-discharge. It is strongly suggested that the polymer hydrogel electrolyte can be potentially applied to EDLCs as a new electrolyte. From a practical viewpoint, homogeneous polymer hydrogel electrolytes with sulfuric acid of higher concentration need to be prepared and characterized as a next challenge. The temperature dependence of the electrochemical characteristics and prolonged stability of the electrolyte should be also examined. Further investigation along these lines, in addition to study on the reason of the suppression of self-discharge, is now in progress.

4. Conclusions

The acidic polymer hydrogel electrolyte prepared from 1 M H₂SO₄ aqueous solution, PVA and GA was applied to EDLCs. In charge–discharge tests, the polymer hydrogel electrolyte successfully worked in an experimental EDLC cell, and the cell with the polymer hydrogel electrolyte showed discharge capacitance and high-rate dischargeability, almost comparable to that with a 1 M H₂SO₄ aqueous solution. Moreover, the self-discharge of the EDLC cell was remarkably suppressed using the polymer hydrogel electrolyte. From these results, it is considered that the

acidic polymer hydrogel electrolyte has a potential applicability to EDLCs.

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