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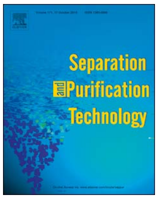

Enhancement of salt removal in capacitive deionization cell through periodically alternated oxidation of electrodes

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ABSTRACT

In capacitive deionization (CDI), the functionalization or modification of carbon electrodes and the mitigation of positive electrode oxidation are effective methods to improve desalination capacity and stability for practical application. Here, the covalent bond attached three-dimensional (3D) graphene/carbon nanotubes hybrid (G-CNTs) with rich conductive channels was chosen as electrode material, and a periodically alternated (positive and negative) voltage operation (1.2/0/–1.2/0 V) was applied that aims to enhance the efficiency and stability of capacity deionization. The desalination capacity of the G-CNTs electrode increased gradually over the first few cycles in this operation, while the usage cycle of CDI could be pronouncedly extended almost six times, compared with the CDI of regular applied voltage operation (1.2/0 V). Through the characterization of electrode and CDI cell, this enhancement of the desalination performance is attributed to the synergistic benefits of alternating oxidation of negative and positive electrode, which can mitigate the oxidation of the positive electrode as well as achieve negative surface charge enhanced negative electrode. Therefore, a periodically alternated voltage operation is an economical and efficient method to control the oxidation of electrodes for enhancing the desalination performance.

1. Introduction

Capacitive deionization (CDI, electrosorption) has emerged as an energy efficient device to treat salt water, especially those with low or moderate salt concentration, compared with other existing technologies [1–8]. Similar to the electric double-layer capacitors (EDLCs) for accumulating of ions at charged electrode-electrolyte interfaces [9,10], when an electrical voltage is applied across the CDI cell, ions are electrostatically stored in electric double layers (EDLs) at the surface of the polarized carbon electrode, and thus the salt is removed from aqueous solution. This process is reversible as the ions can be released from the electrodes by short-circuiting the electrodes for regeneration.

However, the electrodes are not polarized ideally for electrostatic interactions driven by electric field in CDI. A parasitic electrochemical oxidation process takes place in parallel to the electrostatic interactions, which would result in oxygen-containing functional groups formed on the positive electrode and the positive shifting of the potential of zero charge (E_{PZC}) of positive electrode [11,12]. The amount of counter ions adsorbed and desorbed gradually decreases and the amount of co-ions desorbed and adsorbed gradually increases during continuous cycling. As a result, the CDI's desalination performance deteriorate [13], even to the extent where the performance of the CDI becomes inverted [14]. Some authors found that the deionization performance gradually degraded during operation at 1.2/0 V. However, the use of $-1.2/0$ V significantly boosted deionization performance, but this enhancement was not sustained with continued cycling [11,15]. Therefore, the lifetime of electrode material determines the long-term stability of CDI, which is still a major issue to be addressed for practical applications.

Many efforts have been made to achieve CDI's high desalination performance and maintain long-term stability, including to applying ion-exchange membranes (IEMs) [14] or ion-exchange polymer-coating [16,17], employing inverted capacitive deionization (i-CDI) system with surface charge enhanced carbon electrodes [18–20], testing low operation voltage and periodically alternated potential operation [21]. By comparison, the optimization through operation condition can be much easier and more effective than that through modification of electrodes to improve the long term stability of CDI [22]. Low operation voltage mitigates the oxidation of electrode, but often results in low electrosorption capacity. A periodically alternated voltage operation may restrain the electrode oxidation as well. As previously reported, this periodically alternated voltage operation could extend the lifetime of the electrodes and retain good electrosorption capacity in flow-through CDI stack assembled with activated carbon cloth electrodes due to the reduced oxidation rate of the electrodes [21]. More recently, Gao

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et al. used the same voltage operation in flow-through CDI stack configured with carbon xerogel electrodes. They found that this operational method extended the stability of salt removal, while it also led to an arch-shaped plot of salt adsorption capacity versus cycling time. That is, the salt adsorption capacity initially increases and then decreases during long-term operation [23]. Compared with activated carbon cloth electrode, carbon xerogel electrode was seemed more suitable for enhanced capacitive deionization under periodically alternated voltage operation. This periodically alternated voltage operation brought alternated polarization of the electrodes that enabled the negative electrode to have negatively charged oxygen-containing functional groups like the positive electrode in the meanwhile. The oxidation of the positive electrode generally leads to a deterioration of the CDI's desalination performance, but the negative electrode with an appropriate amount of oxygen-containing functional groups can effectively enhance the CDI performance [24]. Therefore, carbon xerogel electrode with less oxygen-containing functional groups revealed better desalination performance compared to the activated carbon cloth electrode under periodically alternated voltage operation. In fact, salt adsorption capacity mainly depends on the pore properties and surface chemistry of electrode [25–28]. Carbon-electrode materials with an appropriate amount of oxygen-containing functional groups can serve as electrode-active material in the CDI device for their good efficiencies and the high capacities [29]. Our previous work [30] also showed that graphene-carbon nanotubes (G-CNTs) electrodes through the moderate oxidation treatment delivered high electrosorption capacity and good recycled stability. This study attempted to provide an oxygen-containing functionalized electrode-based CDI with periodically alternated voltage to obtain better desalination performance of the device and long-term stability. The oxidation degree, capacitance, and potential of zero charge (E_{PZC}) of the electrodes, as well as the internal resistance and potential distribution of CDI cells were determined to detect their influences on the CDI's performance and to better understand the advantage of the periodically alternated voltage operation on CDI's desalination performance.

2. Experimental methods

2.1. Desalination experiment

The graphene/carbon nanotubes hybrid [31] (G-CNTs, Beijing Beifang Guoneng New Material Co., Ltd., Beijing, China) electrode was prepared by mixing 80 wt% of the G-CNTs, 10 wt% of polytetrafluoroethylene (PTFE, 60% water solution, Sigma–Aldrich), and 10 wt% of acetylene black (99.9%, Sigma–Aldrich) slurry. The mixtures were pressed onto the titanium mesh (current collector, ChengZhuo wire mesh products trade Co., Ltd., Hebei, China) with a size of 4.0 cm × 4.0 cm, and then it was dried at 70 °C in an oven overnight. The electrode had a mass of 0.25 ± 0.01 g. Schematic diagram of desalination system was shown as Fig. S1. The CDI cell was assembled by using a pair of G-CNTs electrodes sandwiched together, separated by a Nylon mesh (Sefar Filtration Solutions Co., Ltd., Suzhou, China) which provided the flow channel to prevent the short-circuit of the two electrodes. Titanium plates (5.0 cm × 1.0 cm × 0.1 mm) attached with the electrodes to connect the external circuit. The desalination experiment was conducted in batch mode with a 20 mL NaCl aqueous solution at the concentration of 500 mg/L, which was continuously pumped through the unit cell by a peristaltic pump (BT00-2M, Longer Precision Pump Co., Ltd., Baoding, China) with a volumetric flow rate of 9 mL/min. The electrical conductivity of the NaCl solution was monitored every 10 s at the CDI's outlet using an online conductivity meter (S40, Seven Multi, Mettler-Toledo, USA). Cycles were automatically executed for 30 min at a voltage (1.2 V or −1.2 V) for adsorption and for another 30 min at the short-circuit potential for desorption. A regular potential operation and a periodically alternated voltage operation were conducted in this study. The former was operated at 1.2 V for adsorption and at the short-circuit potential for desorption (1.2/0 V), the later is operated at periodically alternated voltage of 1.2/0 V and −1.2/0 V.

In this experiment, NaCl concentration was calculated based on a calibration curve between conductivity and concentration. The electrosorption capacity (Γ, mg/g) was calculated according to the following equation.

$$\Gamma = (C_0 - C_e) \times V/m \tag{1}$$

where C_o and C_e refer to the initial and final NaCl concentrations, respectively (mg/L), and V is the volume of NaCl solution (L), and m refers to the mass of the electrode materials (g).

2.2. Modeling of the kinetics

Adsorption kinetics, which indicates the adsorption rate, is an important characteristic of adsorbents. It can be determined by using the Lagergren equation, which is often called the pseudo first-order adsorption kinetics and is presented as

$$q_t = q_e(1 - e^{-kt}) \tag{2}$$

where q_e and q_t are the amount of NaCl adsorbed (mg/g) at equilibrium and time t (min), respectively and k is the adsorption rate constant (min^{-1}).

2.3. Characterizations of electrodes in CDI system

X-ray photoelectron spectroscopy (XPS, Thermo Fisher Escalab 250xi, USA) was used to detect the valence state of carbon and oxygen of the electrode surface. Cyclic voltammetry (CV) and electrochemical impedance spectroscopy (EIS) investigations were taken using PGSTAT 128N electrochemical workstation (Metrohm Autolab, The Netherlands) in 1 M NaCl solution. CV was measured in the potential range of −0.5 to 0.5 V. EIS was measured at a scan frequency ranging from 100 kHz to 0.1 Hz. Herein, the specific capacitance was obtained from CV curve by the following equation.

$$C = \frac{\int IdV}{2v\Delta Vm} \tag{3}$$

where C is the specific capacitance (F/g), I is the current (A), v is the scan rate (V/s), $\triangle V$ is the applied potential window (V), and m is the mass of electrode material (g).

The potential distributions for a pair of electrodes was measured in 500 mg/L deaerated NaCl solution in a four-electrode cell using PGSTAT 128N electrochemical workstation [11], when each electrode was tightly placed in the cell so that the distance between the two electrodes was merely 0.5 mm (the same configuration used in the CDI cell, Fig. S2). The short-circuit potential (E_0) vs. SCE was determined by short connecting the negative and positive electrodes, the potential distribution each electrode (E_+ and E_-) vs. SCE was detected by applying a voltage across the two electrodes.

The potential of zero charge (E_{PZC}) information of the electrodes was tested through differential capacitance minimum measurements conducted using electrochemical impedance spectroscopy (EIS) [32]. EIS measurements for electrodes were made using an electrochemical workstation (CHI660D, Chenhua Instruments Co., Ltd., Shanghai, China) in 5 mM deaerated NaCl solution at a frequency of 1 Hz with a sinusoidal voltage perturbation of 5 mV and a potential increment of 2 mV. The value of E_{PZC} was determined through the minimum value of the specific capacitance (C), which was calculated through the imaginary part of the impedance spectra (Z″) and angular frequency (ω) according to the following equation [33].

$$C = \left| \frac{1}{\omega Z^{Prime}} \right| \tag{4}$$