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A Comparative Study between Membrane Capacitive Deionization and Capacitive Deionization from Isotherms and Kinetics

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Abstract: Membrane capacitive deionization (MCDI) is a promising technique to achieve the desalination. This novel technique can largely improve the desalination efficiency of capacitive deionization (CDI) by introducing ion-exchange membranes into CDI. This paper presents a comparative study on the electrosorptive performances of CDI and MCDI based on single walled carbon nanotubes electrodes in NaCl solution from electrosorption isotherm and kinetics analysis. It was found that MCDI exhibits a higher salt removal efficiency of 98% than CDI (52%) and the ions sorption behavior follows Langmuir isotherm in both CDI and MCDI, indicating the monolayer sorption. Furthermore, the kinetics analysis shows that the ion-exchange membranes can speed up the ion transport during the electrosorption process due to restricted co-ions expulsion impaction.

Keywords: Capacitive deionization (CDI); Membrane capacitive deionization (MCDI); Electrosorption; Isotherm; Kinetics

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Introduction

About 98% of earth's water is either sea water or brackish water which is not suitable for direct consumption because of high salinity and currently many countries suffer from a shortage of the fresh natural water. In this case, desalination has emerged as a novel approach to solve this crisis since it can provide clean water by converting the highly saline sea water to fresh water [1-5]. Capacitive deionization (CDI) is an electrochemically induced alternative approach for the removal of salt ions from concentrated aqueous solutions by forcing charged ions into the electrical double layer at an electrode-solution interface when the electrode is connected to an external power supply [6-8]. CDI as an energy-saving and environmental-friendly desalination

technique has attracted enormous attentions in recent years because it is conducted at ambient conditions and low voltages (e.g. 1.2 V) without secondary waste and doesn't require high-pressure pumps, membranes, distillation columns, or thermal heaters [9-18].

Membrane capacitive deionization (MCDI) is a modification of CDI by integrating ion-exchange membranes 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 [19]. 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 [20-22]. Therefore, MCDI should be a promising highly-efficient desalination technology.

In this work, we comparatively study the electrosorption behavior including electrosorptive isotherm and kinetics of CDI and MCDI based on single walled carbon nanotubes (SWCNTs) electrodes in NaCl solution. Through the comparison, it can show us the advantage of MCDI over CDI. Such a study will be helpful to further understand and apply both of CDI and MCDI in practice.

Experiment

Fabrication and characterization of electrode

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), purity ($\geq 90\%$) and diameter (<2 nm). The electrodes were fabricated by mixing 70% SWCNT, 20% graphite (conductive material) and 10% 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 hours. Subsequently, the mixture was pressed on the graphite sheet and after drying in the air it was assembled into a CDI/MCDI unit. Each electrode was 80 mm wide \times 100 mm long \times 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 Ω/m^2 , 80 mm wide \times 100 mm long \times 0.4 mm thick) was selectively permeable to cations and the anion-exchange membrane (20 Ω/m^2 , 80 mm wide \times 100 mm long \times 0.4 mm thick) was selectively permeable to anions. The detailed description of ion-exchange membranes can be found elsewhere [19].

The surface morphologies of SWCNTs electrodes were examined by JEOL-5100 scanning electron microscopy (SEM). Their pore size distribution and Brunauer-Emmet-Teller (BET) 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 (Micromeritics, Norcross, GA).

Batch mode desalination experiment

Batch-mode experiments were conducted in a continuously recycling system including an CDI/MCDI unit, conductivity monitor and current recorder [23,24]. 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, respec-

tively, with an initial conductivity of 100 $\mu\text{S}/\text{cm}$. A direct voltage of 1.2 V was applied between electrodes. The variation of conductivity was recorded and 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 [25,26].

Normally the salt removal is defined as follows:

$$\text{Salt removal}(\%) = \frac{C - C_0}{C} \times 100 \quad (1)$$

Where C is initial conductivity and C_0 is the final conductivity.

Results and discussion

SWCNTs with specific surface area of 448 m^2/g was utilized to fabricate the electrodes for both CDI and MCDI. Fig. 1 shows pore size distribution of SWCNT. The average pore size of 5 nm shows SWCNTs in this work are mainly composed of mesopores (2-50 nm) according to IUPAC classification. Such a mesoporous network structure is further confirmed by SEM image in the inset of Fig. 1. Meso-scale pores allow hydrated ions easily to enter through the pores of the SWCNTs electrode to facilitate ion adsorption [11].

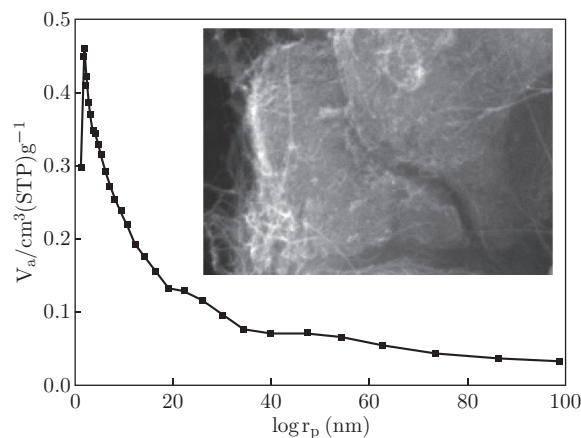


Fig. 1 Pore size distribution and SEM image (inset) of SWCNTs film.

The electrosorption experiments of CDI and MCDI in NaCl solution with an initial conductivity around 100 $\mu\text{S}/\text{cm}$ show the similar process, as shown in Fig. 2(a). When the voltage is applied onto the electrodes, the conductivity sharply decreases with the increasing time. At about 30 min, the electrosorption of CDI and MCDI gradually reaches saturation. The salt removal of MCDI is 98% which is nearly twice as much as that of CDI (52%), indicating the MCDI is better for desalination purpose than CDI. To determine the ion sorption isotherm, several batch electrosorption experiments in NaCl solutions with different initial conductivities were carried out in CDI and MCDI, respectively. The initial conductivities of NaCl solutions were from 50 to 1000

$\mu\text{S}/\text{cm}$ and a direct voltage of 1.2 V was applied. Freundlich isotherm (2) and Langmuir isotherm (3) models were introduced to fit the experimental data,

$$q = K_F C^{1/n} \quad (2)$$

$$q = \frac{q_m K_L C}{1 + K_L C} \quad (3)$$

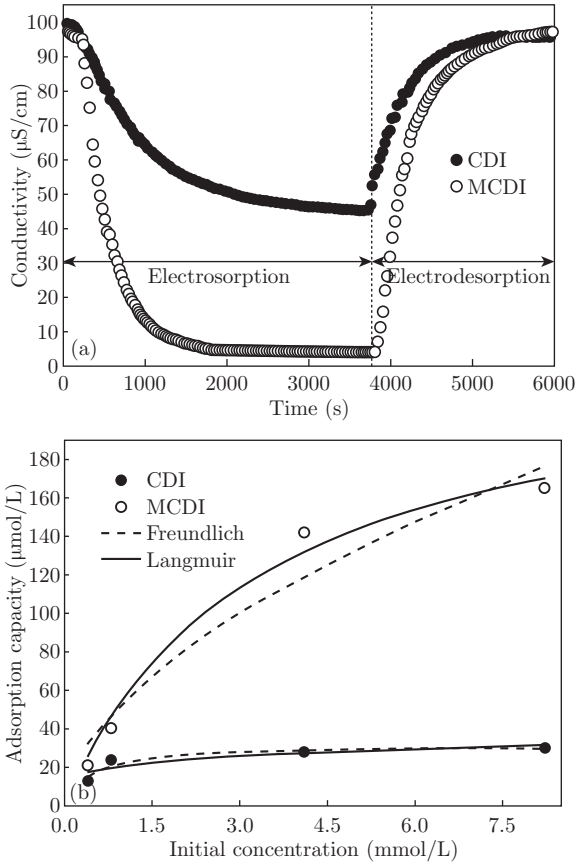


Fig. 2 (a) Desalination performance of CDI and MCDI and (b) the electroadsorption isotherms for CDI and MCDI in NaCl solution.

where C is the equilibrium concentration (mmol/L), q is the amount of adsorbed NaCl (in micromoles per gram of SWCNT electrodes), q_m is the maximum adsorption capacity corresponding to complete monolayer coverage. Fig. 2(b) illustrates the electroadsorption isotherms of CDI and MCDI. It can be observed that CDI and MCDI have similar electroadsorption isotherms, indicating the ion-exchange membranes have little impact on ion sorption behavior during the electroadsorption. Table 1 shows the determined parameters and regression coefficients R^2 , K_L and K_F of Freundlich and Langmuir isotherms for CDI and MCDI, respectively. The regression coefficients R^2 of Freundlich and Langmuir isotherms for MCDI are 0.99 and 0.95 while 0.92 and 0.8 for CDI, implying the Langmuir isotherm describes the experimental data better than Freundlich isotherm

for both cells, which means that although ion-exchange membranes are introduced in MCDI, the electroadsorption of SWCNTs electrode still follows monolayer adsorption. The q_m values calculated from Langmuir equation are 239.56 and $31.57 \mu\text{mol}/\text{g}$ for MCDI and CDI, respectively, indicating the electroadsorption capacity of MCDI is higher than that of CDI which is consistent to the results in Fig. 2(a). The result further confirms that MCDI exhibits better desalination performance than CDI due to the inhibition of co-ions expulsion effect during electroadsorption.

Table 1 The determined parameters from Freundlich and Langmuir isotherms in NaCl solutions for CDI and MCDI

Isotherm	Model equation	Parameters	CDI	MCDI
Freundlich	$q = K_F C^{1/n}$	K_F	20.58	53.98
		n	5.08	1.78
		R^2	0.8	0.95
Langmuir	$q = \frac{q_m K_L C}{1 + K_L C}$	q_m	31.57	239.56
		K_L	2.45	0.3
		R^2	0.92	0.99

Adsorption kinetics, implying the adsorption rate, is often employed to explain the ions behavior during adsorption process [27,28]. Fig. 3 depicts the simulated results of adsorption kinetics associated with CDI and MCDI by considering the Lagergren equation which is often called as pseudo-first-order adsorption model and is as follows:

$$\log(q_e - q) = \log q_e - \frac{kt}{2.303} \quad (4)$$

Where k is the adsorption rate constant (min^{-1}), q_e and q are the adsorption capacities at equilibrium (mg/g) and time t (min), respectively.

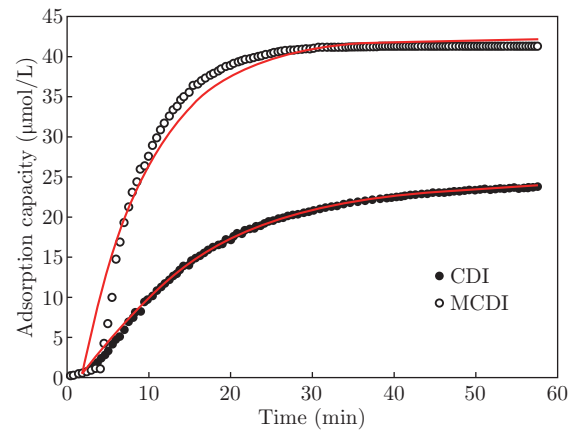


Fig. 3 The electroadsorption kinetics for CDI and MCDI in NaCl solution.

The regression coefficient R^2 , can be used to determine the adequacy of kinetic equation. The coefficient

R^2 for CDI and MCDI are 0.9943 and 0.9675, respectively, which are very close to 1, indicating the adsorption equation fits the experimental data very well. In addition, the rate constant of MCDI is 0.2768, which is much higher than that of CDI (0.1484), which further confirms that the ion transport in MCDI is much faster than that in corresponding CDI, due to the coupling of the ion-exchange membranes with SWCNTs electrodes.

Conclusion

In summary, the desalination performance of CDI and MCDI are comparatively investigated through batch mode experiment and evaluated from isotherms and kinetics. The results show that (i) the desalination performance of MCDI is better than corresponding CDI, due to the minimized co-ions expulsion effect; (ii) the ions sorption behavior followed the Langmuir isotherm in both cells, indicating the monolayer adsorption; (iii) the kinetics analysis confirmed that the ions transport in MCDI is much faster than CDI.

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