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특 집

Electrochemical Properties of Activated Carbon Capacitor Adopting a Proton-conducting Hydrogel Polymer Electrolyte

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수소이온전도성 고분자 겔전해질을 적용한 활성탄소계 전기이중층 캐패시터의 전기화학적 특성

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ABSTRACT : An electric double-layer capacitor (ELDC) of activated carbon electrode is prepared using a proton-conducting hydrogel polymer electrolyte, which is composed of poly(vinyl alcohol), silicotungstic acid, H_3PO_4, and deionized water. A solid film by evaporating the hydrogel polymer electrolyte is also prepared for comparison. The hydrogel polymer electrolyte also acts as a separator with the thickness of about 80 μm and the room-temperature ionic conductivity of 10^{-2} S cm^{-1}. The EDLC containing the symmetric electrodes of activated carbon shows the specific capacitance of 58 F g^{-1} at 100 mV s^{-1} with a good cycle life, implying that the hydrogel polymer electrolyte is very promising for use in EDLCs.

요 약 : 폴리비닐알콜, 규소텅스텐산, 인산 및 수용액으로 구성된 80 μm의 두께의 고분자겔 전해질 필름을 제조하여 활성탄소계 전기이중층 케페시터를 제조하였다. 제조한 고분자겔 전해질 필름은 상온에서 10^{-2} Scm^{-1}의 높은 이온전도도를 나타내었으며, 본 전해질 필름을 적용한 활성탄소계 전기이중층 케패시터는 100 mV/s에서 58 Fg^{-1}의 높은 캐패시턴스 특성과 우수한 수명특성을 나타내었다.

Keywords : electric double-layer capacitor, activated carbon electrode, polymer electrolyte, electrochemical properties

Ⅰ. Introduction

Electric double-layer capacitor (EDLC) is an energy storage system, in which the polarization of electrodes in opposite directions leads to accumulation of opposite charges at the electrolyte/electrode interface.[1] The EDLCs could provide high-power capability (typically within 60-120 s), excellent reversibility (90-95% or higher), and long cycle life (>10^5). It also could achieve 20-200 times larger capacitance per unit volume or mass than conventional capacitors.[2]. The EDLC for reversible electrical energy storage and delivery is comprised in principle of an electrolyte solution and two porous electrodes sandwiching the solution. The electrolyte is consisted typically of one or more solvents containing one or more dissolved ionic species. In many cases, physical and electrochemical properties of the electrolyte become a key factor in determining the internal resistance and power capability of the capacitor. Because of high ionic conductivity, the electrolyte of capacitor has been used in aqueous or organic solution for assembly of capacitor greatly. The liquid electrolyte may result in problems when handling and packaging the capacitor, and moreover, it may leak if it is used for a long time. Thus, replacing liquid electrolyte by solid electrolyte has become the focus of capacitor studies. Recently, many attempts have been made to develop all solid-state capacitor since this approach offers attractive features, such as easy fabrication, rugged construction, no liquid leak, long shelf-life, safety, and a wide range of operation temperature. The all solid-state capacitor could be realized by

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using solid or gel polymer electrolyte.[3]

Heteropolyacid is a good candidate for solid electrolyte due to the high proton conductivity in the solid state, which is an attractive feature in fuel cells and capacitors. Some drawbacks, such as poor film-forming capability and sensitivity to moisture, have so far limited application as solid electrolyte.[4] A study was also tried by incorporating the heteropolyacid in polymer matrix to enable the formation of good solid electrolyte with high conductivity and good mechanical property.[5] That is, an electrochemical capacitor adopting poly(vinyl alcohol) (PVA) and silicotungstic acid (SWA) was suggested as an EDLC with good stability and cycle life over three months. The PVA with SWA could form a solid film, and thereby the film was used as an electrolyte system in an electrochemical capacitor.[4] The PVA has also been used in preparing a number of hydrogels. For instance, an acidic hydrogel electrolyte was successfully prepared from aqueous solution of 4 M H_2SO_4, PVA, and glutaraldehyde to design a capacitor.[6] In this study, a proton-conducting hydrogel polymer electrolyte (HPE) comprising of PVA, SWA, orthophosphoric acid (H_3PO_4), and deionized water is developed and used in the fabrication of an EDLC using activated carbon electrodes.

Ⅱ. Experimental

The precursor solution of the HPE was first prepared by mixing PVA (Aldrich, M_w = 130000, 5 wt.%) as a polymer matrix, SWA ($H_4SiW_{12}O_{40}$, Aldrich, 43 wt.%) as a proton-conducting agent, H_3PO_4 (5 wt.%) as proton-conducting salt, and deionized water (47 wt.%) as a solvent. For the EDLC electrodes, a slurry was prepared by mixing activated carbon (80 wt.%) as an active materials, poly(vinylidene fluoride) (Aldrich, 10 wt.%) as a polymer binder, vapor-grown carbon fiber (Showa Denko, 10 wt.%) as a conducting agent, and *N*-methyl-2-pyrrolidone as a solvent. The viscous slurry was then applied on an aluminum foil, spread by a doctor blade apparatus, and finally evaporated in an oven at 110 ℃ to yield the EDLC electrode.

A symmetric two-electrode EDLC was fabricated with a pair of the activated carbon electrodes (1 cm × 1 cm) and the HPE. The EDLC was assembled as follows: 0.07 ml of the electrolyte precursor solution was spread on the activated carbon electrode with the help of a brush. The coated electrode was slightly air-dried at 25 ℃ to evaporate some of the water component to form the HPE-laminated electrode. The EDLC was then fabricated by fusing two HPE-laminated electrodes together. Figure 1 shows some images of the HPE, HPE-laminated electrode, and the fabricated EDLC device. The HPE was served as separator and electrolyte simultaneously in this study. A solid film of the precursor solution of PVA/SWA/H_3PO_4 was also made by solution-cast method for comparison. The solution was cast onto a clean glass plate for evaporation of excess water at room temperature and then vacuum dried overnight at 40 ℃ to dry the film completely. Figure 1d shows the image of the PVA/SWA/H_3PO_4 solid film polymer electrolyte (SPE). The film was kept in a desiccator to remove moisture. The thickness of the film was about 90 μm. An EDLC was also fabricated by inserting the SPE between the two activated carbon electrodes.

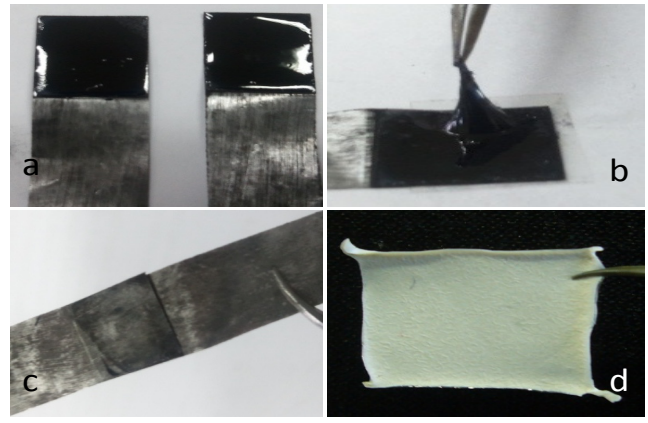

Figure 1. (a) depicts an activated carbon electrode with the laminated HPE; (b) shows tough and adhesive nature of the HPE laminate; (c) shows a fabricated EDLC prepared by fusing two activated carbon electrodes with the laminated HPE together; (d) indicates the SPE.

The electrochemical properties of the EDLC devices were evaluated using cyclic voltammetry and electrochemical impedance spectroscopy. The cyclic voltammetry was carried out using an Autolab imstrument (P/GStat 100, Eco Chemie) at different scan rates of 100-1000 mV s^{-1} in the potential range of 0-1.5 V (vs. Ag/AgCl). A three-electrode cell was used with Ag/AgCl (saturated KCl, 0.222 V vs. SHE) as a reference electrode and platinum as a counter electrode.

Ⅲ. Results and discussion

PVA (-[CH_2-CHOH]$_n$-) is a water-soluble synthetic polymer which has excellent film-forming, emulsifying, and adhesive properties due to its high tensile strength and flexibility. It is an atactic material but exhibits certain crystallinity as the hydroxyl groups are small enough to fit into the lattice without disrupting it.[8] On the other hand, hydrogels are three-dimensional polymeric networks that trap water in the polymer matrices mainly by surface tension and other weak interactions. Hydrogels comprising synthetic polymers, such as PVA, have high structural integrity and good mechanical stability. These hydrogels can also absorb large amount of water in the polymer matrix that helps fine-tuning their ionic conductivity.[9]

However, in many cases, conductivity is not part of the inherent characteristics of the hydrogel and is provided by other elements which are incorporated within the polymer network of the hydrogel (e.g., conductive particles, conducting polymer, etc.). Therefore, it is important to develop a conductive hydrogel system that retains its conductivity at different gel swelling ratios and also displays enhanced mechanical performance.[10]

The prepared PVA-based HPE shows a high proton-conductivity of 10^{-2} S cm^{-1}, which may be considered as a result of synergistic contribution from SWA and triprotic acid (H_3PO_4). The high conductivity of the HPE is also aided by the large amount of water which is trapped in the polymer matrix. The laminated HPE also has a tough appearance (see Figure 1b). The toughness comes from the PVA which has the ability to provide mechanical strength in the hydrogel by H-bond induced crosslinking. In aqueous solutions, entangled aggregates of H-bonded PVA molecules are formed.[11] The hydrogel also has a sticky, adhesive-like appearance. This adhesive-like nature of the HPE ensured a very good contact between the two electrodes. They are inseparable after fusing them together. This tight contact enables the HPE to form good interfacial contacts with the electrode materials.

In order to assess the compatibility of the electrodes and the hydrogel electrolytes, the EDLCs containing the laminated HPE and the SPE were subjected to complex impedance measurements at 25 ℃. Figure 2 shows that there is a vast difference in the impedance characteristics of the EDLCs containing the laminated HPE and the SPE. The ohmic resistance of the EDLC with the SPE is larger than that with the laminated HPE. This is because the proton-conductivity of the SPE is lower than the laminated HPE. The high conductivity of the laminated HPE results from the large amount of water in the polymer matrix. Deducing from the impedance arcs in high-frequency region, the charge transfer resistance at the electrode/electrolyte interface of the EDLC with the laminated HPE is smaller than that with SPE. Thus, the EDLC with the laminated HPE exhibits a better interfacial compatibility between the EDLC electrode and the hydrogel electrolyte.

The cyclic voltammograms of the EDLCs with the laminated HPE and the SEP deviate slightly from ideal rectangular shape. However, the electric double-layer occurs at the electrode/electrolyte interface. Moreover, visible peaks due to redox reactions cannot be observed, which is implying that these electrolytes are stable within the applied potential range and also good capacitor devices in both cases. Again from Figure 3, the voltammogram size of the SPE-based EDLC is very small compared to that of the laminated HPE-based EDLC. This is due to the high ionic conductivity of the HPE-based EDLC. The good electric contacts at the electrode/electrolyte interface and good compatibility of all constituents of the unit capacitor

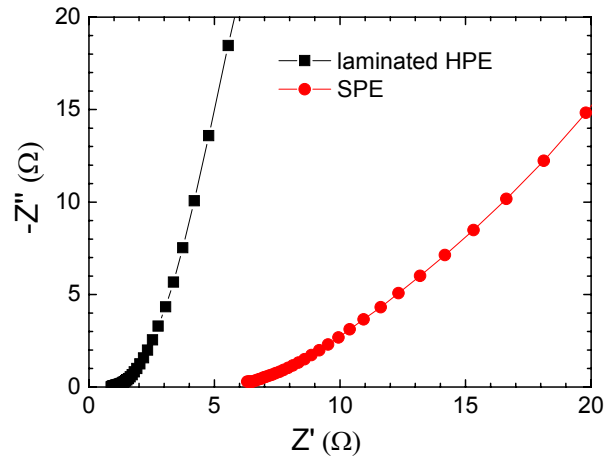

Figure 2. Nyquist plots of the EDLCs containing the laminated HPE and SPE.

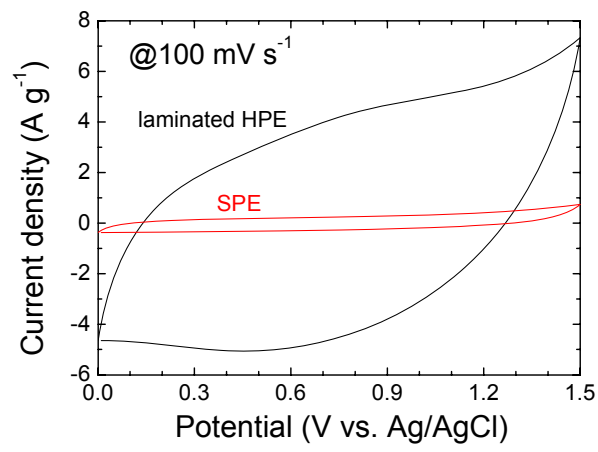

Figure 3. Cyclic voltammograms of the EDLCs containing the laminated HPE and SPE at scan rate of 100 mV s^{-1}.

are responsible for the good electrochemical characteristics in the HPE-based EDLC, comparable to that with the SPE. As shown in Figue 4, both the EDLCs with the HPE and SPE show a decreasing capacitance with increasing the scan rate. However, the specific capacitance of the HPE remains higher than that of the SPE throughout the range up to 1000 mV s^{-1}.

Figure 5a shows three cyclic voltammograms obtained after 100, 500 and 1,000 cycles, respectively, at a voltage sweep rate of 100 mVs^{-1}, for the EDLC containing the HPE. The three voltammograms ae almost overlapping and have a voltage window of 0-1.5 V, suggesting an excellent cycle life. Figure 5b shows the specific capacitance as a function of cycle number for the EDLC containing the HPE at a scan rate of 100 mVs^{-1}. The EDLC with the laminated HPE has a stable specific capacitance of 57 F g^{-1} for the 1000th cycle. The initial

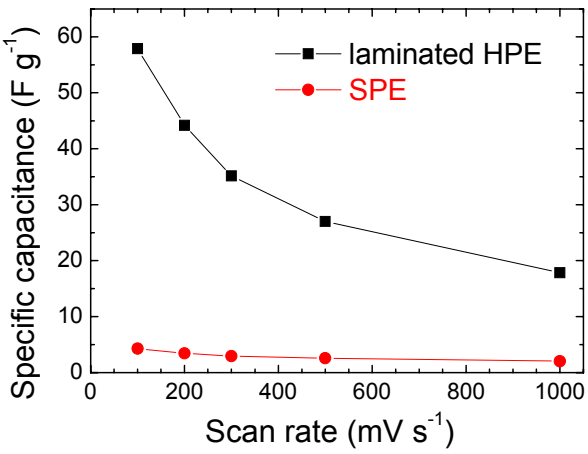

Figure 4. Specific capacitances of the EDLCs as a function of scan rate

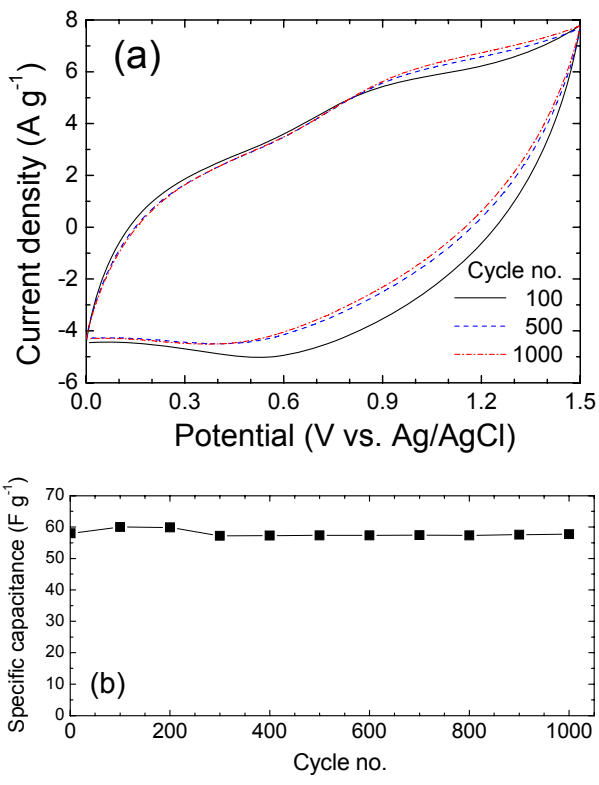

Figure 5. (a) Cyclic voltammograms of the EDLC containing the laminated HPE at 100 mV s^{-1} and (b) the specific capacitance at 100 mV s^{-1} as a function of cycle number.

specific capacitance for the EDLC with the HPE was 60 F g^{-1}, which decreases gradually and attains a stable value of 58 F g^{-1} after the 500th cycle. This excellent tread shown by the EDLC with the HPE makes the HPE a good candidate as a polymer electrolyte system for electrochemical capacitors.

Aside the SWA and H_3PO_4 contributing to the ionic conductivity of the EDLC and leading to high specific capacitance, the PVA as a polymer matrix also plays a significant role in the high specific capacitance of the EDLC. The PVA possess a fairly high degree of hydrophobicity due to the presence of long carbon-chains with few hydrophilic pendant groups,[11] in contrast to hydrogels consisting of natural polymers such as gelatin. The hydrophobic nature of the PVA polymeric component in the hydrogel electrolyte also improves the compatibility between the poly(vinylidene fluoride) binder in the electrode matrix and the hydrogel electrolyte, thereby resulting in good penetrability of the latter within the pores of the electrodes. The PVA also provides the adhesive nature of the laminated HPE ensuring a good contact between the two electrodes with the electrolyte. In addition, the SWA and the H_3PO_4 form a conductive network with the PVA enabling it to provide the required mechanical resistance against the external forces in the HPE.

Ⅳ. Conclusions

In this paper, an EDLC is fabricated using activated carbon electrodes and a proton-conducting adhesive-like HPE, which is started from an aqueous solution of PVA, SWA, and H_3PO_4. Electrochemical tests prove that the EDLC with the HPE has good proton-conductivity, highly stable potential window of 0-1.5 V even though the hydrogel contains the water content of about 50 wt.%. A specific capacitance of 58 F g^{-1} and excellent cycle life for 1000 cycles can be achieved for the EDLC with the HPE at 100 mVs-^{1}, implying that the HPE is attractive for use in electrochemical capacitors.

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