

Desalination performance of a carbon-based composite electrode

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Abstract

In order to enhance the desalination performance of carbon-based composite electrodes, an ion-exchange resin/carbon composite electrode was newly manufactured by mixing activated carbon powders, PTFE binder, and ion-exchange resins. The desalination performance of the electrode was greatly enhanced by about 35% due to enhancement of hydrophilicity compared to that of a conductive carbon black/carbon composite electrode. It was also higher by about 14% than that of a carbon cloth electrode. The results suggest that the desalination performance of the electrode can be improved with the introduction of ion-exchange resins, and the resulting electrode is suitable for use in capacitive deionization.

Keywords: Capacitive deionization; Desalination; Electrosorption; Activated carbon powder; Capacitance

1. Introduction

Capacitive deionization (CDI) is a desalination technology that has been proposed to respond to the demand of economical desalination. It has been recognized as one of the potential technologies reducing operation cost and environ-

mental pollution [1–8]. In capacitive deionization, where inorganic ions are removed by charge separation, carbon electrode is used to adsorb ions on its surface in aqueous solution because it has high surface area, high inorganic ion adsorption in aqueous solutions, cheap price, etc. The materials such as carbon cloth, carbon aerogel, and composite carbon can be used for the

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electrode in CDI. Among the carbon materials, the carbon composite electrode shows the highest capacitance in a 0.5 M NaCl solution and desalination performance [9].

Some studies tried to improve the capacitance of carbon electrodes for various purposes [10,11]. In capacitive deionization for seawater desalination, research for modification of functional groups has been mainly tried to increase the capacitance [12–18], but its effect was not clear.

In this work, we tried to enhance the capacitance and desalination performance of composite electrode by changing it from hydrophobic to hydrophilic. The composite electrode is generally fabricated by mixing activated carbon powders (ACP), binders, and conductive carbons. But capacitance performance of the electrode is somewhat low due to its hydrophobicity. We prepared new composite electrodes by mixing activated carbon powder, polytetrafluoroethylene (PTFE) binder, and ion-exchange resin (IER) to improve capacitance and desalination performance. We examined the morphological characteristics and contact angles of the surface layer of the electrode to investigate its hydrophilicity. And we measured the capacitance and desalination performance of the electrodes and compared it with the electrode fabricated by mixing ACP, binder, and conductive carbon.

2. Experimental

Activated carbon powders (MSP-20, Kansai Coke and Chemicals) serving as the electrode materials were used with a specific surface area of 2340 m²/g. To fabricate various electrodes as shown in Table 1, the slurry mixture consisted of ACP, PTFE and Super-P (SP) or IER was made in isopropyl alcohol solution. Strongly basic anion resins (OH-form) was used as IER (PrAOH, Purolite). The mixture was stirred for 24 h at room temperature. The electrodes were manufactured by pressing the mixture with a roll

Table 1

Electrodes with composition in a different weight ratio

Electrodes	Composition, wt%
CS	ACP:PTFE:SP = 84:4:12
CI-1	ACP:PTFE:IER = 84:4:12
CI-2	ACP:PTFE:IER = 72.4:2.4
CI-3	ACP:PTFE:IER = 60.4:3.6

press. The composition of the electrodes is listed in Table 1.

The contact angles on the surface layers of composite electrodes were tested with a sessile drop method [19]. The electrochemical experiments for cyclic voltammogram (CV) employed an electrochemical analyzer (IM6, Zahner). The cyclic voltammogram was obtained in the potential range of –700 to 700 mV with a scan rate of 2, 6, and 10 mV/s in the three-electrode cell. A three-electrode cell assembly was utilized with an Ag/AgCl reference electrode, a counter electrode of Pt and a working electrode with apparent surface area of 1.0 cm² in 0.5 M NaCl at 25°C.

To compare desalination performance of the CI-1 electrode with the different kinds of electrodes, we tested capacitance and desalination performance of carbon cloth and a general composite electrode. The carbon cloth (CC) made from phenolic resin (Kuraray Chemical, Japan) was used for the test.

3. Results and discussion

To investigate the hydrophilicity of CI electrodes and compare them to that of the CS electrode, we measured their contact angles by fitting a tangent to three-phase point where liquid surface touches the solid surface. We obtained an image of water droplet on the surface of CS, CI-2, and CI-3 electrodes as shown in Fig. 1. We could not obtain image of water droplet on the surface of CI-1 electrode because the water droplet was

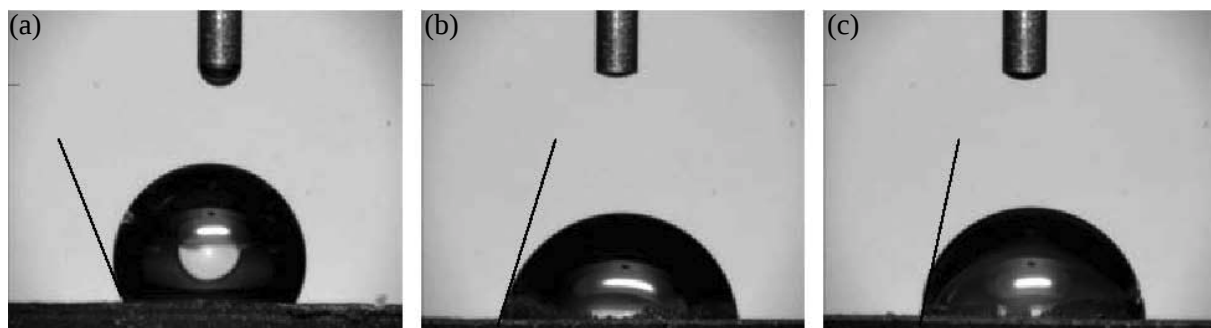


Fig. 1. Contact angle images of water droplet on CS (a), CI-2 (b), and CI-3 (c) electrodes.

absorbed completely as soon as it made contact with the surface of the electrode. The contact angle of CS electrode was 115° . The contact angles of CI-2 and CI-3 electrodes were 75° and 85° , respectively, but the water droplets on the electrodes were absorbed in the electrodes after 3 s. Based on the result, it is obvious that the CS electrode shows stronger hydrophobicity, while the CI electrodes show stronger hydrophilicity, among which CI-1 electrode shows the strongest hydrophilicity.

It can be seen that the hydrophobicity of CS electrode results from the hydrophobicity of all consisting materials: activated carbon powders, PTFE binders, and conductive carbon blacks. It can also be explained that CI electrodes have stronger hydrophilicity than CS electrode because they contain ion exchange resins that have the high capability to absorb water. We believe that CI-1 shows the strongest performance because it contains more activated carbon powders than any other CI electrodes.

SEM images of different composite electrodes are displayed in Fig. 2. CS(a) shows a stronger compactness of carbon powders and carbon blacks. In contrast, CI (b–d) present surfaces that have pores formed by the aggregates of carbon powders and ion-exchange resins. Based on the analysis of the contact angle on the surface of the electrode and the SEM images, we believe that CI electrodes have much more hydrophilic surfaces,

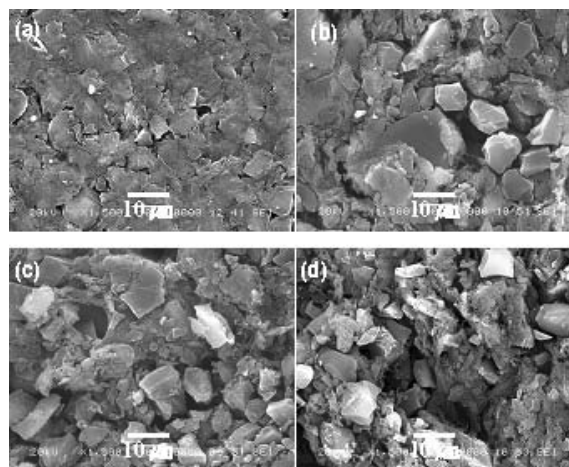


Fig. 2. SEM ($\times 1500$) images of CS (a), CI-1 (b), CI-2 (c), and CI-3 (d) composite electrodes.

which reduce the mass transport limitation from aqueous solution to electrode surface. The pore structure properties of the electrodes were not considered because both carbon powders and ion exchange resins have pores. Although ion-exchange resins have pores, they do not adsorb inorganic ions but they exchange inorganic ions.

Fig. 3 shows the CVs obtained for different electrodes of CS, CI-1, CI-2, and CI-3 at a scan rate of 2 mV/s. The capacitances of the CI electrodes are higher than that of CS electrode. This indicates there is an improvement in capacitive performance as a result of composition of the ACP with the resin. It can be seen that the

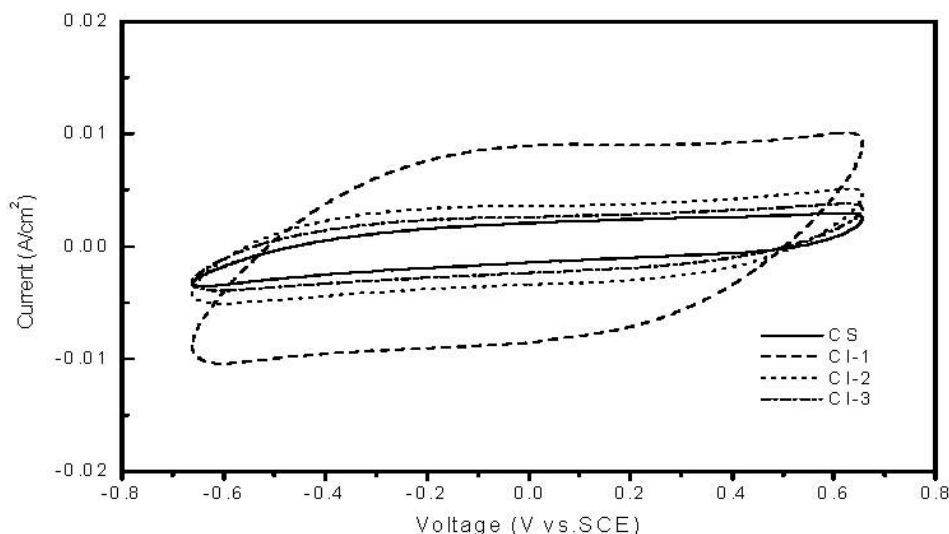


Fig. 3. CVs for CS, CI-1, CI-2, and CI-3 composite electrodes in 0.5 M NaCl at a sweep rate of 2 mV/s.

hydrophilicity of the electrode has a great effect on solvent accessible area. On the other hand, the capacitance of CI-1 electrode is much higher than that of the other CI electrodes. This indicates that the best composition rate is ACP:PTFE:IER = 84:4:12 at low scan rate such as 2 mV/s among the examined in the present study. In our previous paper, we already observed that the one with the composition of carbon powder: binder: conductive carbon black = 84: 4: 12 showed the largest capacity and the best deionization [9].

It can be explained that resins of minimum amounts are needed to be contained in electrodes for hydrophilicity and ACP of maximum amounts are needed to be contained in electrodes for the best desalination performance. The hydrophilicity enhances the capacitance since it helps movement of inorganic ions from aqueous solution to the electrode surface. In our previous paper, we observed the enhancement of the capacitance after the carbon sheet electrode was changed from hydrophobic to hydrophilic by treating it with 1M KOH for 1h at 100 °C [9].

To investigate the desalination performances of the electrodes, CDI cell consisted of two

parallel electrode plates was prepared and 6 electrodes with 100 mm wide × 100 mm long × 0.6 mm thick were used in the cell. NaCl solution with 1,000 ppm NaCl (conductivity of about 2 mS/cm) was used for the test. The solution was pumped in by a peristaltic pump from the bottom and exited from the top of the cell at flow rates of 80 ml/min. And the applied voltage was 1.4 V.

Fig. 4 shows four consecutive operations and regeneration profiles of CS and CIs electrodes. Desalination performances of CS, CI-1, CI-2, and CI-3 electrodes were displayed with the outlet solution conductivity of test equipment. The graphs show the same pattern in 100 cycles except the first cycle. In the first cycles, electrodes do not exert perfect desalination performance due to the dried condition of electrodes. The maximum desalination rate observed after 240 s was 26% for the CS electrode. The maximum desalination rates observed after 120 s were 60% for CI-1, 36% for CI-2, and 33% for CI-3. The desalination rates of all CIs are higher than CS. The desalination rate of the CI-1 is much higher than those of other CIs and is greatly enhanced by about 35% than CS. The results

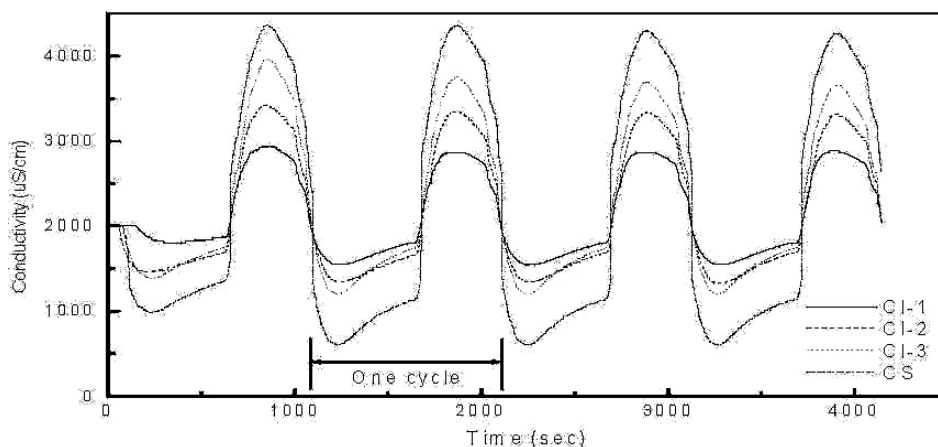


Fig. 4. Desalination performances of CS, CI-1, CI-2, and CI-3 composite electrodes.

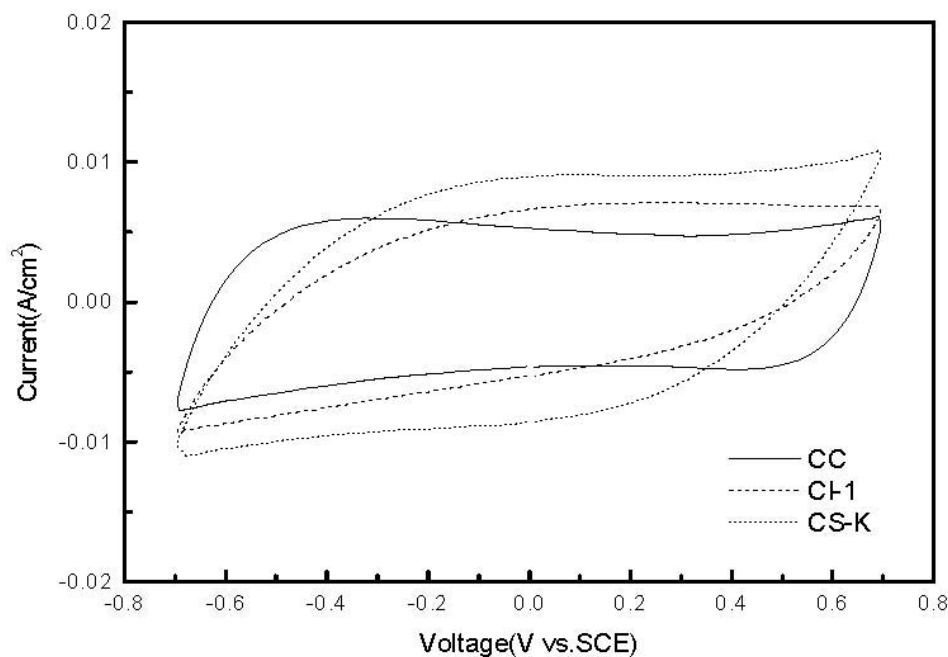


Fig. 5. CVs for CC, CI-1, and CS-K electrodes in 0.5 M NaCl at sweep rate of 2 mV/s.

from Fig. 4 indicate that the order of desalination rate for the electrodes matches with the order of capacitance for the electrodes shown in Fig. 3.

It can be seen that the desalination performance of carbon electrode depends on the hydrophilicity of the electrode and the amount of carbon powders in the electrode. In the hydro-

philic electrode, the hydrated ions are easy to move from water to the surface of carbon pore.

For additional assessment in desalination performance of the CI-1, its capacitance was compared to those of carbon cloth (CC), commercialized carbon material, and CS-K, KOH-treated CS. The CS-K is the carbon sheet electrode

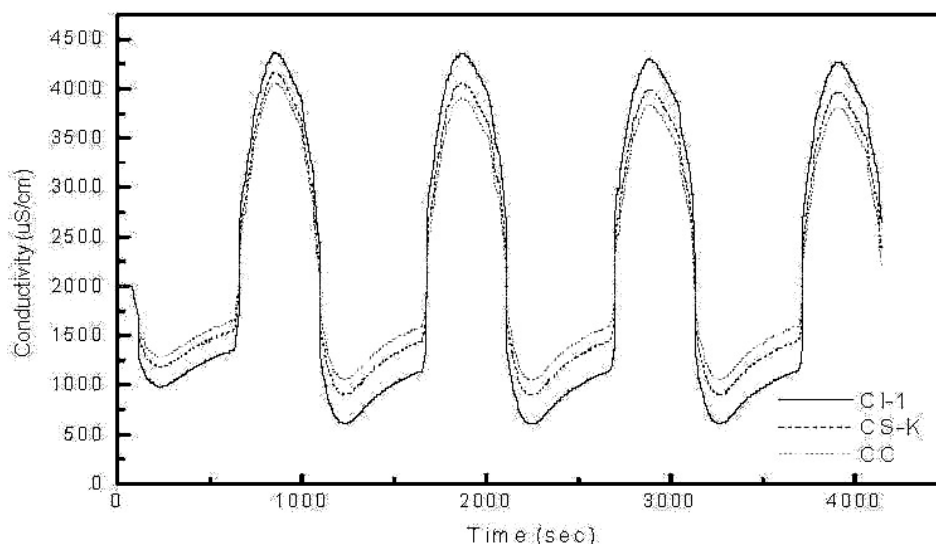


Fig. 6. Desalination performances of CC, CI-1, and CS-K electrodes.

treated with 1 M KOH for 1 h at 100°C. In our previous paper, the CS electrode that showed the best performance was prepared by mixing 84 wt% carbon powder, 4 wt% binder, and 12 wt% conductive carbon black. The capacitance of CS-K was 19.2 F/g in 0.5 M NaCl at 25°C and at the potential of -0.7 – 0.7 V with a scan rate 2 mV/s [9]. Its capacitance was higher than those of carbon aerogel (7.2 F/g), carbon cloth (9.4 F/g), carbon felt (8.2 F/g), and carbon paper (2.4 F/g). The capacitance of CI-1 is higher than that of CC and CS-K as shown Fig. 5.

The desalination performance of CI-1 is also better than the others as shown in Fig. 6. The maximum desalination rates of CI-1 were higher by 14% and 11% than CC and CS-K, respectively. These results match well with the order of capacitance for the electrodes shown in Fig. 5.

4. Conclusions

A new carbon composite electrode that shows better desalination performance, compared to other carbon electrodes such as carbon cloth and

general composite electrode, was developed for capacitive deionization. The new electrode was fabricated by mixing activated carbon powders of 84 wt%, PTFE binder of 4 wt%, and ion-exchange resin of 12 wt%. Compared to the desalination performance of conductive carbon black/carbon composite electrode, the desalination performance of the electrode was greatly enhanced by about 35% because of enhancement of hydrophilicity. It was also higher by about 14% than the carbon cloth electrode. These results suggest that the desalination performance of the electrode with ion-exchange resins can be improved and the electrode can be suitably applied to capacitive deionization.

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