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The study of membrane capacitive deionization from charge efficiency

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ABSTRACT

Membrane capacitive deionization (MCDI) is a promising technology for desalination with the potential of lowering energy consumption and treatment cost. In this paper, batch mode experiments were carried out to evaluate the charge efficiency of the MCDI process. Specifically, charge efficiency is a very functional tool to examine the double layer structure inside of porous electrode. The results show that the charge efficiency in MCDI is a function of both cell voltage and solution conductivity. Specifically, it was found that the charge efficiency was proportional to cell voltage while inversely to solution conductivity. The maximum charge efficiency (0.55) in MCDI was far less than one, indicating the high transient resistivity between membrane and carbon electrodes.

Keywords: Membrane capacitive deionization; Removal amount; Capacitive deionization; Porous electrode; Resistivity; Charge efficiency

1. Introduction

Desalination has emerged as an effective approach to overcome the water shortage worldwide [1–6]. MCDI is a promising desalination technology that may lower the energy demand compared to more established technologies such as reverse osmosis or thermal distillation [7]. MCDI is a modification of capacitive deionization (CDI) by integrating ion-exchange membranes/polymers into the CDI unit. Specifically, ion exchange membranes are added in front of porous carbon electrodes and thereby the salty ions are freely and selectively electrosorbed onto cathode and anode under direct voltage [8–11]. The membrane introduced in this process has the advantages of both minimizing the co-ions (ions of equal polarity as the electrode) expulsion effect to increase the removal capacity and improving the regeneration by means of fully releasing the counter ions back to the solution with a reverse voltage (Fig. 1(a)). Thus, MCDI is a very energy-efficient desalination technology (energy consumption <1 kWh m^{-3}) by compared with current reverse osmosis (2.9–3.7 kWh m^{-3}) or thermal distillation (4 kWh m^{-3}) technologies in which the water is removed instead of ions [7]. To achieve the optimum ion adsorption capacity, the nanocarbon materials with high specific surface area and superior bulk conductivity, such as carbon aerogel and carbon nanotube (CNTs), are often employed as electrodes for CDI and MCDI as well [12–16].

However, the exact role of electrical voltage during adsorption is still unclear. Besides, how to elucidate the CDI performance of diverse carbon materials with a reliable parameter, are not very clear either because of limited effective parameters during electrosorption [17–21]. Charge efficiency, defined as the ratio of adsorption capacity (mol g^{-1}) over charge (C g^{-1}), is thought to be a functional tool to examine the electrical double

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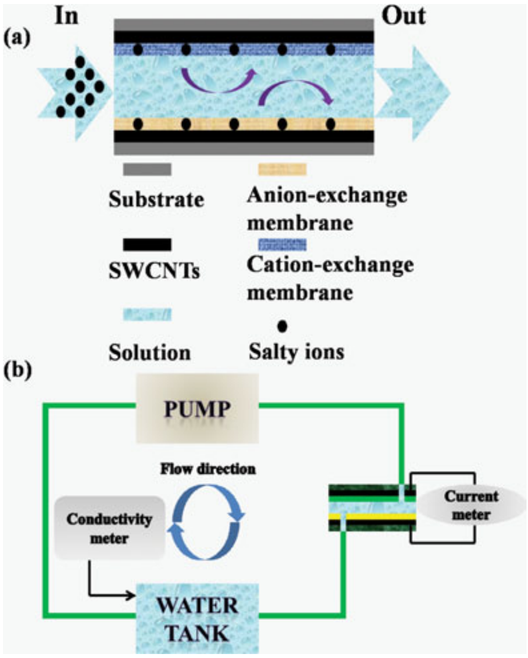

Fig. 1. Schematic diagram of (a) working principle of MCDI, (b) batch mode desalination experiment.

layer inside of porous electrode [22]. The charge efficiency parameter is based on the simplified classic Gouy–Champan–Stern model which is directly related to both sorption capacity and charge. Charge efficiency, as proposed by Biesheuvel et al. [23,24], was recommended to elucidate the desalination performance of CDI unit and to model the dynamic CDI process. Therefore, the charge efficiency model can accurately evaluate the double layer structures of porous electrode and provide an effective approach to optimise the electrode for desalination purpose.

Ideally, the charge efficiency would equal to one if the counterion adsorption fully compensates the electrode charge. However, the actual value of charge efficiency derived from experiment is far less than one because of the existence of co-ions impaction and the electrical current is contributed by the adsorption of counterions and the desorption of co-ions, respectively. In MCDI, the ion-exchange membranes block the co-ions effect by only allowing the counterions to selectively transport into and out of the electrode. The electrical charges can be more effectively used for the adsorption of counterions. Thus, the charge efficiency of MCDI would be highly enhanced by compared to corresponding CDI device.

In this paper, we study the electrosorption performance of MCDI based on single walled CNTs (SWCNTs) in NaCl solution from a point view of charge efficiency. This study strengthens the understanding on the dynamic MCDI process and provides useful information on how to further optimize the MCDI process.

2. Experimental

2.1. Fabrication and characterization

SWCNTs (Nanotech Port Co., Ltd. Shenzhen, China) used for this study had the following properties: length (5–15 µm), ash content (≤2 wt.%), surface area (>400 m^2 g^{-1}), purity (≥90%) and diameter (<2 nm). MCDI electrodes were fabricated by mixing 70 wt.% SWCNTs, 20 wt.% graphite (conductive material) and 10 wt.% polytetrafluoroethene (PTFE, binder agent). Ethanol (10–20 ml) was added dropwise into the mixture during the mixing process and then the mixture was put into ultrasonic bath for 2 h. Subsequently, the mixture was pressed on the graphite sheet and after drying in the air it was assembled into a MCDI unit. Each electrode was 80 mm wide × 100 mm long × 0.2 mm thick, and had a flow-through hole with a diameter of 4 mm. The ion-exchange membranes (Shanghai Chemistry, China) were used to absorb the ions selectively on the electrodes. The cation-exchange membrane (15 Ωm^{-2}, 80 mm wide × 100 mm long × 0.4 mm thick) was selectively permeable to cations and the anion-exchange membrane (20 Ωm^{-2}, 80 mm wide × 100 mm long × 0.4 mm thick) was selectively permeable to anions. The detailed description of ion-exchange membranes can be found elsewhere [25].

The surface morphologies of SWCNTs electrodes were examined by JEOL-5100 scanning electron microscopy (SEM). Their pore size distribution and Brunauer–Emmet–Teller specific surface area were deduced from the N_2 physical adsorption measurement data which were obtained with ASAP 2010 Accelerated Surface Area and Porosimetry System (Micrometitics, Norcross, GA).

2.2. Batch mode experiment

Several experiments were conducted in a continuously recycling system including an MCDI unit, conductivity monitor and current recorder as shown in Fig. 1(b). In each experiment, the analytical pure sodium chloride (NaCl) was used for the aqueous solutions and the solution volume and temperature were maintained at 50 ml and 298 K, respectively, with an initial conductivity of 500 and 1000 µS cm^{-1}. A direct voltage of 0.2–1.4 V was applied between electrodes. It should be noticed that hydrolysis of water was not found when the voltage between the two electrodes was more than 1.2 V because of the existence of resistance in the whole circuit. The variation of conductivity and current were recorded simultaneously and independently. The regeneration experiment was carried out by shorting circuit the electrodes for about 25 min and then applying a reverse voltage of 1.2 V for about 15 min. Due to the strong ion adsorption at the beginning of the experiment, the reversed voltage was beneficial to release the absorbed ions quickly and completely. The correlation of conductivity to concentration was obtained according to a calibration table prior to the experiment, which has been described in our previous works [26–29].

3. Results and discussion

Numerous studies have shown that the adsorption capacity of the electrodes is directly related to their specific surface area, pore size distribution and conductivity [30–32]. SWCNTs with specific surface area of 448 $m^2\ g^{-1}$ are used here for electrodes since they are suitable porous materials for CDI [33,34]. Fig. 2(a) shows pore size distribution of SWCNTs. The average pore size of 5 nm shows SWCNTs in this work are mainly composed of mesopores (2–50 nm) according to IUCPA classification. Such a mesoporous network structure is further confirmed by SEM image in Fig. 2(b). Meso-scale pores allow hydrated ions easily to enter through the pores of the SWCNTs electrode to facilitate ion adsorption [35].

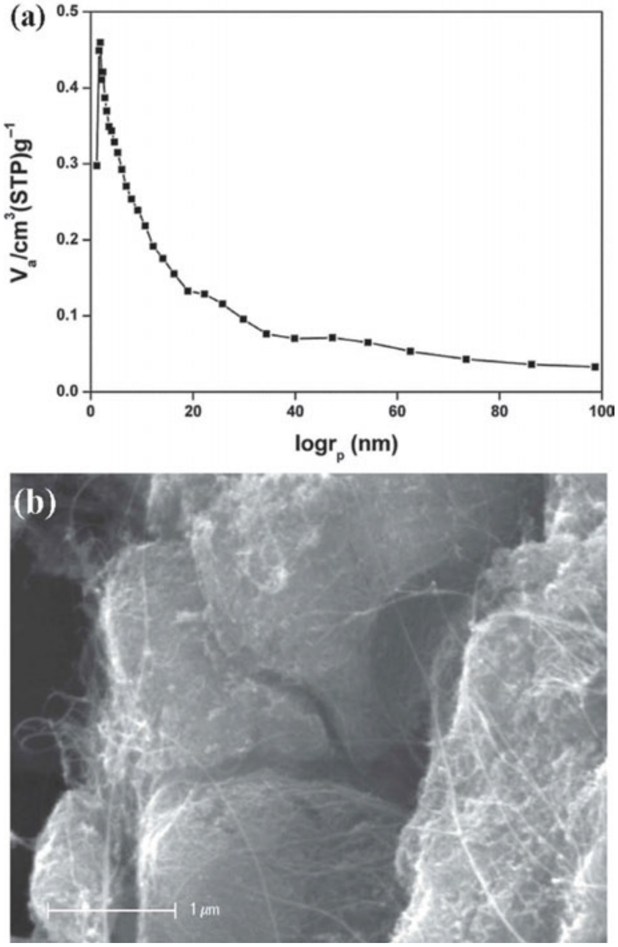

Fig. 2. (a) Pore size distribution, (b) SEM image of SWCNTs.

Fig. 3(a) and (b) depict the typical conductivity and current response in the bench-scale MCDI unit, respectively. It should be noticed that in Fig. 3(a) there is desorption plateau when only short-circuit is used, indicating that a long desorption time is needed in this case. However, an accelerated desorption is observed when 1.2 V reverse voltage is applied, which can release the absorbed ions fast and completely. Fig. 3(c)–(e) show the as-calculated charge, adsorption capacity and charge efficiency at different cell voltages, respectively. As expected, the conductivity and the current dramatically decrease once the cell voltage is applied. High voltage results in high salt removal because of enhanced electrostatic force. Furthermore, once the cell voltage is removed, the conductivity increases rapidly until it becomes stable, indicating the ions are fully released back to solution and the regeneration of electrode ends.

As mentioned above, the charge efficiency is one of most significant tools to elucidate the desalination performance of CDI and MCDI. Ideally, each electron charge will be fully charge-compensated by counterion adsorption and the transfer of one electron from one to another electrode is accompanied by the removal of precisely one salt molecule out of the bulk solution. However, actually, the co-ions are simultaneously expelled from the double layer which accommodates the absorbed ions. It has a negative impact on the charge efficiency. Therefore, charge efficiency (Λ) is used to evaluate whether the electrical voltage has been fully consumed in desalting process and is defined as the ratio of Γ (adsorption capacity, mol g^{-1}) over Σ (charge, C g^{-1}):

$$\Lambda = \frac{\Gamma \times F}{\Sigma} \tag{1}$$

where F is Faraday constant (96,485 C mol^{-1}). Γ is calculated from the adsorption curve where the concentration (mg l^{-1}) is a function as time [22,23] and Σ is obtained by integrating the current. Thus:

$$\Gamma = \frac{(c - c_0) \times v \times 10^{-3}}{58.5 \times M} \tag{2}$$

$$\Sigma = \frac{\int idt}{M} \tag{3}$$

where C and C_0 are the final and initial concentration (mg l^{-1}), v (l) is the volume of test solution and M (g) is the mass of total electrodes.

Adsorption capacity Γ in desalting process is calculated to be 114.3 μmol g^{-1} (the Γ is 22.37 μmol g^{-1} in corresponding CDI) when the initial conductivity of

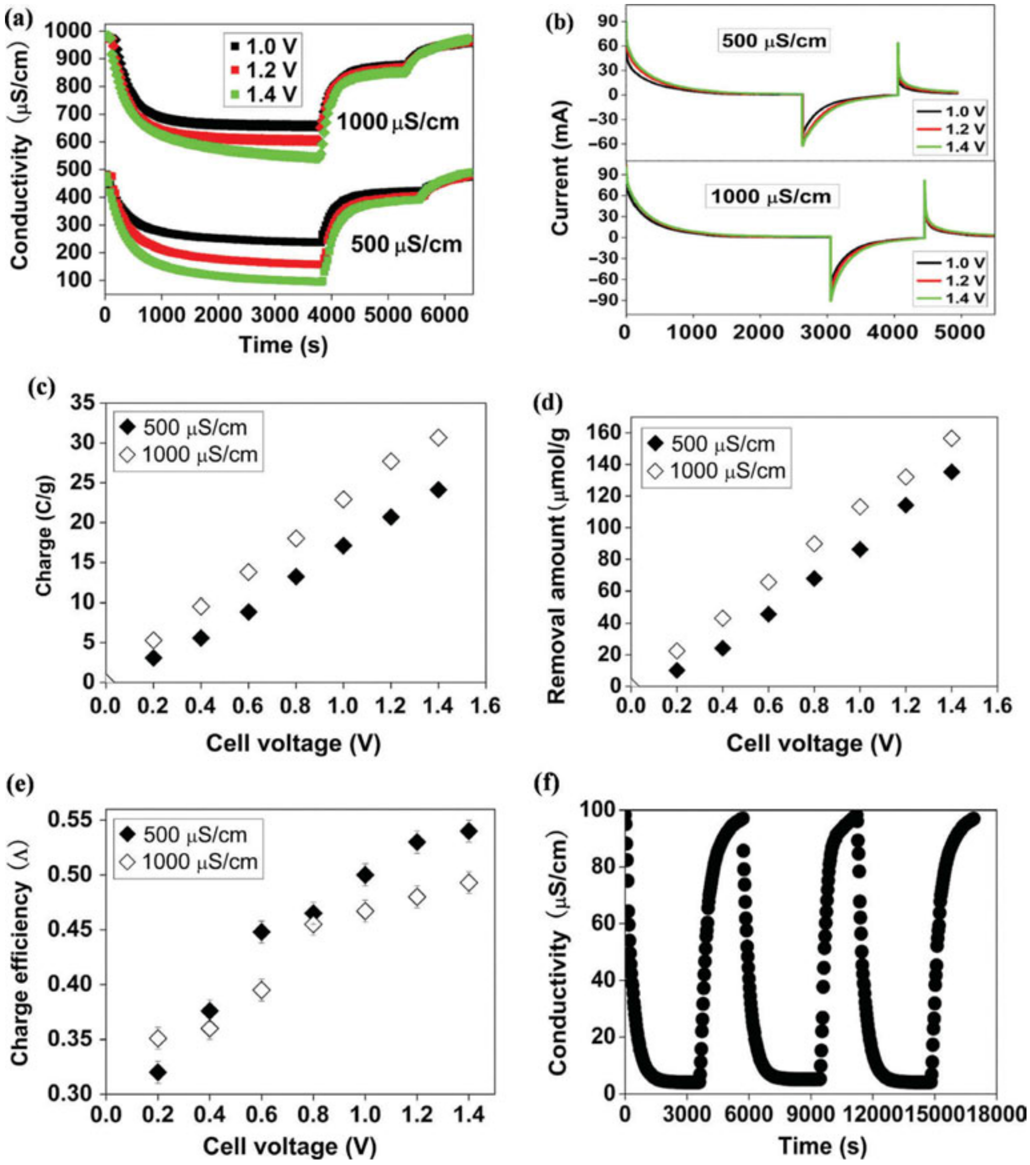

Fig. 3. (a) Conductivity response, (b) current response, (c) charge variation, (d) adsorption capacity variation, (e) charge efficiency variation in MCDI unit with initial solution conductivities of 500 and 1000 μS cm^{-1} at different cell voltages, (f) regeneration experiment in MCDI unit.

solution and the cell voltage are 500 μS cm^{-1} and 1.2 V, respectively. Accordingly, the total charge Σ is 20.7 C g^{-1}. Thus the charge efficiency Λ equals to 0.53, which is much higher than the value for corresponding CDI (0.29), implying the co-ions effect has been effectively blocked. In Fig. 3(c)–(e), it is noticed that the charge, adsorption capacity and charge efficiency increase with the increase of cell voltage. On the other hand, the charge and adsorption capacity at an initial conductivity of 1000 μS cm^{-1} is higher than that at 500 μS cm^{-1} for all voltages while the charge efficiency exhibits an inverse trend. This conclusion was consistent to the corresponding study on CDI [23], showing that there was no change in the working mechanism of MCDI when the ion-exchange membranes are introduced into CDI.

It was observed from Fig. 3(e) that the experimental charge efficiency is still far away from the ideal value even high cell voltage, such as 1.4 V, was applied. The possible reason should be related to the properties of the electrodes, such as the weak adhesion between SWCNTs and substrate. Specifically, the non-conductive PTFE as binder agent had a negative impact on the conductivity of the electrodes. In addition, the weak contact adhesion between the electrodes and ion-exchange membranes may increase the bulk resistivity of the whole unit and thereby limit the total ion adsorption amount and the transient current. Recently, a carbon ion-exchange polymer was proposed to replace ion-exchange membrane in MCDI [36,37], which may solve the problem of weak contact adhesion. However, its influence in charge efficiency is still to be investigated in the future.

Since the regeneration (desorption) is one of most important factors to commercialize the MCDI, a regeneration experiment was performed by using the as-fabricated MCDI unit. Fig. 3(f) clearly shows that the MCDI unit could be regenerated without any decay in adsorption capacity after several cycles.

4. Conclusions

Batch mode desalination experiments were carried out to evaluate the performance of MCDI as indicated by the charge efficiency. The results show that the cell voltage and solution conductivity greatly influenced the charge efficiency in MCDI. The results also show that the ion-exchange membranes play a significant role in blocking the co-ions effect. However, further optimization in the integration of ion-exchange membranes and SWCNT electrodes still needs to be carried out.

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