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Analysis of the desalting performance of flow-electrode capacitive deionization under short-circuited closed cycle operation

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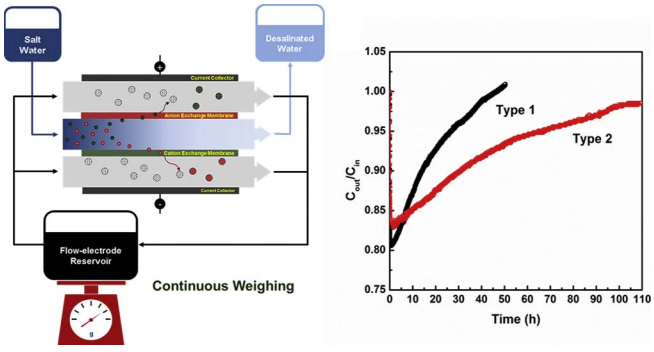
GRAPHICAL ABSTRACT

We report desalting behaviors of FCDI under short-circuited closed cycle operation of the flow-electrode mixing of cathode and anode flow-electrodes.



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ABSTRACT

Flow-electrode capacitive deionization (FCDI) has been studied for its ability to perform continuous deionization; however, there are no reports on the degradation of the desalting performance of FCDI under short-circuited closed cycle operation (SCC) mode. In this study, we observed a gradual decrease in FCDI desalting performance and weight increase of the flow-electrode under SCC mode, which mixes the cathode and anode flow-electrodes. Through an analysis of NaCl and water accumulation rates obtained from the weight variation of the flow-electrode, the gradual decline in the desalting performance was caused by a decrease in the content of activated carbon (AC) with ion adsorption sites in the flow-electrodes. This was driven by water transfer from the feed stream to the flow-electrodes through the ion exchange membrane attributed to hydrated ions and osmosis. We calculated the salt adsorption capacity (SAC) and salt adsorption rate (SAR) based on the variable weight of the flow-electrode. The maximum SAC (mSAC) and average SAR (ASAR) values of the FCDI were higher and lower than those of conventional capacitive deionization systems, respectively. This was likely due to the repetitive use of the flow-electrode and long ion transport pathways in the flow-electrode, respectively.

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1. Introduction

Capacitive deionization (CDI) is a water treatment technology based on electrical adsorption and desorption on the surface of porous electrodes. CDI is generally applied to brackish water desalination due to its higher energy efficiency and relatively easier operation compared to other desalination technologies. However, conventional CDI exhibits desalting limitations associated with highly concentrated feed water because the capacitive electrodes fixed in CDI have ion storage limitations [1]. To overcome the limitations of CDI, numerous researchers have developed CDI technology with innovative architecture, including static electrode architecture (e.g. flow-through electrode CDI [2], membrane CDI [3–6], inverted CDI [7], hybrid CDI [8], wire based CDI [9], and desalination battery [10]), and flow-electrode architecture (e.g. feed-in electrodes [11], feed-between electrodes [1], and membrane flow-electrodes [12]).

Flow-electrode capacitive deionization (FCDI) is a novel capacitive deionization technology that uses a liquid-type flow-electrode separated from the CDI cells that differs from conventional CDI, which uses solid-type electrodes fixed in the cells. To enable flow of the liquid-type flow-electrodes in FCDI, FCDI includes a flow-channel curved along the current collectors. The liquid-type flow-electrode flows through the flow-channel between ion-exchange membranes (IEMs) (or porous separators) and current collectors [11,12]. Regardless of the architecture, FCDI yields continuous desalting performance and electrical current, which differs from conventional CDI because of the infinite ion capacity of the flow-electrode originating from the continuous injection of flow-electrodes in FCDI. In addition, through the continuous desalination of highly concentrated feed water (35 g/L), as demonstrated by Jeon et al. [12], FCDI can overcome the problem of feed water concentration limitations experienced by conventional CDI.

When an infinite amount of fresh flow-electrode is continuously supplied to the FCDI unit cell (i.e. open cycle operation (OC) mode), FCDI performance is maintained without degradation in desalting efficiency. Under the OC mode of fresh flow-electrodes, flow-electrodes have an infinite ion capacity in FCDI systems. However, in practical operation of flow-electrodes in FCDI systems, the flow-electrodes must be performed under closed cycle operation (CC) modes using a limited capacity of flow-electrodes in FCDI systems due to high operation costs. A number of studies have examined FCDI systems under closed cycle operation with a limited capacity of flow-electrodes [13–21].

CC modes of flow-electrodes in FCDI systems can be divided into two modes, isolated closed cycle operation (ICC) mode and short-circuited closed cycle operation (SCC) mode [15]. In ICC mode, the cathode and anode flow-electrodes in FCDI are isolated, and the reservoirs used to store the flow-electrodes are divided into cathode and anode reservoirs. In contrast to ICC mode, the flow-electrodes in SCC mode are operated with only one reservoir, in which the cathode and anode flow-electrodes are mixed during FCDI desalination. Both CC modes result in the continuous accumulation of salt on the flow-electrodes during desalination, which differs from the lack of continuous salt accumulation in the flow-electrodes in OC mode.

ICC and SCC modes differ in the form of the salt that accumulates in the flow-electrode. In ICC mode, salt accumulated in the flow-electrodes exists as cations and anions in the cathode and anode flow-electrodes, respectively. Meanwhile, in SCC mode, the flow-electrodes accumulate both cations and anions during desalination. When flow-electrodes with limited capacities are operated under ICC mode in the FCDI unit cell, the cation and anion capacities in the cathode and anode flow-electrodes, respectively, become saturated during desalination. Therefore, desalting performance is decreased, because ions transferred from the feed stream into the flow-electrode are repulsed by co-ions in the flow-electrode [15]. This is similar to the desalting behaviour of conventional CDI systems [6,22], where the ion capacity saturation in the flow-electrode in FCDI is overcome by a controllable quantity from the flow-electrode. In contrast to FCDI systems in ICC mode, FCDI systems operated in SCC mode with a flow-electrode with a limited capacity, show continuous desalting performance without degradation of the desalting efficiency due to the regeneration of the flow-electrode by ion neutralisation originating from the simple mixing of the cathode and anode flow-electrodes [15,20]. Unlike the deterioration of the FCDI desalting behaviour under ICC mode [15], there are no reports on the degradation of the desalting performance of FCDI systems under SCC mode with a flow-electrode with a limited capacity.

Therefore, in the present work, we monitored the variations in the desalting behaviour of FCDI unit cells depending on the type of IEM used and activated carbon (AC) content in the flow-electrode under SCC mode. First, we performed a continuous weight analysis of the flow-electrode to determine the desalting performance variation of the FCDI system operated in SCC mode. In addition, the salt adsorption capacity (SAC) and salt adsorption rate (SAR) values based on the variable weight of flow-electrodes were obtained. Based on the results, maximum SAC (mSAC) and average SAR (ASAR) were defined for the first time under SCC mode.

2. Materials and methods

2.1. Preparation of the flow-electrode and saltwater for SCC mode

To generate the flow-electrode, specific quantities of NaCl were added to deionized (DI) water in 500-mL beakers and dissolved using a magnetic stirring bar. Subsequently, spherical AC (BEAPS-AC0830; Asahi Organic Chemicals, Japan) was added and homogeneously mixed in aqueous electrolyte solutions containing NaCl for 24 h. Table 1 lists the weight ratios of DI water, AC, and NaCl used in the flow-electrodes and flow-electrode notations used hereafter. To prevent clogging of the flow-electrodes in the flow channel originating from large impurities in the AC, before adding the AC to the electrolyte solutions, large impurities were removed by passing through a sieve with an aperture size of 150 μm and wire diameter of 100 μm [21]. The morphology, average specific surface area, average pore diameter, and total pore volume of AC used in this experiment is listed in our previous work [20]. The influent saltwater was prepared by adding 3.5 g NaCl per 100 g DI water. The original electrical conductivity of the prepared saltwater used as the influent was ~54.3 mS cm^{-1}.

2.2. Experimental set up of the FCDI unit cell

Fig. 1 shows the experimental set up for the characterisation of the FCDI system. The structures and materials of the FCDI unit cells were similar to those used in our previous work [20], except for the material used for the cation- and anion-exchange membranes. We used two types of cation- and anion-exchange membranes in this study, CEM & AEM Type 1 and CEM & AEM Type 2 (FUJIFILM Europe, Japan). Immediately after swelling CEM & AEM Type 1 and Type 2 in 0.5 M aqueous solution for 24 h, they used for FCDI unit cell assembly. The FCDI unit cell was composed of a pair of graphite current collectors, cation- or anion-exchange membranes, a silicone gasket, a polyester spacer, and one pair of polyvinyl chloride end plates. The thickness of the silicone gasket and polyester spacer was approximately 0.3 mm. The dimensions of the graphite current collectors and the carved flow channel were the same as those in our previous work [20]. The contact

Table 1
Weight ratio of deionized water (DI) water, activated carbon (AC), and NaCl used in the flow-electrode.

Notation	DI water (g)	AC (g)	NaCl (g)
AC 11.11 wt%	200	25	7
AC 9.09 wt%		20	5
AC 6.98 wt%		15	3