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Temporal and spatial distribution of pH in flow-mode capacitive deionization and membrane capacitive deionization

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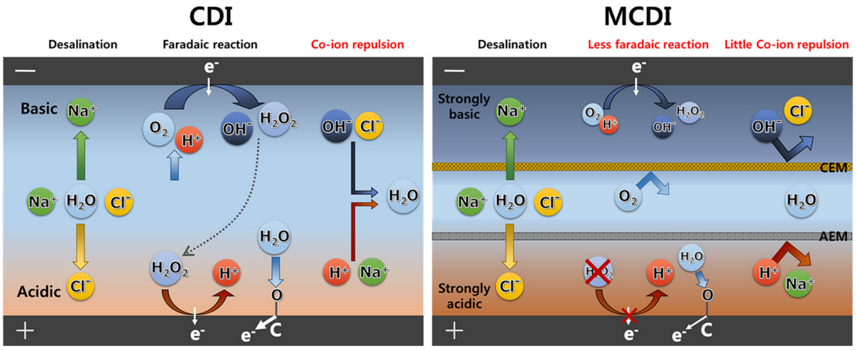
GRAPHICAL ABSTRACT



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ABSTRACT

Capacitive deionization (CDI) is a desalination technique that removes salt from saline water by applying a potential difference between two porous activated carbon electrodes. Although undesirable Faradaic reactions causing a deterioration in the desalination performance in long-term operation have been reported with pH fluctuations and hydrogen peroxide generation, the effect of the temporal and spatial pH distribution and quantitative analysis of charge consumption have rarely been reported or interpreted, especially in membrane capacitive deionization (MCDI). In this study, more detailed and precise investigations were quantitatively conducted to determine the charge consumption for ion adsorption, Faradaic reaction, the co-ion repulsion by analyzing the pH distribution on the electrode surface, the H_2O_2 and salt concentration, and the current profiles for short-term and long-term operations of CDI and MCDI. As major results, active Faradaic reactions caused a decrease in the deionization performance in the short-term operation, whereas in the long-term operation of CDI the sustained oxidation of carbon electrode caused its performance to decrease even further. On the other hand, regardless of a short or long term operation, less Faradaic reactions and less oxidation of the carbon electrode were observed with a superior deionization performance in MCDI.

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1. Introduction

Capacitive deionization (CDI) is a desalination technique that removes salt from saline water by applying a potential difference between two porous activated carbon electrodes [1–8]. CDI has the benefit of high energy efficiency for low saline water and low material and operating costs compared with reverse osmosis (RO) [9–13]. In addition, Membrane CDI (MCDI), which is one of the widely used CDI systems, is constructed by introducing ion-exchange membranes (IEM) in front of the carbon electrodes [14–16]. MCDI has a superior desalination performance compared to CDI which is often explained by the reduction of the co-ion repulsion using IEM [17–21].

However, the oxidation of the carbon electrodes resulting in the deterioration of the long-term performance of CDI and MCDI has been reported as one of the disadvantages of (M)CDI systems [15,22–26]. The oxidation of the carbon electrodes is seen by the changes in oxygen content and a potential of a zero charge at the carbon electrodes [27–30], and H_2O_2 generation and pH fluctuation of the effluent was shown to occur under a typical (1.2 V) or lower potential (0.7–0.9 V) [31–34] resulting in a decrease of the CDI performance [15,32,33,35–40]. More specifically, recently, Waite et al. reported faradaic reactions of H_2O_2 generation resulting from oxygen reduction with pH change in batch-mode (M)CDI systems [38,39,41], and Yoon et al. reported similar faradaic reactions in the flow-mode CDI process in long-term operation [40].

Nevertheless, the quantitative interpretation of the temporal and spatial pH distribution and hydrogen peroxide formation has rarely been reported for either short-term or long-term (M)CDI operations taking into consideration the charge consumption characteristics of the ion adsorption, Faradaic reactions, and co-ion repulsion, all together.

Therefore, the aim of this study was to understand the charge consumption characteristics of the ion adsorption, Faradaic reactions, and co-ion repulsion, all together, by thoroughly analyzing the temporal and spatial distribution of the pH and charge consumption in the short-term and long-term operation of CDI and MCDI. To this end, the pH and H_2O_2 concentration in the effluent, the pH at the surface of the electrode and the IEM were measured, and the surface properties of the carbon electrodes were analyzed especially focusing on the oxygen functional groups. In addition, the charge consumption corresponding to Faradaic reactions and co-ion repulsion as well as the ion adsorption was compared in a short-term and long-term (M)CDI system.

2. Materials and methods

2.1. Electrode fabrication

Carbon composite electrodes for the CDI and MCDI systems were fabricated with a mixture of 86 wt% activated carbon (MSP-20X, Kansai Coke and Chemicals, Japan), 7 wt% carbon black (Super P, Timcal, Switzerland) and 7 wt% polytetrafluoroethylene (PTFE, Aldrich, USA) following procedures described in previous studies [42,43]. The activated carbon and carbon black were thoroughly mixed for one night and then pasted with PTFE and several drops of ethanol. The mixture was rolled to become a flat sheet carbon electrode by a roll presser at 60 °C and 200 rpm. This fabricated carbon electrode (thickness of ~300 μm) was dried overnight under a vacuum condition at 120 °C. The BET specific surface area the activated carbon (MSP-20X) was approximately 2078 $m^2 g^{-1}$ and that of carbon electrode with the activated carbon was about 1706 $m^2 g^{-1}$.

2.2. Capacitive deionization experiments

CDI and MCDI systems were tested in a three electrode flow mode system cell (refer to Fig. S1 in the SI for details) which is capable of investigating the deionization and electrochemical performance of the electrodes. A three electrode (M)CDI flow mode system cell was operated in a mode with two-electrode system where a reference electrode was located inside. A reference electrode (Ag/AgCl (KCl sat'd)) and the anode which were connected to another battery cycler to measure the potential of the anode versus reference electrode. Constant potentials of 1.2 V were applied between the cathode and the anode for 15 min during the charging step while the discharging step was done with a short circuit (zero potential) for another 15 min.

Two fabricated carbon electrodes were cut into a round shape (20 mm in diameter with a 3 mm center-hole in diameter) and placed on each graphite sheet (current collector) connected by a cycler (WBSC3000, WonATech, Korea). For the MCDI system, a cation exchange membrane and anion exchange membrane (CMX and AMX, Neosepta, ASTOM Co., Japan) were placed on the cathode and anode respectively. A nylon spacer (25 mm diameter) was placed between the electrodes or the ion exchange membranes for water passage. As a feed solution, 10 mM solution of sodium chloride was supplied at 2 mL/min by a peristatic pump. The effluent conductivity (3574-10C, HORIBA, Japan) and pH (9618-10D, HORIBA, Japan) were continuously measured, and their measurements were used to calculate the salt adsorption capacity and efficiency.

2.3. Measurement of pH of electrode surface and effluent H_2O_2

For the spatial pH measurement, pH values at the surface of the positive and negative electrodes and at the ion-exchange membranes were measured with a flat tip pH electrode (HANNA HI 1413B, HANNA instruments, USA) after charging for 5 min. The concentration of H_2O_2 was measured by the 2,9-dimethyl-1,10-phenanthroline (DMP) method with 0.1 M phosphate buffer solution [44] at 454 nm with UV–vis spectroscopy (Agilent 8453, Agilent Life Sciences and Chemical Analysis, USA).

2.4. Electrode characterization

The potential of zero charge (E_{pzc}) of the long-term cycled carbon electrode including a pristine carbon electrode was analyzed by cyclic voltammetry (CV). CV was carried out in a three-electrode coin cell in which the round-shaped electrode had a diameter of 18 mm. Ag/AgCl (KCl sat'd) and a pristine carbon electrode were used as the reference electrode and counter electrode, respectively. 100 mM NaCl was used as the electrolyte, and the scan rate (1 mV/s) was adjusted with a potentiostat (PARSTAT 2273, Princeton Applied Research, USA). The potential range of the working electrode (-0.4 to 0.8 V) was determined based on the galvanostatic charge/discharge (GCD) results. The GCD experiment was performed with the identical three electrode flow cell which was used for the (M)CDI system to measure the cell voltage and working potential of each electrode. The cell was charged and discharged within 0–1.2 V at a constant current (2.5 $mA\ cm^{-2}$) with a 10 mM NaCl feed solution. The working potential of the anode and cathode was simultaneously measured with the Ag/AgCl (KCl sat'd) reference electrode. FT-IR (Jasco Model FT-IR 200, Agilent, USA) spectra were obtained for the pristine and long-term cycled carbon electrode. Before the FT-IR measurement, the electrodes were thoroughly rinsed and dried. The wavenumber range was 2000–800 cm^{-1}.

2.5. Faradaic reactions in CDI operation

When a potential of 1.2 V was applied to a pair of electrodes, the potential about 0.8 V and -0.4 V (vs. Ag/AgCl (KCl sat'd) were applied to the cathode and the anode, respectively, as shown in Fig. S2. Therefore, Faradaic reactions shown below (Rxn (1)–(6)) were plausible [31]. The redox potential of each reactions were determined by