



Optimization of the voltage window for long-term capacitive deionization stability



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ABSTRACT

Capacitive deionization (CDI) is an energy efficient desalination technology. In this study, we conducted CDI experiments under different conditions and observed severe performance degradation from 7.3 to 0.5 mg/g after 70 cycles in symmetric 1.2/0 V operation because of anode oxidation under polarization. To eliminate the degradation, different charging and discharging voltages were tested in an asymmetric cell and 0.8/−0.4 V was selected as the optimized voltage window. Under the optimized voltage window, a capacity of 6.3 mg/g was obtained, only somewhat lower than that of the 1.2/0 V experiment, and the stability and charge efficiency were much higher by greatly mitigating the electrode corrosion. In addition, the process had a lower energy consumption. The stable performance in air- and oxygen-saturated conditions indicates that the optimized CDI has superior capacity and better performance than conventional CDI.

1. Introduction

Water shortage is one of the most challenging problems in the 21st century [1]. For industrial use, recycling water by desalinating brackish water to increase water usability has been facilitated by a variety of traditional technologies such as distillation, reverse osmosis, and dialysis. In these methods, water is removed, and impurities are condensed and removed as brine. However, these processes require complex pre-treatment, harsh operating environments, and high energy input [2]. For water of low saline concentration, these methods are highly energy intense and uneconomical.

Recently, a new high efficiency, low-energy technology, capacitive deionization (CDI), has emerged [3]. This technology utilizes electrical fields to remove ions, where ions are extracted, possibly selectively, from brackish water [1,4–7]. This process is based on the formation of an electrical double layer (EDL) among electrode particles under a constant charging voltage or current [8–10]. To maintain electric neutrality, the positively charged anodes attract anions and negatively charged cathodes attract cations, immobilizing the ions at the electrodes [11–13]. The materials used in CDI are carbon with a large surface area and wide pore size distribution [14], including activated carbon, carbon fiber, carbon aerogel, ordered carbon, carbon nanotubes, and carbon wires [15–21]. Furthermore, much work has, to date, focused on hybrid materials and materials enhanced with metal oxides such as MnO₂, TiO₂, and MoS₂ [22–28]. In addition, various new CDI methods such as membrane capacitive deionization, inverted capacitive

deionization, and enhanced capacitive deionization have been investigated [29–33].

Although there have been breakthroughs in CDI through enhancing surface morphology and improving the electrochemical properties, CDI suffers severe performance decay after long-term operation, and this aspect has also attracted significant attention. In CDI, the current is, theoretically, only used for capacitive behavior and no faradaic reactions occur [34–36]. However, water splitting occurs, even at voltages under the voltage for water electrolysis, in actual process conditions, as well as other faradaic reactions [37–40]. Notably, carbon redox reactions reduce not only the desalination capacity but the electrode properties, where negative charges on the surface have been observed [41–43]. These observations indicate that carbon oxidation results in residual surface charges and severe performance degradation [44,45]. As the number of CDI cycles increased, an inversion peak appears, and a significant capacity loss occurs, which hinders the industrial use of CDI because of the higher maintenance required [46,47]. However, the CDI performance degradation can be mitigated by the addition of an ion-exchange membrane, a change in the operational mode such as inverted-operation and polarity alternation, or the electrode modification [28,48–50]. We have conducted experiments in the conventional 1.2/0 V voltage window and tested the process stability and performance for long-term experiments in both air- and oxygen-saturated solutions. Furthermore, we have optimized the operating conditions to yield a steady desalination capacity and high charge and energy efficiency, even after long-term polarization.

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2. Materials and methods

2.1. Electrode fabrication

Electrodes were manufactured with activated carbon. As-received activated carbon powder (Tianjin Fengchuan Chemical Reagent Technologies Corp.) was soaked in 0.1 mol/L HCl solution at 80 °C for 2 h, followed by boiling in deionized water for 2 h to remove impurities. Finally, the carbon was dried at 120 °C for 12 h. The washed carbon is denoted AC in the text. Thereafter, the AC was treated with sulfuric acid and stirred at 140 °C for 2 h, washed until pH neutral to condition the surface character, and dried at 120 °C for 12 h. The modified AC is denoted SA-AC in this paper. Carbon slurries were fabricated by mixing 82 mass% carbon powder, 10 mass% carbon black, and 8 mass% polyvinylidene fluoride (PVDF) with *N*-methyl-2-pyrrolidone (NMP). After mixing for 12 h, the slurries were cast on graphite current collectors with a wet thickness of 500 μm and dried in vacuum at 80 °C for 12 h.

2.2. Characterization

The surface structure and morphology were monitored using a scanning electron microscope (S-4800, Hitachi). Fourier transform infrared spectroscopy (FT-IR, TENSOR27, Bruker Corp.) was used to identify functional groups by tableting activated carbon and KBr into thin slices at a mass ratio of 1:100 within the wavelength range of 400–4000 cm⁻¹ for 64 scans. Raman spectroscopy (inVia Reflex, Renishaw) was used to determine the degree of graphitization at an excitement wavelength of 532 nm. X-ray photoelectron spectroscopy (XPS, Escalab 250Xi, Thermo Fisher) was used to investigate the sample composition.

Electrochemical impedance spectra (EIS) were obtained using an electrochemical workstation (CHI 660D, CHI instruments) using a three-electrode system in a 0.01 mol/L KCl solution at a frequency of 0.1 Hz at a amplitude of 5 mV in increments of 10 mV [51]. In addition to activated carbon working electrodes, a graphite rod electrode was used as the counter electrode and a saturated calomel electrode (SCE) was used as the reference electrode. The specific capacitance (*C*) was calculated via Eq. 1.

$$C = \left| \frac{1}{\omega Z''} \right| \quad (1)$$

where Z'' is the imaginary part of the impedance and ω the scanning frequency.

2.3. CDI setup and desalination test

The CDI cell contained one pair of as-prepared electrodes, 20 cm long by 2 cm wide. The setup configured with the AC electrodes is called the symmetric cell and the setup assembled with an AC electrode and a SA-AC electrode is referred to as the asymmetric cell in this text. Fig. 1 shows the schematic of CDI experiment. During experiments, 5 L of air-saturated KCl solution was circulated through a 1-mm thick flow channel into the cell with a peristaltic pump (YZ1515X, Longer Precision Pump Corp.) at a rate of 6 mL/min. The concentration was maintained at 0.01 mol/L by the large volume ratio between the reservoir and the cell. During experiments, a voltage difference was applied to the electrode pair and controlled by a direct current power supply (M8811, Maynuo Electronic Corp.) with *a/b* V operation indicating charging at *a* V and discharging at *b* V. In the experiments, each cycle consisted of an adsorption stage for 20 min and a desorption stage for 20 min. Each stage was sufficiently long to ensure equilibrium, where the conductivity returned to the inflow value. At the same time, the conductivity was monitored online with a conductivity meter (Rex DDSJ-308F, INESA Scientific Instrument Corp.)

The salt adsorption capacity (Γ) was calculated according to Eq. (2),

and the charge efficiency (Λ), which is the total adsorption capacity divided by the charge consumption, was calculated via Eq. (3). The energy consumption (*E*) was calculated via Eq. (4).

$$\Gamma = \int \frac{(\sigma_0 - \sigma)MQ}{136.95m} dt \quad (2)$$

$$\Lambda = \frac{\Gamma m F}{\int I dt} \quad (3)$$

$$E = \frac{\int I U dt}{m} \quad (4)$$

In these equations, σ_0 is the inflow conductivity, σ is the real-time outflow conductivity, *M* is the molar mass of KCl, *Q* is the volumetric flow rate, *m* is the weight of activated carbon, 136.95 is the slope of the conductivity correlation curve, *F* is the Faradic constant, and *I* and *U* represent the current and voltage, respectively.

All data were calculated according to the weight of carbon, and the masses shown in the text are also the carbon mass, rather than that of the whole electrode.

3. Results and discussion

3.1. Characterization

Scanning electron microscope (SEM) images of the surface morphology are shown in Fig. 2a and b. SEM photos show that AC carbon particles lumped together whereas after the sulfuric acid treatment, SA-AC was corroded and the surface was rougher than that of AC. After corrosion with sulfuric acid, more voids were formed after the sulfuric acid excavation comparing to the AC sample, whose carbon particles were packed densely.

FT-IR measurements were used to identify the surface functional groups in the AC and SA-AC samples. As shown in the spectrum in Fig. 2c, the band at 610 cm⁻¹ in the SA-AC spectrum corresponds to the C–S bond, and peaks at 1100 and 1200 cm⁻¹ can be attributed to stretching vibrations of the S=O bond [7], which correspond to the sulfonic groups on SA-AC. These results demonstrate that sulfonic groups had been attached to SA-AC successfully.

Raman spectroscopy can be used to assess the defects and disorder of the sample. In Fig. 2d, the D band represents amorphous and disordered structure whereas the G band represents symmetric structures, and these bands were found at 1340 and 1590 cm⁻¹, respectively. The I_D/I_G ratio, the relative peak ratio of the D band to the G band, was 1.006 for AC and 1.017 for SA-AC, indicating that sulfuric acid treatment slightly increased the degree of defects and the disorder.

XPS measurements were made to further examine the surface chemical composition on sample surface [52]. Fig. 2e shows the XPS spectra and Table 1 addresses the content of S, O and C in the sample. The S content was 0.64% in the AC sample and 1.26% in the SA-AC sample. The increase in the S content in SA-AC confirmed the successful attachment of the sulfonic groups.

3.2. Conventional CDI operation test

Desalination tests, as described in Section 2, were conducted. CDI in a symmetric cell was performed in a 1.2/0 V voltage window, and the collected data are shown in Fig. 3. As the potential difference was applied, as shown in Fig. 3a, the outflow conductivity decreased rapidly to 1100 μS/cm, forming an adsorption valley, then bouncing back to the inflow conductivity. Then, when the desorption voltage was imposed, a desorption peak formed, reaching 1650 μS/cm. Finally, the conductivity fell to that of the inflow conductivity. However, as the experiment continued, a gradual performance loss was observed, and, between the 65th and 70th cycles, an inversion peak occurred. This is a desorption phenomenon during the charging phase, followed by an adsorption

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