



Short Communication

Hydrogen peroxide generation in flow-mode capacitive deionization

Taeyoung Kim^a, Jihyun Yu^a, Choonsoo Kim^a, Jeyong Yoon^{a,b,*}^a School of Chemical and Biological Engineering, College of Engineering, Institute of Chemical Processes (ICP), Seoul National University (SNU), Gwanak-gu, Daehak-dong, Seoul 151-742, Republic of Korea^b Asian Institute for Energy, Environment & Sustainability (AIEES), Seoul National University (SNU), Gwanak-gu, Daehak-dong, Seoul 151-742, Republic of Korea

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ABSTRACT

Capacitive deionization (CDI) is a process that uses the potential difference developed between two porous electrodes to remove dissolved salts from water known as desalination. In a typical CDI cell consisting of carbon electrodes, a non-Faradaic reaction usually controls the desalination process. However, undesirable Faradaic reactions have been reported which can lower the energy efficiency leading to unexpected side reactions. Among the various side reactions discussed so far, hydrogen peroxide (H₂O₂) generation has been suggested to occur on the cathode due to the pH fluctuation. The H₂O₂ generation was recently observed in a batch-mode CDI operation, but little is known about the H₂O₂ generation in a flow-mode operation and the range of applied potentials to each electrode for producing H₂O₂. In this study, the generation of H₂O₂ was quantified during the charging step in a flow-mode CDI operation with supporting electrochemical characterizations on cathode and anode, which constantly produced approximately 0.1 mg of H₂O₂ for 50 cycles at applied voltage of 1.2 V. The applied potentials to cathode and anode were in the range for H₂O₂ production and carbon oxidation reactions. It can provide one of explanations to the pH increase in the effluent at the beginning of the CDI operation since oxygen and proton are consumed to produce H₂O₂ (O₂ + 2H⁺ + 2e⁻ = H₂O₂). Considering a typical applied voltage for CDI operation (<1.2 V), the generation of hydrogen peroxide is inevitable on the cathode due to the thermodynamic redox potential under neutral pH condition. The quantification of H₂O₂ is significant finding in that it contributes to better understanding Faradaic reaction in CDI and providing foundation to further studies about detrimental effects in long-term operation or prevention of biofouling by employing hydrogen peroxide, which is a typical problem in most water treatment processes.

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1. Introduction

Capacitive deionization (CDI) has received much attention as a desalination process lately [1–6]. CDI desalinates brackish water when passed between two porous electrodes, mostly made of activated carbons, by applying an electrical potential which is followed the formation of a double layer. CDI consists of two main processes, charging and discharging. In the charging process, ions are attracted and stored in the electrodes, and consequently, the solution passing between the electrodes can be desalinated. In the discharge process, the stored ions are released by reversing the potential of each electrode, and therefore the electrodes can be regenerated. CDI is an electrochemically driven process in which a non-Faradaic reaction intended process controls the desalination process. Therefore, the appropriate operation is required to achieve efficient desalination without any undesirable energy loss.

To avoid various Faradaic reactions for an energy-efficient process, the applied potential has been typically limited to 1.2 V [7–10] because the electrolysis of water is negligible in this potential range. However, unexpected side reactions have been reported in an early CDI study [7] even when the applied potential was kept below 1.2 V. Incomplete decay of the current was proposed as evidence for parasitic electrochemical reactions together with current leakage. Afterwards, several Faradaic reactions were postulated by altering the applied potential and following the pH changes [11]. Reduction of dissolved oxygen (pH increase) and oxidation of the carbon electrodes (pH decrease) were suggested as possible explanations for the pH changes during the process. Another study revealed that dissolved oxygen could be involved in the side reactions by observing the cumulative charge and pH changes with and without nitrogen purging [12]. Changes of pH was also examined using a 3-electrode system by varying applied potentials [13]. Increasing the applied voltage above 1.2 V caused more side reactions, which decreased the effluent pH below 5 and induced discrepancy between effluent conductivities and ion concentrations [14].

So far, evidence for unexpected side reactions has been provided using various experimental approaches such as nitrogen sparging, pH changes, and potential adjustments. Previous studies have reported

* Corresponding author at: Daehak-dong, Gwanak-gu, Seoul 151-742, Republic of Korea.

E-mail address: jeyong@snu.ac.kr (J. Yoon).

the oxidation of the carbon in the anode by using X-ray photoelectron spectroscopy (XPS) analysis and observing the change in potential of zero charge [12,13,15]. On the other hand, Faradaic reactions in the cathode have been poorly investigated; several electrochemical reactions related to the reduction of dissolved oxygen were suggested to explain the effluent pH fluctuations [11–13]. Recently, Faradaic reactions in a batch-mode CDI was examined, which reported produced H_2O_2 and decreased dissolved oxygen concentrations [16]. However, such measurements were performed in a batch-mode CDI operation and applied electrode potentials for driving Faradaic reactions remain unclear. Therefore, a suitable electrochemical analysis supporting the reactions that occur on the cathode could provide a better understanding of the CDI process and its mechanism. Herein, we investigated the generation of H_2O_2 as one of postulated Faradaic reactions in flow-mode CDI operation. As evidence of oxygen reduction, hydrogen peroxide was specifically detected together with pH changes in the effluent. In addition, the applied potential to each electrode was separately measured using a reference electrode, and current profiles in the corresponding potential region were observed to examine possible Faradaic reactions.

2. Materials and methods

2.1. Capacitive deionization experiments

CDI experiments were conducted in a custom-built polycarbonate CDI module, in which 50-mm-diameter electrodes can be installed. Two pieces of activated carbon fibers (CH900-20, BET specific surface area = $2183 \text{ m}^2 \text{ g}^{-1}$, pore volume = $0.89 \text{ cm}^3 \text{ g}^{-1}$, thickness = $500 \mu\text{m}$, Kuraray Chemical Co., LTD, Japan) with filter paper (Whatman, USA) in between were installed inside the module. A feed solution (10 mM NaCl) was supplied using a peristaltic pump at a flow rate of 10 ml/min . The solution was injected through a hole (4 mm in diameter) located in the center and then spread radially outside. The outlet conductivity and pH were continuously measured with a conductivity meter (3574-10C, HORIBA, Japan) and a pH meter (9618-10D, HORIBA, Japan). The solution was discarded after measuring pH instead of being recycled (single-pass mode). A constant voltage (1.2 V) was applied to the CDI module for 6 min using a cycler (WBSC3000, WonATech, Republic of Korea) and short-circuited for 6 min .

2.2. Determination of hydrogen peroxide

The concentration of hydrogen peroxide was determined with the 2,9-dimethyl-1,10-phenanthroline (DMP) method [17]. During CDI operation, 1 ml of the effluent was collected every 2 min followed by mixing with 1 ml of DMP solution (1 g of neocuproine (Aldrich) dissolved in 100 ml of ethanol), 1 ml of 0.01 M copper (II) sulphate (Aldrich), and 7 ml of deionized water. Then, the absorbance of the mixed solution was measured at 454 nm (Agilent Technologies, USA). The concentration of H_2O_2 was calculated with the following equation:

$$[\text{H}_2\text{O}_2] = (A_{\text{sample}} - A_{\text{blank}}) / 1500$$

where $[\text{H}_2\text{O}_2]$ is the concentration of the hydrogen peroxide (M); A_{sample} is the absorbance of the sample, and A_{blank} is the absorbance of the blank. The blank was taken from the effluent before the CDI experiment was started. For a long-term experiment, the effluent during the charging step (6 min) was collected (60 ml) in a glass bottle, and 1 ml of the collected sample was used to determine the concentration of H_2O_2 .

2.3. Electrochemical characterizations

Electrochemical characterizations were carried out in a custom-built electrochemical cell consisting of a polytetrafluoroethylene (PTFE) housing and two graphite current collectors. Two pieces of round-

shaped activated carbon fibers (18 mm in diameter) were assembled with a separator (cellulose nitrate, Advanced Microdevices, India). After the installation, the cell was filled with an electrolyte (1 M NaCl) and tightly pressed. First, the cell was charged and discharged at a constant current (2.5 mA cm^{-2}) within 1.2 V using a cycler, which is the typical working voltage for CDI operations. Meanwhile, the potential of each electrode was separately measured using a reference electrode (Ag/AgCl in a saturated KCl solution). Cyclic voltammetry (CV) was performed for each electrode; the potential range (-0.7 to -0.1 V and -0.1 to 0.5 V vs. reference electrode for the cathode and the anode, respectively) was determined based on the galvanostatic charge/discharge test. The current profile was recorded at a scan rate of 2 mV s^{-1} using a potentiostat (PARSTAT 2273, Princeton Applied Research, USA).

3. Results and discussion

Fig. 1a shows the representative conductivity and pH profiles during CDI operation. The conductivity profile decreased and increased upon charging (1.2 V , 0 – 6 min) and discharging (0 V , 6 – 12 min) which represents the typical behavior of desalination and regeneration [2,9,18]. Together with the conductivity, the pH was simultaneously recorded during the operation. The pH increased up to 11 during the charging step, indicating either hydroxide production or proton consumption. Note that such a high pH level could contribute to an increase in conductivity, and thus the effluent conductivity was significantly affected by this pH effect (Fig. S1) [14]. The increase in pH is quite different compared to the previously reported pH response during CDI operation, in which a pH decrease was observed when charging [12]. However, the charging step of the previous study was much longer (240 min vs. 6 min) when obtaining the pH profile, and a sharp peak was also observed prior to the decrease. In addition, other studies reported an increase in pH at the beginning of the charging process [11,14,16], which is relevant to what we observed in this study. Obviously, the increase in pH suggests that unexpected Faradaic reactions did occur under the CDI working voltage (1.2 V), even though it is not expected to generate any other side reactions including water electrolysis.

Among the various possible electrochemical reactions, H_2O_2 generation by oxygen reduction has been proposed in CDI [11], which is a well-known reaction in other fields using a carbon electrode as a cathode [19, 20]. In order to confirm H_2O_2 generation during the charging step of the CDI operation, the amount of H_2O_2 in the effluent solution was measured by applying different cell voltages. As can be seen in Fig. 1b, the higher applied voltage produced more H_2O_2 , for which $0.094 \pm 0.015 \text{ mg}$ of H_2O_2 was produced after 6 min of charging under the typical CDI operating voltage (1.2 V). When considering the charge efficiency loss due to this Faradaic reaction, the amount of charge consumed for H_2O_2 generation appeared to be insignificant (below approximately 5%, data not shown). Further increasing the voltage to 1.6 V produced a slightly more increased H_2O_2 of $0.097 \pm 0.005 \text{ mg}$, which is relevant result to the previous study reporting rather decreased H_2O_2 generation at an elevated applied voltage (1.5 V) in a batch-mode CDI operation [16]. At an applied voltage of 0.6 V , a considerable amount of hydrogen peroxide ($0.047 \pm 0.009 \text{ mg}$) was still generated, indicating that this reaction is inevitable when using a CDI cell consisting of carbon electrodes. An insignificant amount of H_2O_2 was detected when the applied voltage was 0.2 V .

Fig. 1c shows the long-term cycle performance of the conductivity change and the concentration of the hydrogen peroxide generated during the charging steps. The CDI performance gradually deteriorated up to 10 cycles and leveled off for the next 40 cycles. In particular, the conductivity profile for the first charging step was quite different from the subsequent cycles (higher than the influent conductivity at the end of the charging step), which might be due to the repulsion of impurity ions or the abrupt increase in ionic species generated by Faradaic reactions (e.g., OH^-). The degradation could be attributed to the oxidation

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