

Synthesis of cation exchange membranes for capacitive deionization based on crosslinked polyvinyl alcohol with citric acid

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ABSTRACT

Constructing new cation exchange membranes (CEM) has been regarded as an easy and effective approach to improving the capacitive deionization (CDI) system. In this study, a new method of fabrication of CEM was introduced by crosslinking sulfosuccinic acid (SSA) and citric acid (CA). The SSA and CA were crosslinked with polyvinyl alcohol (PVA) to fabricate CEMs in a series of conditions. The ion transference number for each fabricated membrane was tested to select the optimal recipe. The membrane fabricated by the selected method was then tested in the CDI system and the results show that the total percentage of SSA could be reduced from 5% to 1% by adding 5 g of non-toxic and inexpensive CA. The cost of preparing the membrane also decreased from US\$0.18 per square meter to US\$0.03. The adsorption capacity and the charge efficiency of membrane capacitive deionization system (MCDI) coated with a PVA/SSA/CA layer (mass ratio 10:1:5) was compared with the normal CDI and the MCDI coated with the original membrane (PVA:SSA = 19:5), which is named O-MCDI). The results show that with the modified membrane, the adsorption capacity and the charge efficiency can be enhanced by 18% and 28% compared with the CDI. In addition, although the cost is reduced, the desalination efficiency is still guaranteed. The adsorption capacity and charge efficiency are still increased by about 3% compared with the O-MCDI.

Key words | cation exchange membrane, citric acid, membrane capacitive deionization, polyvinyl alcohol

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INTRODUCTION

Capacitive deionization (CDI), as an emerging desalination technology, has attracted great research interests for decades because it is cheaper and consumes less energy than reverse osmosis and electrodialysis (Oren 2008; Porada *et al.* 2013). Each CDI unit consists of a pair of paralleled porous electrodes that are placed opposite each other with a spacer. After applying a low voltage between the positive and negative electrodes, the ions and the charged particles in the feed solution migrate to the two electrodes under the action of the electric field force and the concentration gradient, and are adsorbed on the surface of the electrode to form an electric double layer (EDL), thereby purifying the water (Bazant *et al.* 2004; Biesheuvel 2009; Biesheuvel *et al.* 2009). When the electrodes are short-circuited or a reverse voltage is applied, the absorbed ions are released into the bulk solution and the concentration of the solution increases. This is the process of a CDI unit adsorption and

desorption. However, there are some structural problems with the CDI system during the desorption process (He *et al.* 2016). In particular, when a reversed voltage is applied to the electrode for desorption, the charged ions originally absorbed on the electrode will desorb and move to the bulk solution, while the counter-ions are again adsorbed from the solution to the electrode surface. This phenomenon will lead to incomplete electrode regeneration, thereby reducing the ability of the electrode to adsorb salts, and resulting in higher energy consumption and lower operation efficiency (Lee *et al.* 2006; Tang *et al.* 2017). At the same time, Faradaic reactions (i.e. redox reactions both on the surface and within the carbon electrodes) may lead to the formation of chemical by-products and/or pH fluctuations of the produced water, which ultimately reduces the long-term stability and performance of the electrode (He *et al.* 2016; Tang *et al.* 2017).

To overcome this weakness, membrane capacitive deionization (MCDI) was introduced by Lee *et al.* (2006). As the modification of CDI, MCDI uses anion and cation exchange membranes (CEM) on the surface of anode and cathode, respectively. Such a simple modification allows the counter-ions to freely enter the pore structure, while the co-ions are blocked off, which leads to an increase in the desalination efficiency and capacity (Zhao *et al.* 2013; Kim *et al.* 2015). The counter-ions can also be completely discharged from the electrode region during the regeneration step compared to the CDI system (Biesheuvel *et al.* 2014; Kim *et al.* 2015). Therefore, the most critical part of MCDI is the design and application of membranes.

Basic research on ion membranes began in 1925, when Michaelis and Fujita studied the homogeneous weak acid colloid membrane (Michaelis & Fujita 1925). Around 1940, the demand of industrial application promoted the development of synthesis of ion-exchange membranes based on phenolic condensation (Wassenegger & Jaeger 1940). In the 1970s, the sulfonated polytetrafluoroethylene 'Nafion series' CEM developed by the Dupont Company of the United States realized its large-scale application in the chlor-alkali production industry, energy storage and conversion systems (such as fuel cells) (Kerres 2001). It has been found that Nafion is rarely used in water treatment due to excessive swelling and high cost (Kim *et al.* 2004). Many researchers have therefore focused on the development of good mechanical properties and chemical stability membranes with lower cost to achieve the goal of commercialization of CDI (Lee *et al.* 2005).

Polyvinyl alcohol (PVA) has the advantages of strong film-forming ability and good hydrophilicity. It is a common polymer matrix and its mechanical properties and thermal stability can be improved through freezing, heat treatment, irradiation and chemical crosslinking (Lebrun *et al.* 2002; Bolto *et al.* 2009). However, PVA itself does not have a fixed charge and is poorly hydrophilic. It is usually necessary to use organic functional groups such as hydroxyl, amine, carboxylate, sulfonate, and quaternary ammonium to provide hydrophilic or ionic groups. All poly-functional compounds capable of reacting with hydroxyl groups can usually be crosslinked with PVA to obtain a spatial network structure (Kim *et al.* 1992; Krumova *et al.* 2000).

Kim *et al.* studied the crosslinked CEM by PVA and sulfosuccinic acid (SSA), and applied it in the field of MCDI. They reached the conclusion that the use of composite membranes could enhance the desalination ability of CDI (Kim & Choi 2010). During the preparation process of CEM,

SSA can be used as a crosslinking agent and a donor of the hydrophilic group ($-\text{SO}_3\text{H}$). In our previous study (Chen *et al.* 2020), we found the optimal reaction conditions and parameters for the preparation of a crosslinked SSA/PVA composite membrane. It turns out that the CEM significantly increases the adsorption capacity by more than 15%, and the charge efficiency increases by about 25% on average when 5% SSA was used and the crosslinking temperature reached 100 °C. However, SSA is expensive (about US\$0.4 per gram), and so we introduced cheap citric acid (CA, US\$0.003 per gram) to reduce the mass of SSA. Although reducing the cost of the membrane, it also successfully achieved high desalination efficiency. Compared with the original membrane, the crosslinked membrane modified by CA increased the charge efficiency and the adsorption capacity by about 3%. In this study, the desalination efficiency of different mass of CA/SSA/PVA composite membranes were investigated. Here, we expect that the crosslinked CA/SSA/PVA composite membrane results in high desalination efficiency due to the addition of sulfonic acid groups and carboxyl groups, which do not participate in the crosslinking reaction. The important thing is that the modified membrane is inexpensive, which is about US\$0.03 per square meter, much lower than 5% SSA/PVA membrane (US\$0.18 per square meter). At present, the price of ion-exchange membranes (homogeneous membranes) on the market is generally higher than US \$142.7 per square meter, and even the heterogeneous membranes cost about US\$70.

MATERIALS AND METHODS

Materials

Fully hydrolyzed PVA (average $M_w = 75,000\text{--}80,000$) and the CA_SSA (70 wt% solution), which acted as a crosslinking agent as well as a donor of the hydrophilic group with the sulfonic and carboxyl group ($-\text{SO}_3\text{H}$ and $-\text{COOH}$), were purchased from Aldrich Chemical Co. (Milwaukee, WI, USA). The NaCl, KCl, NH_4Cl , CaCl_2 , and MgSO_4 used in the experiments were of analytically grade and acquired from Sinopharm Chemical Reagent Co. (Shanghai, China).

Preparation of the carbon electrodes

First, the solvent N-methyl-2-pyrrolidone (NMP, Aldrich) and the polymer binder poly(vinylidene fluoride) (PVDF, $M_w = 275,000$, Aldrich) were mixed at a ratio of 31:1. This

was then heated and stirred for several hours to be clear and transparent. After that, the activated carbon powder (YP-50F, KURARAY) was added to the homogenous slurry. The slurry needs to be ball milled and defoamed before it can be used. Finally, the slurry was cast onto a graphite sheet to a thickness of 200 μm and dried at room temperature for 2 or 3 days.

Fabrication of the CEM

Aqueous 10 wt% PVA solution was prepared by dissolving dry PVA in water and then heating at 90 $^{\circ}\text{C}$ for 6 h. The PVA solution was mixed together with SSA solution, and the mixture was vigorously stirred at room temperature for 24 h. The amount of SSA was 1 wt% of the total solution. After mixing, an appropriate amount of CA solution was added dropwise into the solution and then heated at 60 $^{\circ}\text{C}$ for 3 h. The obtained homogeneous polymer solution was casted onto the prepared carbon electrode, and the thickness of the film was controlled with a four-sided preparation device (SZQ type, Tianjin Kexin Testing Machine Factory Co., China, selecting a side with a thickness of 200 μm). The electrode was then dried in a vacuum oven at 60 $^{\circ}\text{C}$ for 1 h to evaporate the excess solvent. After that, the temperature was increased to 100 $^{\circ}\text{C}$ so that further crosslinking reactions between the polymers occurred to form a CEM. Finally, the membrane electrode with a thickness of 100 μm was obtained. The reaction mechanism of PVA, SSA, and CA is shown in Figure 1.

Open-circuit voltage testing

The selective permeability of the counter-ions through the ion-exchange membrane is measured by the ion transference number (Buck *et al.* 2002). It is related to the ratio of the concentration of ion-exchange groups in the membrane (fixed ion concentration) to the concentration of the external solution. In general, there are two methods for measuring

the ion transference number: membrane potential method and electrodialysis (Forland & Ostvold 1974; Zhao *et al.* 2010). In this experiment, the ion transference number and the selective permeability were estimated using the testing membrane potential method, which uses a NaCl solution (the mobility of Na^+ and Cl^- is almost equal).

The measurement of transference number is performed in a dual pool instrument, as shown in Figure 2. The membrane samples were immersed in a 1 mol/L NaCl solution for more than 2 h, and were transferred between the two chambers. The same volume of NaCl solution was injected into the two tanks for at least 5 min before measuring (the concentration of the dilution solution (C_1) was 5 mmol/L, but the concentrated solution (C_2) was changed (5–500 mmol/L)). The open-circuit voltage (OPV) was measured using a pair of Ag/AgCl reference electrodes (washed thoroughly with water and allowed to stand overnight). In general, when the ratio of C_2 to C_1 was relatively high, the measured membrane potential was also higher.

During the experiment, the CEM has selective permeability, allowing only cations to pass; therefore, the ion concentration on both sides of the membrane will be different and the membrane potential will be generated. The cation mobility can reflect the ion selectivity of the CEM. The higher the mobility, the better the selectivity.

When an electrolyte solution with a 1:1 valence is used and the potential difference between the reference electrode and its surrounding solution is ignored, the transference number of cations can be calculated according to Equation (1) (Nagarale *et al.* 2004):

$$V_M = (2\bar{t}_+ - 1) \frac{RT}{F} \ln \left(\frac{a_{\pm 2}}{a_{\pm 1}} \right) \quad (1)$$

where $a_{\pm 1}$ and $a_{\pm 2}$ are the average ion activity of C_1 and C_2 , respectively; F is the Faraday constant; V_M is the membrane potential; R is the gas constant; T is the temperature; and \bar{t}_+ is the transference number of cation in the membrane.

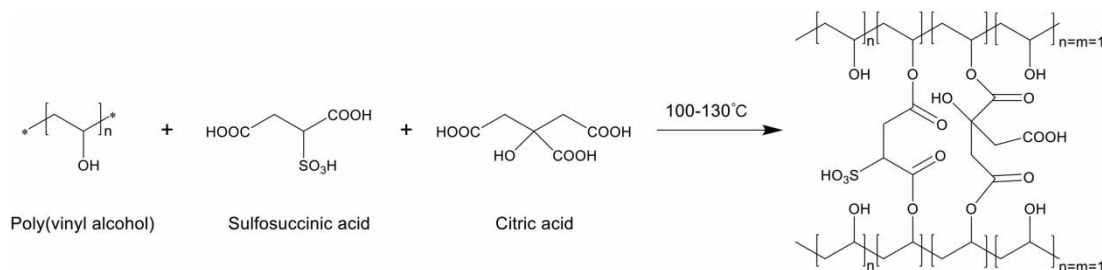


Figure 1 | Possible reaction mechanism of PVA/SSA/CA.

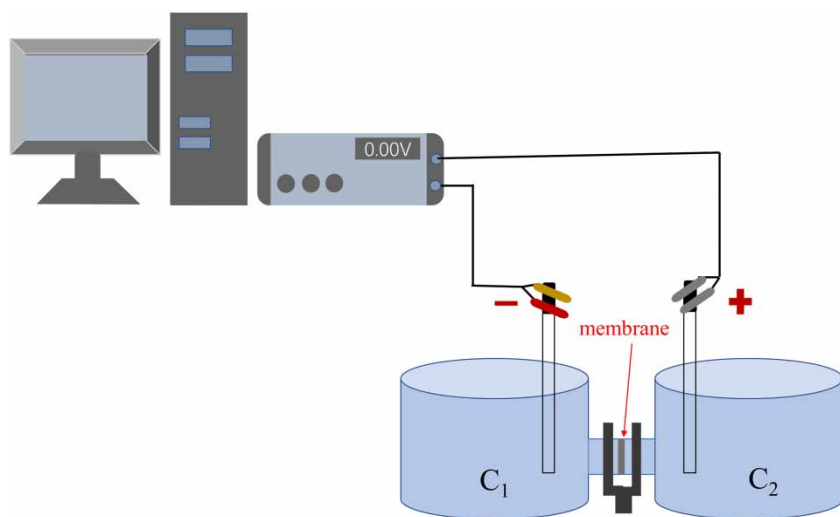


Figure 2 | Schematic diagram of the dual pool instrument.

When using an electrolyte solution with a valence of 2:1, the membrane potential can be calculated using Equation (2):

$$V_M = \left(\frac{3}{2}i_+ - 1 \right) \frac{RT}{F} \ln \left(\frac{a_{\pm 2}}{a_{\pm 1}} \right) \quad (2)$$

Desalination experiments

Five pairs of electrodes were used in the experiments. Each unit cell consisted of two relatively parallel electrode sheets, $60 \times 60 \text{ mm}^2$ with a 1.3-cm-diameter hole in the middle. The reverse of the electrodes were made of flexible graphite sheets as inert current collectors, and adjacent electrode sheets were separated by a spacer to prevent short circuits. In the experiments with membranes (denoted as the MCDI), the CEM electrode acted as the cathode and the pure carbon electrode acted as the anode.

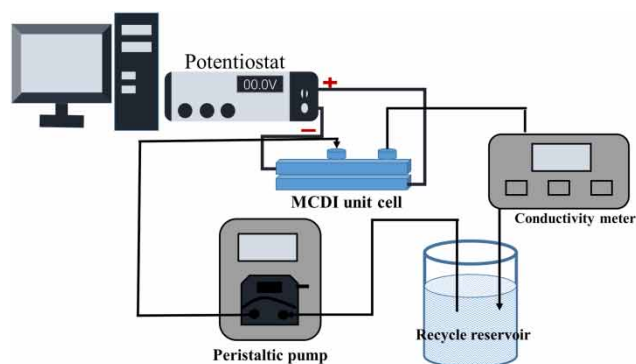


Figure 3 | Schematic diagram of experimental setup and MCDI unit cell configuration.

Electrosorption experiments were carried out in a batch mode, depicted in Figure 3. Using a peristaltic pump (YZ1515×, Longer) during the experiments, the NaCl solution flowed through the stack from a small reservoir. The conductivity meter was connected to a data-acquisition system (LEICI DDSJ-308A, INESA (Group) Co., Shanghai, China) and was immersed in the effluent water to measure the conductivity. The adsorption and desorption processes of the solution were designed by the electrochemical workstation (ZF-100, Shanghai and Zhengfang Electronic Appliance Co., China).

RESULTS AND DISCUSSION

Ion transference number

In the previous study (Chen *et al.* 2020), we obtained the highest ion mobility and the highest charge efficiency when the mass fraction of SSA was 5% and the crosslinking

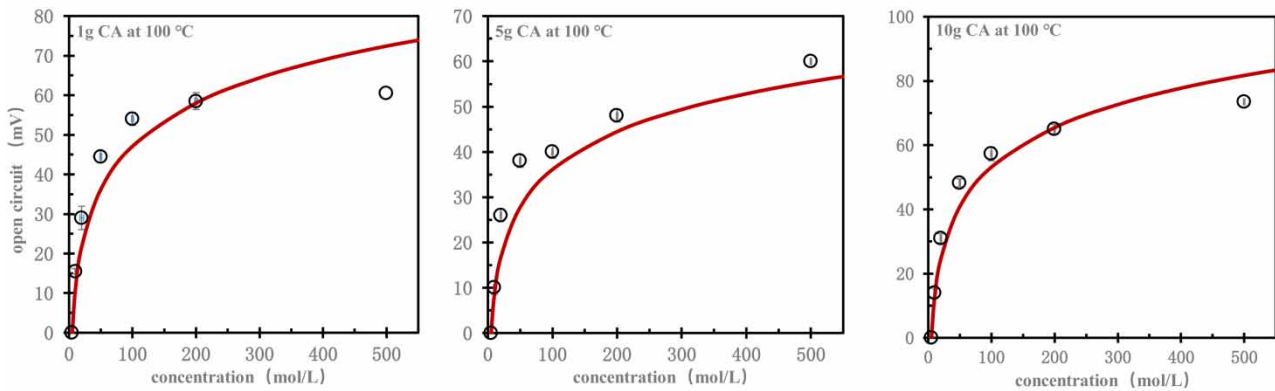


Figure 4 | Membrane potential and theoretical fitting results at different mass of CA.

temperature was 100 °C. The degree of crosslinking of PVA/SSA membrane significantly affects its ion selectivity. Under 100 °C, the crosslinking degree of the polymer composite membrane is at the optimal level, which not only retains the space structure sufficient for transporting ions, but also introduces a sufficient number of ionic groups, and so the ion selectivity of the membrane is optimal. SSA is expensive, and we tried to replace it with cheap crosslinking agents with functional groups (such as CA). Figure 4 shows the sodium ion transference number of the PVA/1%SSA/CA membrane calculated from the membrane potential at different mass of CA. When the mass of CA is 5 g, the ion selectivity of the membrane is optimal. The following experimental data of each group are obtained by averaging the results of the last three cycles (the experiment was unstable in the first and second cycles, so was not used).

The results revealed that the mobility of the modified membrane was 0.8061, 0.8642 and 0.8454, respectively. Each value corresponds to a different amount of CA (1 g, 5 g, and 10 g). It can be seen that when the mass of CA is 5 g, the ion selectivity is optimal. The crosslinking degree of

the PVA composite membrane significantly affects its ion selectivity. Considering both the space in the polymer electrolyte that can accommodate and transfer hydrated ions and the number of ionic groups, the optimal mass of CA is 5 g, as shown in Figure 5. The degree of crosslinking, the polymer space and the number of ionic groups are at an optimum level to optimize the selectivity.

Desalination performances of the CDI and MCDI cells

Capacitive deionization tests were performed on the two systems (CDI and MCDI) and the results are shown in Figure 6.

The NaCl concentration was determined from the linear relationship between NaCl concentration and conductivity (Equation (3)):

$$C = \left(\frac{\sigma - 4.5}{121.29} \right)^{1/0.9826} - 0.13 \quad (3)$$

where σ is the conductivity recorded during the experiments.

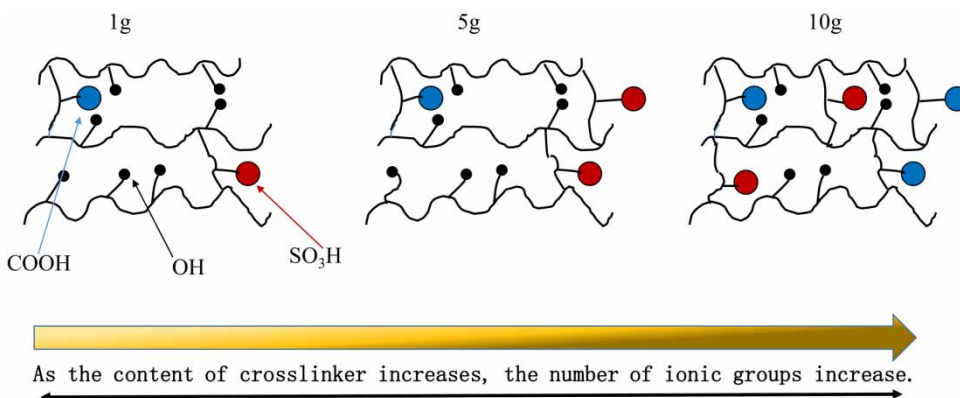


Figure 5 | Different crosslinking degree at different mass of CA.

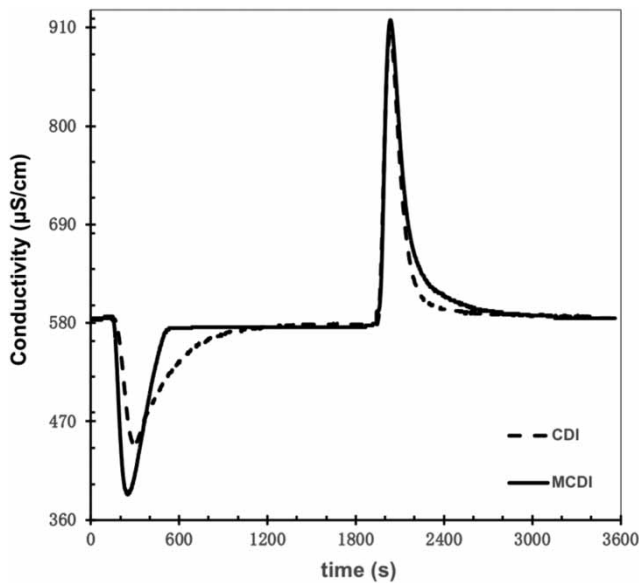


Figure 6 | Conductivity curve of CDI and MCDI.

The desalination capacity and charge efficiency of the two systems were analyzed and compared. In this study, the desalting ability, that is, the amount of NaCl adsorbed by the activated carbon electrode, was calculated using Equation (4):

$$\tau = \phi \int_0^t (C_0 - C_{eff}) dt \quad (4)$$

where C_0 and C_{eff} are the inflow and outflow concentrations of the salt solution, respectively, and ϕ is the flow rate of the peristaltic pump (Biesheuvel *et al.* 2011).

From the data, it can be found that MCDI is more powerful than CDI. Figure 7 shows that apart from during the first cycle when the system is still in the self-balancing state, the desalination capacity of MCDI increased by more than 18% in all subsequent cycles. I also increased by about 3% compared to the system without adding CA.

Another important parameter is charge efficiency, also known as adsorption efficiency, which is a characteristic parameter in the CDI process, defined as the ratio of salt to charge. First, the amount of charge can be calculated simply by integrating the measured current and time over the adsorption cycle:

$$Q = \int_0^t Idt \quad (5)$$

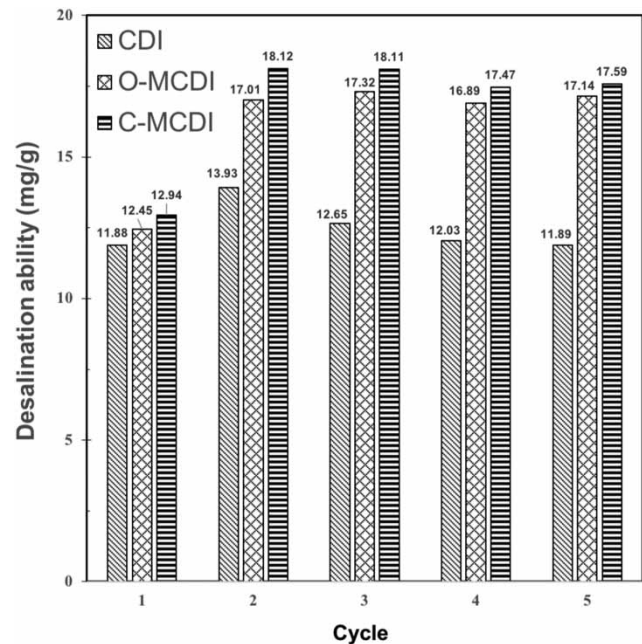


Figure 7 | Desalination ability comparison of CDI and MCDI.

Then, the Faraday constant F is multiplied by the salt adsorbed by the electrode (Equation (6)), and divided by the calculated charge amount, which is the charge efficiency:

$$\Lambda = \frac{\tau * F}{Q} \quad (6)$$

The Faraday constant F is 96,485 C/mol. As can be seen from Figure 8, compared with CDI, the charge efficiency of MCDI has increased by more than 28% and it has also increased by about 3% compared to the system without adding CA.

CONCLUSIONS

In this paper, a composite membrane-coated carbon electrode was successfully synthesized using a chemical crosslinking method. The electrode has both the high capacitance of the carbon electrode and the selectivity of the ion-exchange membrane. The optimal preparation process conditions for the CEM were explored in detail, and it was found that with the addition of CA, the mass of SSA could be reduced from 5% to 1%, which greatly reduced the experimental cost from US\$0.18 to US\$0.03

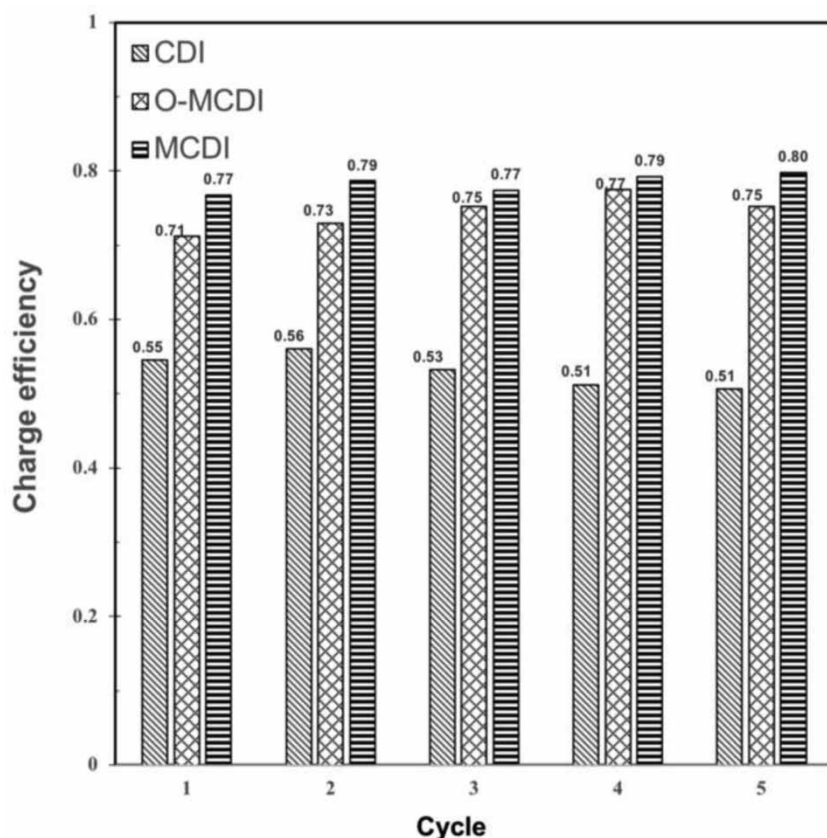


Figure 8 | Charge efficiency comparison of CDI and MCDI.

per square meter. In addition to reducing the cost of the membrane, it also successfully achieved a high desalination efficiency. Compared with the original membrane, the cross-linked membrane modified by CA increased the charge efficiency and the adsorption capacity by about 3%. The prepared CEM was used in CDI, which not only met the characteristics of EDL adsorption and desorption, but also had the typical charge and discharge behavior of EDL capacitors. The MCDI coated with CEM was compared with pure CDI. It was found that the CEM greatly increased the adsorption capacity by more than 18% and enhanced the charge efficiency by about 28%.

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