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A carbon electrode fabricated using a poly(vinylidene fluoride) binder controlled the Faradaic reaction of carbon powder

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ABSTRACT

A carbon electrode for capacitive deionization (CDI) was fabricated by casting a slurry that was a mixture of activated carbon powder (ACP) and poly(vinylidene fluoride) (PVdF) dissolved in di-methylacetamide (DMAc) on the current collector. Electrochemical properties and adsorption/desorption behaviors of the carbon electrodes prepared with different PVdF contents (9–18 wt%) were characterized using cyclic voltammetry, chronoamperometry, and impedance spectroscopy methods. From the SEM images, carbon powders were coated with the PVdF binder and bound together. Capacitances of carbon electrodes were estimated in the range of 75.3–69.6 F/g, decreasing in tandem with PVdF contents, but the decrease was not significant. From cyclic voltammetric and chronoamperometric measurements, the electrochemical behaviors of the carbon electrodes were dependent not only on the electric double layer capacitance, but also on Faradaic reactions. However, Faradaic currents resulted from an electrochemical redox reaction of carbon surface controlled by the polymer binder. These results indicate that the electrochemical reaction on the carbon surface was suppressed due to the PVdF binder.

1. Introduction

The removal of ionic species from aqueous solutions is of great importance in environmental and industrial processes such as desalination of seawater, removal of hardness species for boiler feed water, and production of ultrapure water [1,2]. The main conventional desalination processes include thermal evaporation, ion exchange, reverse osmosis (RO), and electrodialysis (ED). Among these processes, a proper process is selected and applied according to the types of ions and the concentration of salt. Each of these methods has some advantages and drawbacks. In thermal evaporation, the operating principle and equipment are simple, but the energy consumption is very high. Using the ion exchange method, a high concentration of salt waste is generated during the regeneration of ion exchange resins. The RO and ED cause problems with flux decline due to the membrane contamination [3].

Concerns about environment and energy problems have increased over recent years from a global viewpoint. As a promising answer to these problems in desalination technology, many studies have been performed on capacitive deionization (CDI) [4–11]. CDI (or electrosorption) is defined as potential-induced adsorption of ions on the surface of the charged electrode. One of the big advantages in CDI technology is that it reduces power consumption because it operates at lower electrode potential (about 1–2 V) at which no electrolysis reactions occur. During the CDI operation, charged ions are held in the electric double layer (EDL) at the electrode surface, and once the potential is removed, adsorbed ions are quickly released back to the bulk solution. Thus, CDI has been touted as an environmentally friendly process because no acid, base, or salts are required to generate the surface [10,12,13].

Because the CDI process uses an adsorption reaction on the electrode surface, it is very important to increase the specific capacitance of the electrode. Accordingly, many studies have been conducted to manufacture an electrode for the CDI process from activated carbon cloth [14,15], carbon felt [16], carbon nanotubes [17,18], and carbon aerogels [5,6,9,19–21]. Even though these carbon materials are known to have high specific surface area and excellent electrical conductivity, these electrode materials have the disadvantages of relatively complicated manufacturing processes and higher costs for CDI application. Activated carbon powder (ACP) is known to be an inexpensive yet good electrode material with a high specific area. However, to manufacture an electrode, it is necessary to fix ACP by adding a polymer binder. In general, the process of manufacturing an electrode using ACP involves blending the ACP and polymer powder, coating the current collector, and compressing the resulting mixture with a roll press at a higher temperature [22].

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The basic operating principle of CDI is similar to the electric double layer capacitor (EDLC). Both CDI and EDLC use adsorption and desorption processes in an electrical double layer at the electrode surface. However, the electrode properties required for CDI differ from those of EDLCs. In EDLCs, the electrolyte is maintained in a stagnant state, whereas the brine solution flows between the electrodes for CDI. Accordingly, the electrode for CDI should have a higher mechanical strength than that of EDLCs. In addition, the Faradaic current in EDLCs, which contributes pseudocapacitance, could increase the capacitance of the capacitor [23,24], whereas the Faradaic reaction can diminish the sorption efficiency and change the pH of effluent by an electrochemical reaction in the CDI process. Hence, it is necessary to make an electrode for CDI application that has a proper mechanical strength and that suppresses the Faradaic reaction on the carbon surface.

In this study, we fabricated a carbon electrode through a drying process after casting a slurry blended with ACP in a polymer solution on the current collector. The effect of the polymer binder on the electrochemical properties and electrode reaction was investigated for electrodes prepared with various polymer binder contents. Electrochemical methods such as cyclic voltammetry (CV), chronoamperometry (CA), and impedance spectroscopy (IS) were applied to characterize the electrochemical properties of the electrodes.

2. Materials and methods

2.1. Fabrication of carbon electrodes

To fabricate a carbon electrode, a carbon slurry was prepared by mixing a solution of activated carbon powder (P-60, Daedong AC Corp., specific surface area = 1260 m^2/g) and poly(vinylidene fluoride) (PVdF, M.W. = 275,000, Aldrich) dissolved in di-methylacetamide (DMAc, Aldrich). The mixture was stirred for 12 h to ensure homogeneity. The slurry was then casted on a graphite sheet (F02511, Dongbang Carbon Corp., Korea) using a doctor blade 300 μm thick. The coated electrode was dried at 50 °C in a drying oven for 2 h and then in a vacuum oven at 50 °C for 2 h to remove all organic solvents remaining in the micropores of the electrode. After the electrode was dried, the weight was measured to determine the amount of carbon coated on the graphite sheet. Four carbon electrodes samples were prepared with different PVdF contents (9–18 wt%). The compositions of the carbon electrodes are summarized in Table 1.

The carbon electrodes were soaked in 0.5 M KCl solution for 24 h to analyze electrochemical properties. Prior to electrochemical measurement, the carbon electrodes were vacuum impregnated in the electrolyte to remove any adsorbed gases from the inner pore volume [25].

2.2. Physical and electrochemical characterization of the carbon electrodes

The surface and cross-section of the electrode were observed with SEM (JSM-6335F, JEOL) to determine the physical structure of the manufactured carbon electrode.

Table 1
Compositions of the carbon electrode prepared in this study.

Electrodes	ACP (g)	PVdF (g)	DMAc (g)
PVdF09	10.0	0.99	25.0
PVdF12	10.0	1.36	25.0
PVdF15	10.0	1.77	25.0
PVdF18	10.0	2.20	25.0

To examine the electrochemical properties and electrochemical behaviors of the prepared carbon electrodes, cyclic voltammetry (CV), chronoamperometry (CA), and electrical impedance spectroscopy (EIS) were measured using a 3-electrode system. The carbon electrode specimen was inserted into the specimen holder with an exposed surface area of 1.77 cm^2. A platinum net and a saturated Ag/AgCl electrode were used as a counter electrode and a reference electrode, respectively.

Voltage on the test electrode was controlled by an AutoLab PGST30 potentiostat combined with a FRA impedance analyzer. The electrolyte solution used was 0.5 M KCl. All experiments were maintained in water bath at 25 ± 0.1 °C.

Cyclic voltammetric measurements for the electrodes were made in the potential range of −0.5 to 0.5 V (vs. Ag/AgCl). The potential scan rate ranged from 5.0 to 15 mV/s. The current decay transient measurement (chronoamperometry) was measured to investigate changes in charging and discharging current. For this measurement, a charging potential of −0.15 V (potential step, ΔE = 50 mV) was applied for 10 s from −0.10 V followed by discharging at −0.10 V for 10 s, and the resulting current transients were obtained every 0.1 s by the potentiostat.

To examine inner resistance and capacitance according to frequency, an impedance measurement was performed with an AutoLab FRA impedance analyzer on the carbon electrodes. The impedance spectra were obtained at a potential of 0.0 V in the frequency range of 100 Hz to 20 mHz. An alternating sinusoidal signal of 25 mV peak-to-peak was superimposed on the dc-potential.

3. Results and discussion

3.1. Surface structure measurement

Fig. 1 shows the SEM images of the cross-section of the manufactured carbon electrode. Activated carbon powders of diverse particle size formed a uniform electrode layer. The thickness of the electrode was about 130 μm. Although the electrode slurry was cast to be 300 μm thick, it was reduced by more than half during the drying process.

As shown in Fig. 1, ACP was covered with PVdF binder, and they bound together. Actually, ACPs of the carbon electrodes prepared in this study did not fall off when the electrode surface was rubbed by hand. Judging from this test, the carbon electrodes appeared to have enough mechanical strength to be durable against the shear stress of the influent flow. On the contrary, it is anticipated that the specific capacitance and electrical resistance of the electrode can be increased by the PVdF binder.

3.2. Cyclic voltammetric analysis

The cyclic voltammetric measurement on the carbon electrodes was conducted within a potential range of −0.5 to 0.5 V vs. Ag/AgCl. Fig. 2 shows the cyclic voltammograms obtained from the PVdF15 electrode at different potential sweep rates. Voltammograms were nearly rectangular in shape within applied potential ranges in which current quickly reached a plateau value after reversal of the potential sweep. This means that ions were adsorbed or desorbed according to the applied potential effectively within the electric double layer at the electrode surface by the electrostatic force [24,26]. Also, the anodic and cathodic charging currents linearly increased according to the potential sweep rate in the cyclic voltammograms.

An ideal capacitor would create a rectangular shape on a cyclic voltammogram. As can be seen in Fig. 2, however, a gradual increase of anodic (I_a) and cathodic (I_c) currents at about 0.1 and −0.1 V, respectively, was observed for the carbon electrode. It is

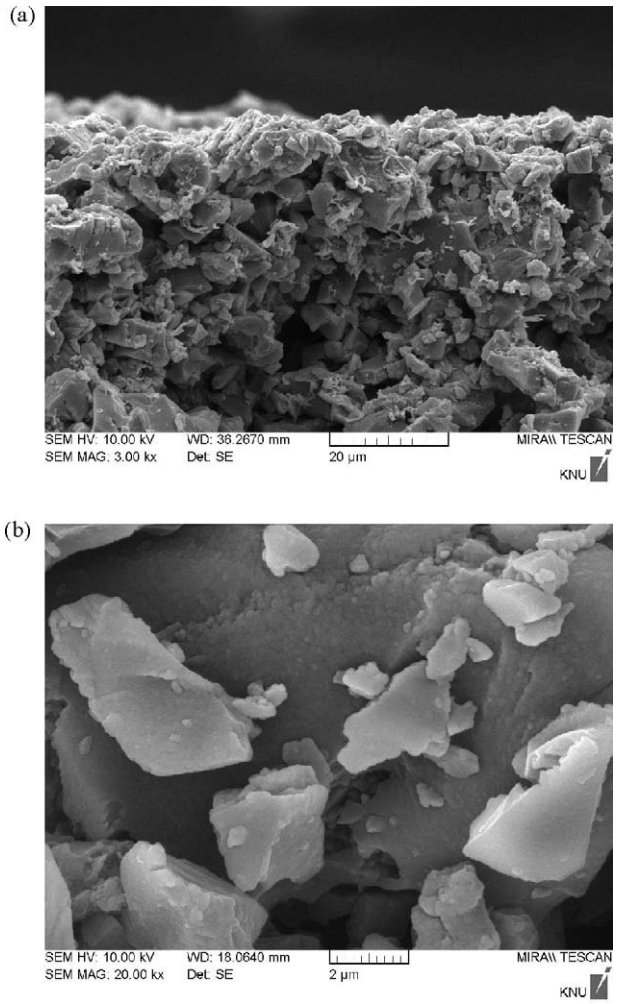

Fig. 1. SEM images of the PVdF15 electrode: (a) cross-sectional view (3000×) and (b) top view (20,000×).

known that the deviation from the rectangular shape of cyclic voltammogram is due to the Faradaic current [24]. The functional groups on the carbon surface, i.e., carbonyl and quinine groups, influence current changes by electrical oxidation and reduction reactions. From the cyclic voltammograms, the electrochemical

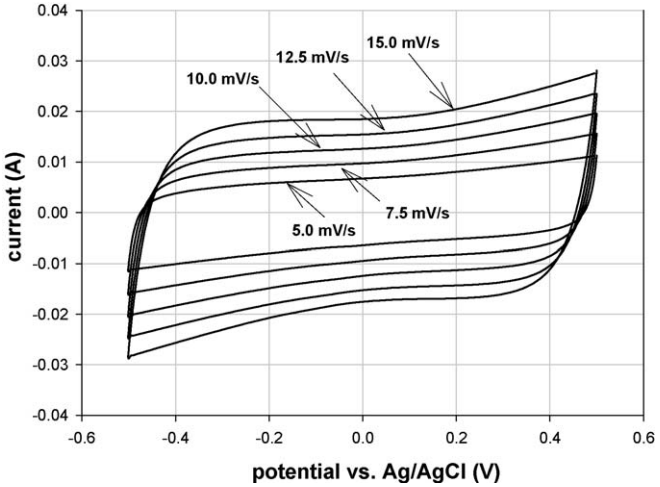

Fig. 2. Cyclic voltammograms measured on the PVdF15 electrodes at different potential sweep rates.

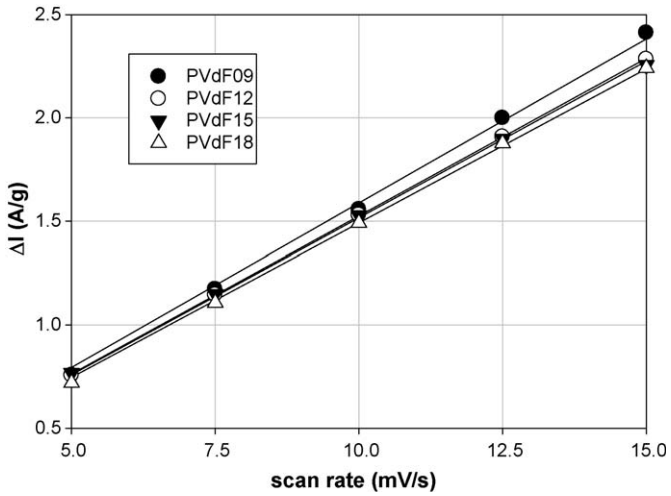

Fig. 3. Variation of ΔI (the difference between anodic and cathodic charging current) with potential sweep rate in cyclic voltammograms.

behavior of the prepared carbon electrodes appeared dependent not only on the charging current in the electric double layer, but also on the Faradaic currents [23,24,27].

The best way to calculate capacitance from the cyclic voltammograms with a finite Faradaic current is to conduct measurements over a range of sweep rates, obtaining the capacitance from the plot of $\Delta I(=I_a - I_c)$ against the potential sweep rate [28]. The ΔI values at a certain sweep rate were found to be nearly invariant over the majority of potential range. The values of ΔI of different electrodes obtained with various sweep rates are shown in Fig. 3. The capacitance of the electrodes can be estimated from the slope of the linear relationships in Fig. 3. Calculated capacitances are listed in Table 2. As can be expected, the specific capacitance decreases slightly with the PVdF contents, which may be attributed to the PVdF binder that covers the ACP surface, resulting in a reduction of surface area of the carbon powder. It is noticeable that the reduction of specific capacitance was not significant even when the polymer content increased in preparation for the electrode.

3.3. Chronoamperometric analysis

To understand the charging/discharging behaviors and the electrode reaction mechanism, a potential step method (chronoamperometry) was performed on the prepared carbon electrodes [29]. A charging potential of −0.15 V (potential pulse = 50 mV) was applied from −0.10 V, followed by a discharging potential of −0.10 V, and the resulting current transients were obtained. Resulting chronoamperograms for the PVdF12 electrode are shown in Fig. 4. When a potential was applied to the electrode, the current exponentially decreased and approached zero. Notably, the current for the sorption process was clearly higher than that for the desorption process. If no Faradaic reaction occurred on the

Table 2
The specific capacitances determined by various electrochemical methods.

Electrode	Specific capacitance (F/g)			
	Cyclic voltammetry	Chronoamperometry	Impedance spectroscopy	Average
PVdF09	79.4	73.4	73.1	75.3
PVdF12	76.3	70.7	69.0	72.0
PVdF15	75.8	69.0	67.8	70.9
PVdF18	74.6	68.2	66.0	69.6

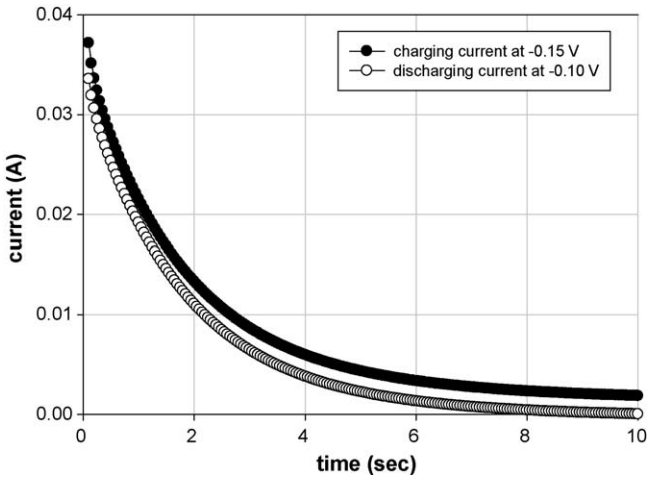

Fig. 4. The changes in current with time during the charging and discharging process for the PVdF12 electrode.

electrode surface, the charging current would converge to zero. Thus, the current responses of chronoamperogram indicate that Faradaic reactions occurred when a charging potential was applied.

Capacitances were estimated from the chronoamperometric results by fitting the current transients with the following equations; the results are listed in Table 2 [29].

$$I(t) = \left(\frac{\Delta E}{R}\right)\exp\left(\frac{-t}{RC}\right),$$

where ΔE is step potential, R is equivalent series resistance, and C is the specific capacitance. The capacitance values determined by chronoamperometry methods were slightly lower than were those obtained from a cyclic voltammetry method.

The effect of PVdF content on the Faradaic current was investigated. Faradaic current at a certain time corresponds to the current difference between charging and discharging current. Fig. 5 shows the Faradaic current as a function of time for different carbon electrodes. Faradaic current decreased slightly as time went on. Moreover, the current was reduced with increasing PVdF content. Especially, the Faradaic current sharply decreased for the PVdF18 electrode. These results indicate that the electrochemical reaction on the carbon surface was suppressed due to the PVdF binder.

Faradaic current is an electric current that corresponds to electron transfer between electrode and chemical species resulting in oxidation or reduction of the species. It has been known that the oxygen functional groups on carbons such as carbonyl- or quinine-type functional groups can induce Faradaic current [24]. As can be seen in the SEM image of the carbon electrode, activated carbon powders were covered with PVdF polymer binder. It is suggested that the redox activity of the functional groups on carbons is affected by the coverage of the PVdF polymer binder. As a consequence, the Faradaic current was found to decrease with the extent of the polymer binder.

CDI technology may be attractive for desalination of low salinity brackish water and for removing trace contaminants such as hardness and metal species. Obviously the carbon electrode having much larger specific adsorption capacity is profitable for the CDI application. However, one of the drawbacks that limit the commercialization of CDI process is scaling by precipitation of sparingly soluble salt. Scale formation in the CDI process can be occurred in the cathode because the cations adsorbed on the cathode such as calcium, magnesium, and heavy metal ions can make easily insoluble salt by combining with the hydroxyl ions generated from the electrochemical reaction. Therefore, it is very important to control the electrode reaction on the carbon surface. The addition of a polymer binder is a feasible solution to control the redox reaction that occurred in the carbon electrode.

3.4. Impedance spectroscopic analysis

The best method to measure double layer capacitance is to assess electrochemical impedance spectroscopy measurements [28]. Specific capacitance (C) can be derived from the imaginary part (Z'') of the impedance spectra according to [30]:

$$C = \left|\frac{1}{\omega Z''}\right|,$$

where ω denotes the angular frequency of the applied ac-signal.

Specific capacitances determined by impedance spectroscopy are shown in Fig. 6 as a function of frequency.

Capacitances increased steeply with decreasing frequency up to about 0.2 Hz. The ac-signal can attain and charge more inner surface sites of the carbon electrode with decreasing frequency, resulting in a higher capacitance. At frequencies below 0.2 Hz, the signal attains almost the total surface of the carbon, so that the capacitance remains at almost a constant value [25,30]. As shown in Fig. 6, capacitances decreased with PVdF binder content

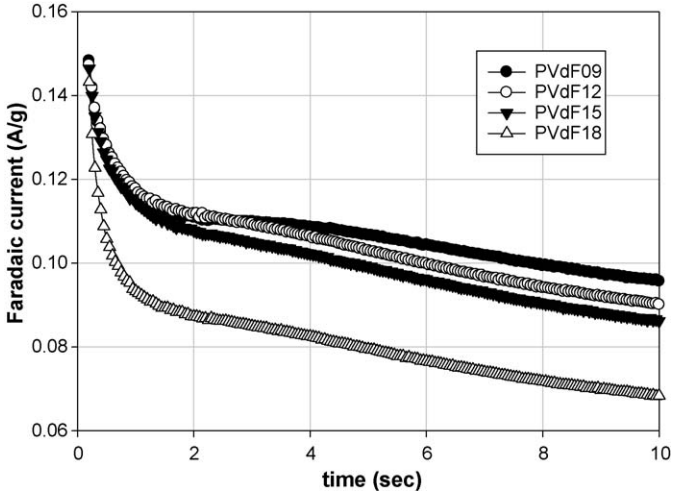

Fig. 5. Faradaic current (the difference between charging and discharging current) for the carbon electrodes prepared with different PVdF contents.

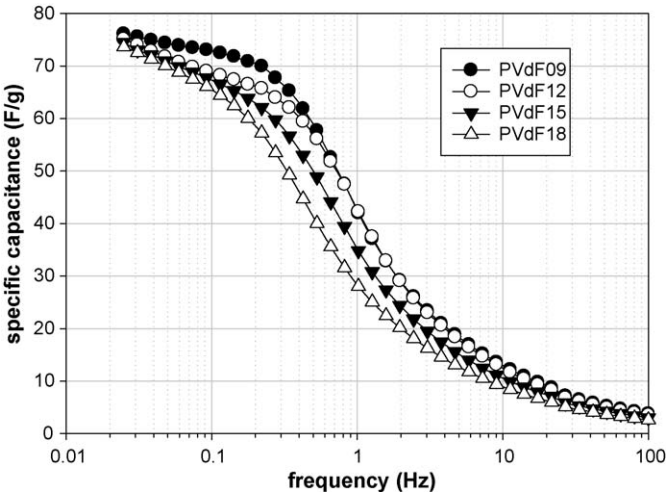

Fig. 6. Specific capacitances of the various carbon electrodes derived from impedance data as a function of frequency.

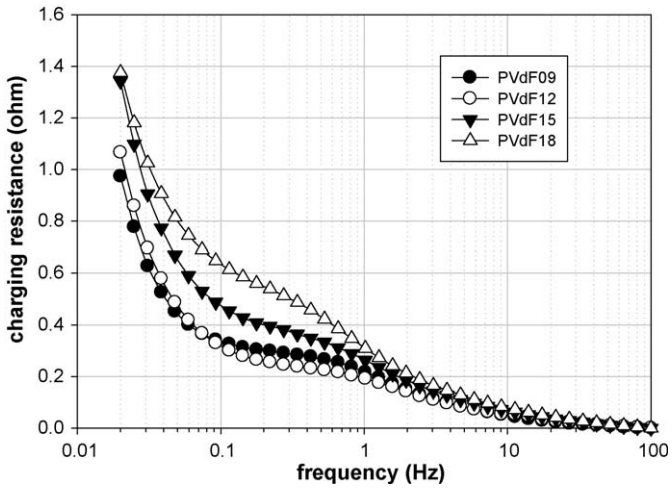

Fig. 7. Charging resistance of the various carbon electrodes derived from the impedance data as a function of frequency.

throughout the entire range of frequencies measured. Capacitances at the frequency of 0.1 Hz are listed in Table 2. Specific capacitances obtained by various electrochemical methods have showed similar values. Thus, CV, CA, and EIS methods effectively determine the capacitance of the carbon electrode.

Propagation of the ac-signal into inner pore structures includes longer electrolyte pathways, which results in an increasing real component (charging resistance) of the impedance [30]. Charging resistance corresponds to real part of the impedance minus the high frequency resistance (at 100 Hz) [25]. Fig. 7 shows the charging resistance for various carbon electrodes as a function of frequency. For all electrodes, no significant changes in charging resistance were observed up to about 1 Hz, but the charging resistance showed definite differences at frequencies below 1 Hz, and these differences increased with PVdF content. This effect can be ascribed to narrow pathways in the carbon powder due to the PVdF binder.

4. Conclusion

An electrode for a CDI application should have higher specific capacitance and proper mechanical strength to withstand the shear stress of flow passed through the electrode surface. For these purposes, a carbon electrode was fabricated through a drying process after casting a slurry blended with ACP in a polymer solution on the current collector.

From the SEM images, ACP was covered with the PVdF binder, and they bound together, which led to high mechanical strength. Specific capacitances decreased with increasing the PVdF binder content, but reduction of specific capacitance was not significant even with polymer content increases. Moreover, charging currents of the carbon electrodes were dependent not only on the electric double layer capacitance, but also on the Faradaic reactions. However, the Faradaic currents resulted from an electrochemical redox reaction at the carbon surface were controlled by the polymer binder. The experimental results of this study indicate that a carbon electrode fabricated with a mixture of activated carbon powder and polymer binder may yield an effective and applicable electrode for the CDI process.

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