



Electrode reactions and adsorption/desorption performance related to the applied potential in a capacitive deionization process

Jae-Hun Lee^a, Wi-Sup Bae^b, Jae-Hwan Choi^{a,*}

^a Department of Chemical Engineering, Kongju National University, 275, Budae-dong, Seobuk-gu, Cheonan, Chungnam, 331-717, Republic of Korea

^b Department of Earth and Environmental Sciences, Sejong University, 98 Gunja-dong, Gwangjin-gu, Seoul, 143-747, Republic of Korea

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ABSTRACT

Desalination experiments were performed by constructing a capacitive deionization (CDI) unit cell with a carbon electrode prepared from activated carbon powder (ACP). Through CDI experiments, the mechanism of adsorption, desorption and electrode reactions were investigated by measuring conductivity, effluent pH, and the current passed through the cell under different electrode potentials. The salt-removal efficiency increased with increasing potential at the range of 0.8–1.5 V. Additionally, the pH of the solution varied significantly with a change in potential. At potentials less than 1.0 V, the pH increased due to the reduction of dissolved oxygen and the pH decreased at potentials over 1.2 V due to oxidation reactions at the anode. The change in current revealed that adsorbed ions were not completely desorbed and a fraction of ions were retained at the carbon electrode. These accumulated ions were re-adsorbed at the electrode surface when a potential was re-applied, which led to a decrease in the salt-removal efficiency of CDI.

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1. Introduction

Due to the recent focus on issues related to energy and the environment, the study of capacitive deionization (CDI), a salt-removal technology, is actively pursued [1–3]. CDI uses the principles of ionic adsorption on the electrode surface due to electrostatic force. When the electrode is charged, ions with opposite electric charge move to the electrode and form an electric double layer (EDL). When the electrode is discharged, ions are desorbed from the electrode surface and move back into bulk solution [4].

The CDI process is simple to operate because ions can be readily adsorbed or desorbed by changing the potential of the electrode. CDI is an environmentally friendly process because contaminants are not produced during the regeneration of electrodes. Energy consumption is also greatly reduced because CDI is operated at a low potential and electrolysis does not occur at the electrode [5–8].

Most studies related to CDI have focused on the preparation of electrodes in order to increase capacitance. Various carbon materials with a high specific surface area and good conductivity have been used to produce electrodes for CDI. High-performance carbon electrodes have been developed with materials such as carbon cloth, carbon nanotubes, and carbon aerogels [9–15].

To increase the capacitance of the electrode, the efficiency of salt-removal in CDI must be improved. However, even if an electrode has a constant capacitance, the efficiency of salt-removal can vary greatly

depending on the mechanism of adsorption and desorption on the electrode surface. If all ions adsorbed onto the electrode cannot move back into the bulk solution during the desorption process, the ion concentration on the electrode surface will increase. Thus, when a potential is applied, ions present on the electrode surface are re-adsorbed onto the electrode and the amount of ions transported into the bulk solution is reduced, leading to lower salt-removal efficiency. Therefore, the mechanisms of ion adsorption and desorption, which are related to the applied potential, effect the efficiency of desalination in CDI, and information regarding these processes can be used to improve performance. While most studies related to CDI have focused on improving the performance of the electrode, to date, there have been almost no studies on ionic adsorption and desorption mechanisms relating to the applied potential.

CDI should be operated at the highest possible potential to adsorb more ions onto the electrode. However, an increase in electrode potential is limited because electrode reactions can occur at higher potentials, which not only decrease the efficiency of salt-removal, but also cause serious problems in CDI operation. For example, if hard species or heavy-metal ions are present in the influent, scale can be deposited on the electrode surface as the pH increases. While electrode reactions are obviously an important factor in CDI, to date, no reports on the interpretation of electrode reactions have been published.

In this study, a salt-removal experiment was performed with a CDI unit cell made with a carbon electrode prepared from activated carbon powder. Salt-removal efficiency and electrode reactions were investigated in relation to the applied potential by measuring the electrical conductivity and effluent pH at different applied potentials.

* Corresponding author. Tel.: +82 41 521 9362; fax.: +82 41 554 2640.

E-mail address: jhchoi@kongju.ac.kr (J.-H. Choi).

Adsorption and desorption performances were analyzed by interpreting the correlation between the current passed through the cell and the conductivity of the effluent.

2. Experimental

2.1. Fabrication of porous carbon electrode

To fabricate a carbon electrode, a carbon slurry was prepared by mixing activated carbon powder (P-60, Daedong AC Corp., specific surface area = $1260 \text{ m}^2/\text{g}$) and poly(vinylidene fluoride) (PVdF, M.W. = 530,000, Aldrich) dissolved in dimethylacetamide (DMAc, Aldrich). The mixture was stirred for 12 h to ensure homogeneity. The slurry was then cast onto a graphite sheet (F02511, Dongbang Carbon Corp., Korea) using a doctor blade. 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. The PVdF polymer content of the dried carbon electrode was 10 wt.%.

2.2. Capacitive deionization experiments

Capacitive deionization experiments were conducted in a flow-through system, depicted in Fig. 1. The system consisted of a reservoir, peristaltic pump, CDI unit cell, and conductivity meter. The CDI unit cell consisted of two parallel carbon electrode sheets separated by a non-conductive spacer (nylon cloth, $100 \mu\text{m}$ thick). This prevented an electrical short and allowed liquid to flow. The size of the carbon electrode was $100 \text{ mm} \times 100 \text{ mm}$. Graphite sheets were used as inert current collectors on the back side of the carbon electrodes. A Plexiglas plate was used to assemble the upper and lower parts of the unit cell.

A flow channel was created by punching a hole with a diameter of 1 cm in the center of the electrode so that the solution was in contact with all sides of the electrode and could flow through a spacer to the central hole. A solution with 200 mg/L NaCl was supplied to the cell using a peristaltic pump at a flow rate of 20 mL/min .

A given potential was applied to the CDI cell using a potentiostat (WPG100, WonA Tech Corp.). An adsorption test was conducted while applying a pre-established potential for 10 min and a desorption test

was conducted for 5 min immediately following the adsorption test by changing the electrode potential to 0 V. The conductivity and pH of the effluent passing through the cell were measured by connecting a conductivity (CON-BTA, Vernier Corp.) and pH sensor (Orion 8102BNUWP, Thermo Electron Corp.) to the exact location of the cell where the solution was released. The conductivity and pH were automatically measured at intervals of 1.0 s by connecting the conductivity and pH sensor to the interface (LabQuest, Vernier Corp.). CDI was conducted at 0.8, 1.0, 1.2, and 1.5 V potentials to compare the efficiency of salt-removal at these potentials.

3. Results and discussion

3.1. Conductivity changes of effluent with varying applied potential

Fig. 2 shows the conductivity of the effluent as the applied potential was varied from 0.8 to 1.5 V.

As soon as a potential was applied, conductivity was abruptly reduced as ions were adsorbed onto the surface of the electrode. As the potential increased, a further reduction in conductivity was observed. When potentials of 0.8, 1.0, 1.2, and 1.5 V were applied to the CDI cell, the conductivities were reduced by 112, 94, 63, and $29 \mu\text{S/cm}$, respectively. The conductivity increased slowly as the sorption capacity of the electrode became saturated. As calculated from conductivity results, the amounts of NaCl adsorbed over 10 min under varying potentials were 5.64, 8.24, 12.22, and 15.42 mg , respectively. Thus, the amount of NaCl adsorbed increased linearly as the potential increased.

Changes in the conductivity of effluent during desorption are also shown in Fig. 2. Here, a potential was applied for 10 min and a desorption potential of 0.0 V was applied immediately after adsorption. Conductivity rapidly increased after the desorption potential was applied, as ions were immediately desorbed. The amount of desorbed ions increased according to the prior adsorption potential and when 1.5 V of potential was applied, the conductivity increased up to $2653 \mu\text{S/cm}$ during desorption. In the desorption process, most of the adsorbed ions were desorbed within 2 min of applying a desorption potential. This indicates that desorption proceeded rapidly and the regeneration of the electrode during CDI was facile. Thus, the recovery ratio of the influent can be increased by reducing desorption time.

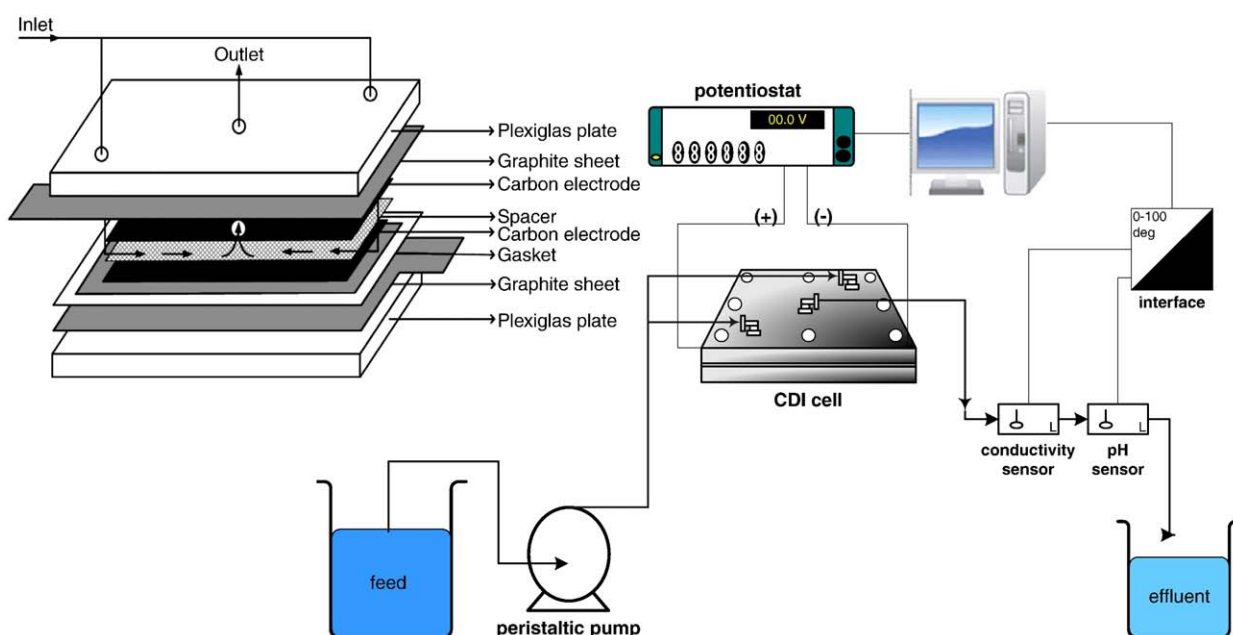


Fig. 1. Schematic diagram of capacitive deionization (CDI) experiments.

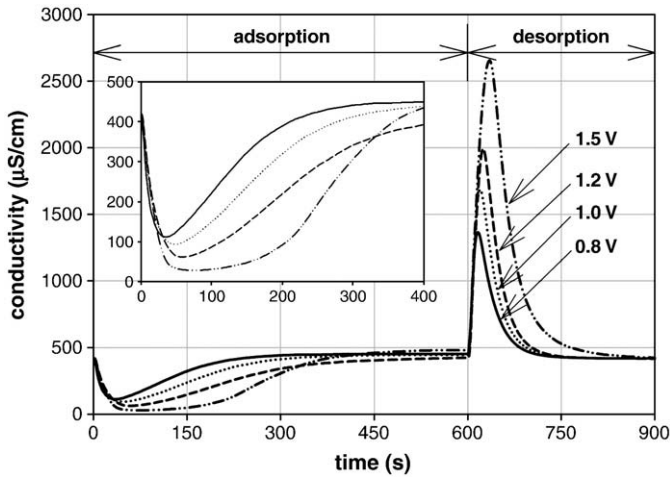


Fig. 2. Changes in conductivity at various applied potentials.

At each potential, the salt-removal efficiencies (η_t) as a function of adsorption time t , were calculated with the following equation and the results are shown in Fig. 3.

$$\eta_t(\%) = \left(1 - \frac{\int_0^t C_{\text{eff}} dt}{tC_0}\right) \times 100 \quad (1)$$

where C_0 is the initial concentration of feed solution, C_{eff} is the effluent concentrations and t is an adsorption time. The salt-removal efficiency increased as the cell potential increased: when 1.5 V was applied, the salt-removal efficiency up to 83.4% could be obtained. The removal efficiency decreased over time because the adsorption capacity of the electrode became saturated and the salt concentration of the effluent increased. If a salt-removal efficiency of 80% or above is the goal for CDI under a potential of 1.2 V, then the flow rate should be reduced. Conversely, a salt-removal efficiency over 80% could be obtained with an adsorption time of 250 s at 1.5 V and a flow rate of 20 mL/min.

3.2. Electrode reactions and the change in pH according to the applied potential

The pH of the effluent was measured at several applied potentials and the results are shown in Fig. 4. At potentials less than 1.0 V, the pH rapidly increased and reached a constant value as the potential was

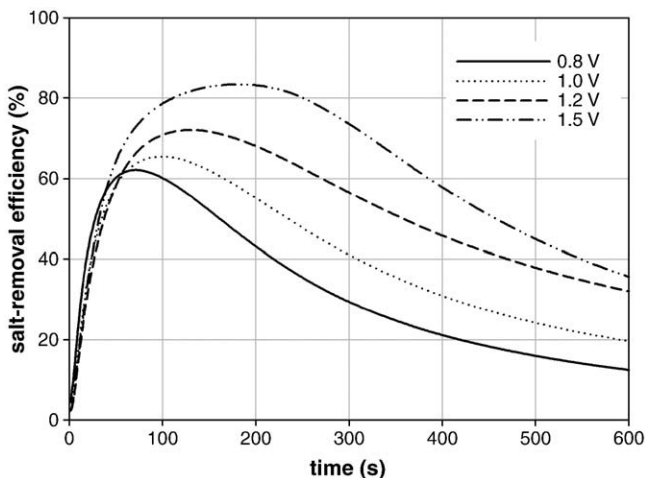


Fig. 3. Changes in salt-removal efficiencies as a function of adsorption time at various applied potentials.

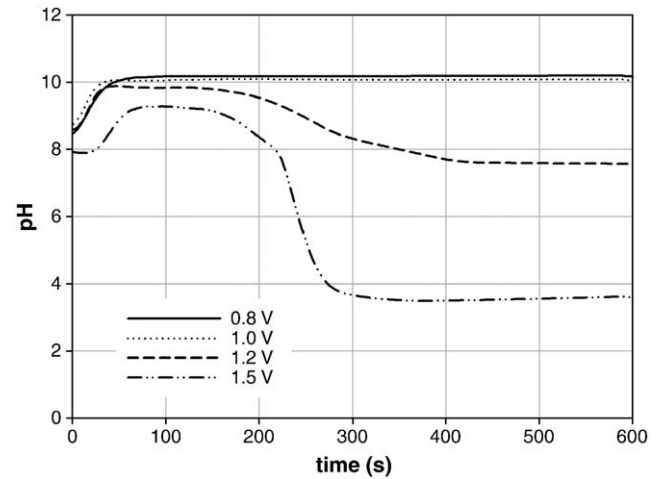


Fig. 4. Change in the effluent pH during adsorption at different potentials.

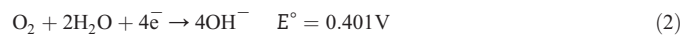
applied. However, at potentials over 1.2 V, the pH initially increased and then decreased, reaching a constant value that was lower at higher potentials.

The change in effluent pH is caused by reactions at the electrode and by the adsorption of ions with different equilibrium constants for hydrolysis. In this work, however, the pH changes induced from the adsorption of ions could be ignored because the feed solution was prepared by dissolving NaCl. CDI is generally operated within a potential range where electrode reactions do not occur [16,17]; however, as evidenced in the pH results, reactions occurred at the electrode at a low potential of 0.8 V.

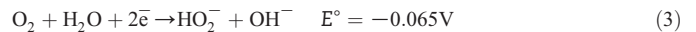
Reactions at the carbon electrode can vary greatly depending on the surface functional groups present on the electrode and the species present in the influent. The pH rapidly increased and remained constant at a value of 10.1 when the potential was 0.8 V or 1.0 V. A basic and constant effluent pH indicates that a reaction generating OH^- is occurring at the cathode at a constant rate. This may be caused by the reduction of dissolved oxygen (DO) from the influent.

Under alkaline conditions, dissolved oxygen is known to undergo reduction reactions on the surface of a cathode through two pathways, as shown below [18].

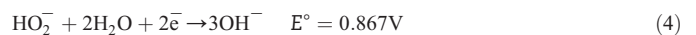
(1) Direct four-electron pathway:



(2) Peroxide pathway:



followed by the reduction of peroxide:



In the first pathway, DO is directly reduced on the surface of the cathode and OH^- is produced. In the second pathway, DO is reduced to form peroxide, which is reduced to OH^- . Regardless of the pathway, OH^- is produced when DO is reduced at the cathode. Hydroxyl ions generated from the reduction of DO move to the anode where oxidation of hydroxyl ions can occur to produce oxygen (reverse reaction of Eq. (2)).

At potentials over 1.2 V, the pH of the solution gradually decreased, and at 1.5 V, the pH decreased to 3.5. The pH did not decrease

immediately; rather, it increased for a period of time and then rapidly decreased. The pattern of pH change is likely caused by the oxidation of Cl^- at the anode by the following oxidation reaction [19];



followed by the disproportionation of chlorine:



When a potential is applied, the concentration of Cl^- on the surface of the anode gradually increases as Cl^- is adsorbed on the anode. At early stages of potential application, the pH increases because the reaction in Eq. (5) does not occur to a significant extent. Chloride oxidation is not prevalent at early stages because the concentration of adsorbed Cl^- is not high enough for the reaction to proceed appreciably. However, as adsorption progresses and the concentration of Cl^- increases, the pH rapidly decreases due to the oxidation of chloride.

Another reaction at the anode which can decrease the pH of the solution is the oxidation of the carbon electrode itself. The mechanism of the electrochemical oxidation of carbon is postulated to be



In practice, anode potentials of 0.7 to 0.9 V (vs. NHE) are required to oxidize carbon [18].

From the change in effluent pH with varying cell potential, electrochemical reduction of dissolved oxygen occurs at the cathode. At the anode, oxidation of hydroxyl ions produced from the reduction of oxygen, oxidation of chloride in the feed solution, and oxidation of carbon (electrode) occur, depending on the cell potential. The oxidation of chloride and carbon (electrode) occurs at a cell potential of 1.2 V or above.

The change in solution pH during CDI can cause serious problems. If Ca^{2+} or Mg^{2+} is included in the influent, scale can be produced when the pH of the solution increases. Because the presence of DO in the influent increases the pH of the solution, it is desirable to remove DO or protect the electrode from contact with DO. Recently, a membrane capacitive deionization (MCDI) process, where an ion-exchange membrane protects the electrode surface, was introduced and reported to greatly enhance the salt-removal efficiency of CDI [16,20]. In MCDI, the permselectivity of the ion-exchange membrane increases the efficiency of salt removal and protects the electrode from contact with DO, effectively controlling the pH of the solution.

3.3. Adsorption and desorption mechanisms in CDI operation

Fig. 5 shows the current supplied to the CDI cell at each applied potential: at higher applied potentials, more current flowed. At early stages of potential application, an initial current of 5–8 mA/cm² was rapidly reduced to 1.5 mA/cm² in the first 50 s and slowly reduced thereafter. When an influent of 200 mg/L NaCl was fed at a flow rate of 20 mL/min, approximately 1.1 mA/cm² of current was required to adsorb all ions. However, a much higher current was supplied at the initial stage. This change in current can be explained by the mechanism of ion adsorption and desorption at the electrode interface. When a desorption potential was applied after adsorption was complete, ions adsorbed on the electrode moved back into bulk solution to balance the electroneutrality of the solution. However, ions of opposite charge can simultaneously move toward the electrode from the bulk solution. As a result, all adsorbed ions were not desorbed from the electrode surface and a portion remained inside the porous carbon electrode. When the sorption potential was

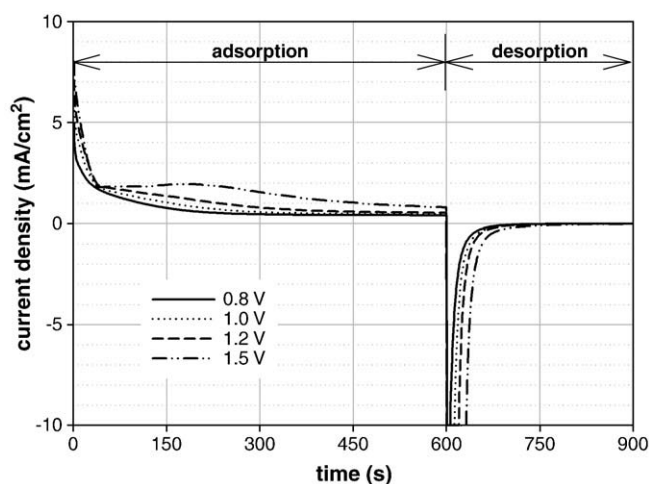


Fig. 5. Changes in current density during adsorption and desorption at various cell potentials.

applied again, the ions inside the electrode were re-adsorbed. Thus, a large amount of current flow at the early stage of potential application was due to the re-adsorption of ions present in the pores of the carbon electrode.

Current change during desorption represents the rate of desorption from the electrode. As shown in Fig. 5, when a desorption potential was applied, current flowed at a constant level of 10 mA/cm², which is the maximum level supplied by the potentiostat. The current then abruptly declined and, after 100 s, almost no current flowed. This result indicates that desorption of ions from the electrode proceeded very quickly, as shown in Fig. 2.

Fig. 6 shows the cumulative charges flowed through the cell during adsorption and desorption.

During the total adsorption time of 10 min, total charges flowed through the cell were 43.4, 54.0, 66.2, and 96.5 C, at potentials of 0.8, 1.0, 1.2, and 1.5 V, respectively. Charges flowed during desorption at the same potentials were 17.4, 23.5, 30.1, and 43.9 C, respectively, which are about 40–46% of those during adsorption. For an ideal CDI operation with no electrode reactions, the amount of charge during adsorption and desorption should be identical. However, the charges flowed during adsorption was greater than twice the charges of desorption. This discrepancy is attributed to electrode reactions that occurred when the potential was applied. Electrochemical reactions at the electrodes can

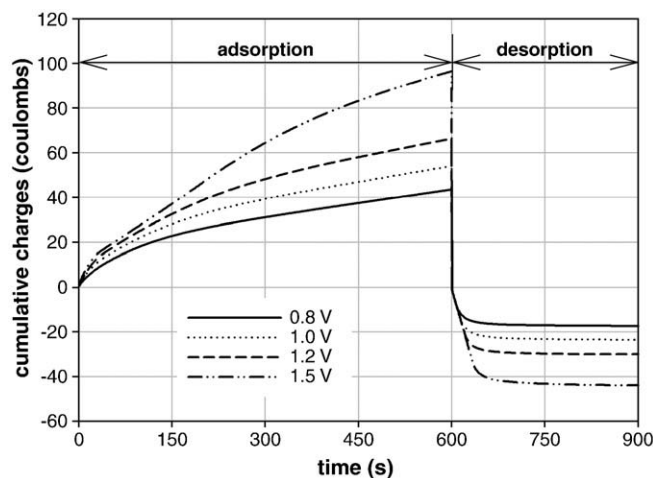


Fig. 6. Changes in cumulative charges flowed during adsorption and desorption at various cell potentials.

cause reductions in current and salt-removal efficiency and a change in the pH of the solution, which can have a serious impact on CDI. Thus, for stable CDI operation, the development of an electrode and cell configuration that can control reactions at the electrode is a significant unmet need.

4. Conclusions

Investigation of the mechanisms of adsorption and desorption, along with examination of reactions at the electrode surface, is important for enhancing the efficiency of CDI and for stable CDI operations. In this study, a carbon electrode was prepared using activated carbon powder and desalination experiments were performed with a CDI unit cell. By measuring the conductivity, effluent pH and current at different applied potentials, electrode reactions and the performances of adsorption and desorption were investigated.

In adsorption experiments with 0.8–1.5 V of applied potential, the efficiency of salt removal increased with increasing potential. However, the pH of the solution also changed considerably with applied potential. The change in solution pH was caused by reactions at the electrode. The solution pH increased at a potential of 1.0 V due to the reduction of dissolved oxygen. However, the pH rapidly decreased at potentials of 1.2 V or greater due to the oxidation of chloride at the anode. From the change in current, it was discovered that adsorbed ions were not completely desorbed and a fraction of the ions were retained in the carbon electrode. Because these accumulated ions were re-adsorbed at the electrode surface when a potential was applied, the efficiency of salt removal decreased. The control of electrode reactions was found to be important for the efficiency of salt removal and stability of CDI.

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