Electrochemical properties of MCDI-utilized PVA/SSA/GA cation exchange membrane

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Abstract

Membrane capacitive deionization (MCDI), an alternative desalination technology that uses a voltage between two electrodes that are covered with ion-exchange membranes to remove salt, has been drawing a lot of research attention. It has been demonstrated that the desalination performance in terms of salt removal and energy efficiency can be maximized when ion-exchange materials are incorporated on the electrodes in MCDI. In this study, the electrochemical properties of the MCDI electrodes coated with PVA/SSA/GA cation exchange membrane were intensively investigated, specifically the effect of sulfosuccinic acid (SSA) and glutaric anhydride (GA) content in the cross-linking reaction with polyvinyl alcohol (PVA). The presence of SSA in the cation exchange membrane helps improve its conductivity, as proven by the electrochemical measurements via cyclic voltammetry and galvanostatic charge-discharge. As a result, the salt adsorption capacity was also enhanced in the addition of SSA and GA into the PVA chain. The PVA/SSA/GA cation exchange membrane is proved to be an inexpensive, environmentally friendly and suitable candidate to be utilized in the MCDI systems.

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Từ khóa
Cation exchange membrane, capacitive deionization, polyvinyl alcohol, sulfosuccinic acid, glutaric anhydride

1 Introduction

In recent years, capacitive deionization (CDI) has been emerging as an alternative desalination process, thanks to its high efficiency, easy operation, low energy consumption, and reduced secondary pollution, especially with brackish water with low salt content [1,2]. Membrane capacitive deionization (MCDI), a modification of the conventional CDI, can help inhibit the movement of the ions by only allowing the similarly charged ions to pass [3] by attaching the cation exchange membrane (CEM) or anion exchange membrane (AEM) onto the electrode surface [1,4], which brings about greater salt removal efficiency [5-8], higher current efficiency [7-10], faster salt removal rate [6], lower energy consumption [9,11], and better energy recovery [12,13]. Ion exchange membrane (IEM) is one of the key components that influence the efficiency of an MCDI device [14]. The matrix and the charged functional groups are the two components that have an impact on the properties of the membranes: the membrane matrix can change the thermal and chemical stability, together with mechanical resistance and water uptake; while the functional groups can adjust the ion adsorption capacity as well as the ion selectivity of the membrane [15].

In this study, the preparation of PVA/SSA/GA cation exchange membrane from the cross-linking reaction of polyvinyl alcohol (PVA), sulfosuccinic acid (SSA) and glutaric anhydride (GA), and its incorporation on the carbon electrode was presented. In addition, the investigation into the effect of SSA and GA content on

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the electrochemical properties of the MCDI electrodes was also intensively conducted.

2 Materials and methods

2.1 Materials and chemicals.

PVA (98 %, M = (146,000-186,000) g·mol^{-1}) and GA (95 %) was purchased from Acros, Belgium. Commercial activated carbon (AC) was obtained from Trabaco (Viet Nam). Multi-walled carbon nanotube (MWCTN) was acquired from nTherm (USA). SSA, concentrated nitric acid, concentrated sulfuric acid, hydrochloric acid (37 %), and ammonia solution (25 %) were secured from Sigma Aldrich (USA) and were used without any further purification. Graphite sheet (thickness of 200 µm) was obtained from Mineral Seal (USA).

2.2 Fabrication of MCDI electrodes

Preparation of the carbon electrodes. First, 6.122 g PVA powder was stirred in 93.878 g deionized water for 24 h at 90 °C. After the obtained 6 % PVA solution was cooled down to room temperature, 0.818 g GA was added and the mixture was kept stirring for 1 h. After that, 0.614 g MWCNT was added and the mixture was stirred for another 1 h. The resulting slurry was homogenized in 10 minutes at 15,000 rpm with the addition of 60.386 g AC. Electrode coating was proceeded using the doctor blade method with a graphite sheet (20 cm × 30 cm, the thickness of 200 µm) as a base. In the end, the carbon electrodes were dried at 120 ^{0}C for 4 h [16].

Preparation of MCDI electrodes. Firstly, a 6 % PVA solution was similarly prepared. Next, the SSA solution was slowly added into the PVA solution, and the mixture was kept stirring at 50 ^{0}C for 4 h. After that, GA was also added to the reaction mixture to obtain the PVA/SSA/GA composite solution, which was used to coat the carbon electrodes. Finally, the MCDI electrodes were dried at 120 ^{0}C in 4 h, then was used to perform electrochemical measurements [16].

Different concentration of SSA and GA were employed, the name and composition of the MCDI electrodes were presented in Table 1.

Table 1 Composition of the composite membranes

Sample	**SSA concentration (%)**	**GA concentration (%)**
PS5.0	5.0	0.0
PS7.5	7.5	0.0
PGS5.0	5.0	5.0
PGS7.5	7.5	5.0

2.3 Electrochemical properties of the MCDI electrodes

Cyclic voltammetry (CV) was performed on Autolab 302 N potentiostat/galvanostat using three-electrode cells which included Pt as counter electrode, Ag/AgCl as reference electrode, and MCDI electrode (3.0 × 2.5) cm as working electrode, in an aqueous 0.5 M NaCl electrolyte. The electrodes were immersed in 0.5 M NaCl solution for 1 h before the experiment, each sample was measured three times from −0.5 V to 0.5 V at a scanning rate of 5 mV·s^{-1} at room temperature. From the CV plots, specific capacitance values of the composite membrane electrodes were calculated using Equation 1:

$$C_S = \frac{1}{2 \times m \times v \times \Delta E} \times \int IdE \quad (1)$$

in which C_S (F·g^{-1}) is the specific capacitance, $\int$ IdE is the integrated area of the CV curve, m (g) is the mass of the MCDI electrode, v (V·s^{-1}) is the potential scan rate, ΔE (V) is the width of the potential window.

The galvanostatic charge-discharge (GCD) behaviours were investigated using a measurement system consisting of two symmetrical MCDI electrodes of (1.0 × 1.0) cm in aqueous 0.5 M NaCl for 1,000 cycles. Specific capacitance values of the MCDI electrodes from the GCD plots were calculated following Equation 2:

$$C_S = \frac{I \times t}{m \times V} \quad (2)$$

in which C_S (F·g^{-1}) is the specific capacitance, I (A) is the applied potential, t (s) is the charge – discharge time, m (g) is the mass of the electrode, V (V) is the width of the potential window.

2.4 Desalination performance of the MCDI electrodes

The salt adsorption capacity of the MCDI electrodes was measured using the CDI system, which comprises of a CDI cell, a NKP-DCL-S10B peristaltic pump, and a Jenway 3540 conductivity meter (**Figure 1**) [16]. The CDI cell consisted of a pair of electrodes (3.0 × 2.5) cm (thickness of 100 µm) parallel and separated from each other by an insulating plate. 30 mL of 200 ppm NaCl solution as feed water was pumped through the CDI cell at a constant rate of 10 mL·min^{-1}. The conductivity (G) of the inlet solution was observed until remain unchanged (G_0). Next, the potential of 1.2 V was applied to the CDI cell, and the decreasing specific conductivity (G_t) was noted every 30 seconds until remain unchanged (G_c).

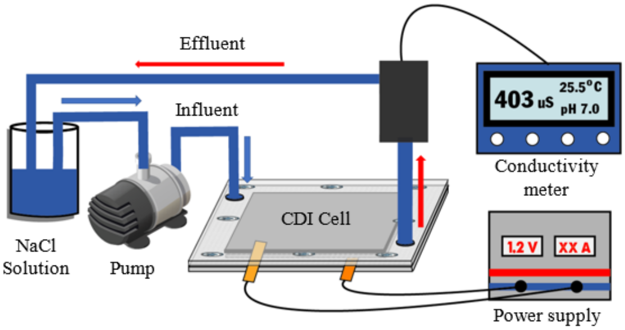

Figure 1 CDI system [16]

Salt adsorption capacity (SAC) and maximum salt adsorption capacity (mSAC) were calculated from Equations (3a and 3b):

$$\mathrm{SAC} = \frac{(C_0 - C_t) \times V}{m} \qquad (3a)$$

$$\mathrm{mSAC} = \frac{(C_0 - C_c) \times V}{m} \qquad (3b)$$

Salt adsorption rate (SAR) and average salt adsorption rate (ASAR) were determined by Equations (4a and 4b):

$$\mathrm{SAR} = \frac{\mathrm{SAC}}{t} \qquad (4a)$$

$$\mathrm{ASAR} = \frac{\mathrm{mSAC}}{t} \qquad (4b)$$

where SAC (mg·g^{-1}) is the salt adsorption capacity; ASAR [mg·(g·min)$^{-1}$] is the average salt adsorption rate; C_0, C_t and C_c (mg·L^{-1}) are concentration of the NaCl solution which were calculated from the conductivity of the solution at the beginning, at t (minutes) and at the end (G_0, G_t and G_c), respectively; V (L) is the volume of the NaCl solution; m (g) is the mass of the electrode; and t (minute) is the adsorption time.

3 Results and discussions

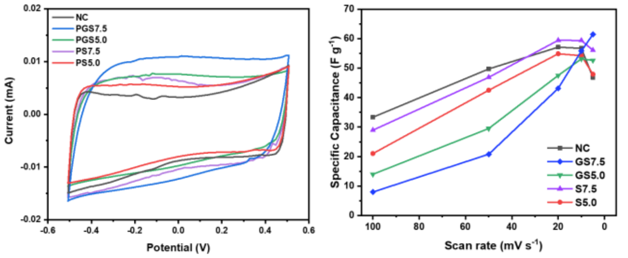

Figure 2 (a) CV plots at scan rate of 5 mV·s^{-1} and (b) specific capacitance value at different scan rate of different MCDI electrodes

At low scan rate of 5 mV·s^{-1}, the CV curves of all samples (Figure 2a) displayed the characteristics of an electrochemical double layer capacitor. No Faradaic current was observed in the potential range of (–0.5-0.5) V. The CV curves of the PVA/SSA and PVA/SSA/GA electrodes are wider and larger than that of the non-coated (NC) electrode. It can be explained that, at low scan rate the charge had enough time to pass through the membrane, resulting in higher charge storage capacity higher and a widened CV curve. In addition, at low scan rate, the charge storage capacity of the electrode was also enhanced by the SSA content in the ion exchange membrane, leading to a much wider CV curve of the GS7.5 electrode compared to the NC and other MCDI electrodes.

The effect of scan rate on specific capacitance of different electrodes at different scan rates were investigated, and the results were shown in Figure 2b. At high scan rate of 100 mV·s^{-1} the NC electrode possessed the highest specific capacitance value of 33.33 F·g^{-1}, while the GS7.5 electrode has the lowest specific capacitance value of 7.97 F·g^{-1}, which was much lower than the others. As the scan rate decreased, the specific capacitance values of the electrodes increased. For the NC and PVA/SSA electrodes, the specific capacitance reached their highest values at the scan rate of 20 mV·s^{-1}, then decreased as the scan rate continued to decrease. At the scan rate of 20 mV·s^{-1}, the specific capacitance value of the NC electrode was 57.12 F·g^{-1}, which was 71.38 % higher than that at the scan rate of 100 mV·s^{-1}. The specific capacitance value of the S7.5 electrode was 59.46 F·g^{-1} (105.39 % higher) and that of the GS7.5 sample is 43.14 F·g^{-1} (441.28 % higher), indicating a more significant increase of specific capacitance value of the GS7.5 sample compared to other electrodes. The change in specific capacitance with scan rate depends on the double layer charge process, which is related to the kinetics of the adsorption process of the ions in the electrolyte solution onto the electrode surface. This process is usually controlled by the properties of the electrode capillary and surface, which means that the ions need to diffuse rapidly through the capillary system and then adsorb onto the electrode surface. In addition, at very slow scan rates (5-20) mV·s^{-1}, the double-layer charge is no longer dependent on the adsorption kinetics, but instead the capacitance will depend mainly on the double layer charge current [C = I : (dE/dt)].

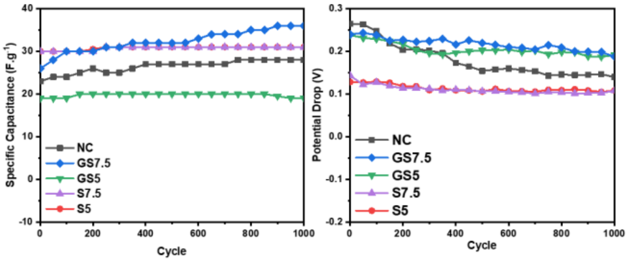

Figure 3 (a) Specific capacitance and (b) potential drop of different MCDI electrodes after 1000 cycles at current density of 0.5 A g^{-1} calculated from GCD plot

The specific capacitance values of different electrodes over 1000 measurement cycles were calculated from the GCD plots (Figure 3a), showing an increased specific capacitance value of GS7.5 electrode and a negligible change of specific capacitance value of other electrodes. In addition to the specific capacitance value, a potential drop over 1,000 cycles can also be obtained from the GCD curve through the potential drop present on the discharge line. Figure 3b shows that the potential drop of the electrodes all decreased after 1,000 cycles. This phenomenon can be explained that the electrodes were better activated after many cycles of charging and discharging, therefore the resistance of the membrane will decrease and the potential drop of the electrode will also decrease.

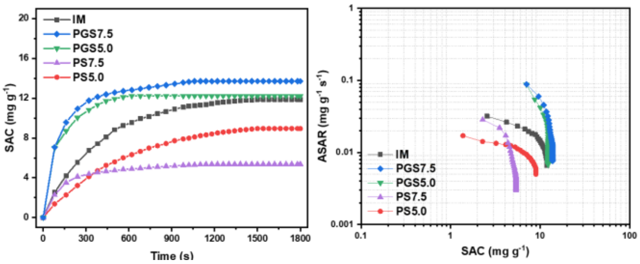

Figure 4 (a) SAC value as a function of desalination time and (b) Kim-Yoon plot for CDI process using different MCDI electrodes (Applied voltage: 1.2 V, flow rate: 10 mL·min^{-1})

The salt adsorption investigation using the industrial-membrane-coated electrode (IM, provided by Liaoning Yichen Membrane Technology) and different PVA/SSA/GA electrodes was performed in a 200 ppm NaCl at a voltage of 1.2 V, a flow rate of 30 mL·min^{-1}, at room temperature, and the results were illustrated in Figure 4a. It can be seen that the electrodes coated with the membranes synthesized from the reaction between PVA and SSA displayed a faster saturation time than the IM electrode. However, the SAC values of the membranes without GA were lower than that of IM, specifically the SAC values of IM, S5 and S7.5 were (11.87, 8.95 and 5.37) mg·g^{-1}, respectively. In contrast, the membranes containing GA displayed higher SAC values compared to IM, with the SAC values of GS5 and GS7.5 being 12.23 and 13.71 mg·g^{-1}, respectively, which is the highest among all investigated electrodes. Thus, it can be concluded that the addition of GA helps the ion exchange membrane to outperform in terms of both saturation time and adsorption capacity.

Kim-Yoon plot is a useful method to evaluate the desalination efficiency of CDI system as well as MCDI system, in which salt adsorption rate (SAR) is plotted against salt adsorption capacity (SAC) (Figure 4b). As a result, the electrode with the Kim-Yoon plot on the upper right corner of the graph will exhibit better desalination capability, indicating that the GS5 and GS7.5 electrodes could achieve much higher efficiency compared to the industrial-membrane-coated electrode as well as other PVA/SSA electrodes.

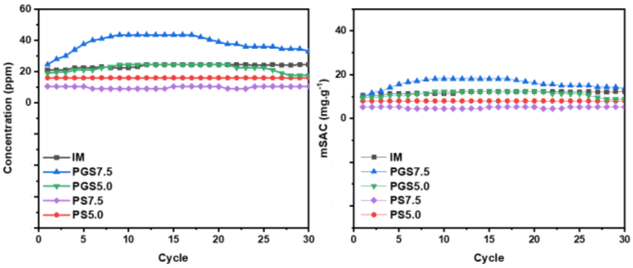

Figure 5. (a) Salt concentration and (b) mSAC value of different MCDI electrodes after 30 cycles of CDI process using different MCDI electrodes (Applied voltage: 1.2 V, flow rate: 10 mL·min^{-1})

The adsorption capacity as well as the durability of the electrodes after many cycles were also examined, and the results were displayed in Figure 5. Similar to the above SAC value, the membranes containing GA gave higher adsorption capacity value compared to the other membrane, with the best being the GS7.5 electrode. The adsorption capacity of the electrodes increased and reached the highest value after the 10th cycle, then decreased slightly from the 20th cycle. Once again, it has been proven that the addition of GA into the cation exchange membrane enhanced the desalination efficiency. Additionally, all of the electrodes still exhibited good desalination efficiency after 30th cycles, which is consistent with the durability investigation through the GCD.

4 Conclusion

PVA/SSA/GA cation exchange membrane and MCDI-utilized electrodes was successfully fabricated from PVA and the crosslinking agents such as SSA and GA. The addition of SSA and GA helped enhance the electrochemical properties of the MCDI electrodes, as the achieved specific capacitance value reached 61.47 $F \cdot g^{-1}$, and could be maintained after 1,000 GCD cycles. The MCDI electrode also exhibited improved desalination capability, with the SAC values of GS5 and GS7.5 being (12.23 and 13.71) $mg \cdot g^{-1}$, which was higher compared to the industrial membrane. The fabricated membrane could also be employed for 30 cycles of desalination process without any deterioration in the salt adsorption capacity, indicating that the PVA/SSA/GA membrane is a suitable candidate to be utilized in the MCDI systems, which is inexpensive, environmentally friendly, and easy to fabricate.

Acknowledgments

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Conflict of Interest

The authors declare that there is no conflict of interest.

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Khảo sát các tính chất điện hóa của màng trao đổi cation PVA/SSA/GA ứng dụng làm điện cực trong công nghệ MCDI

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Tóm tắt Công nghệ điện dung khử ion kết hợp màng trao đổi ion (Membrane capacitive deionization – MCDI), sử dụng dòng điện giữa hai điện cực được phủ màng trao đổi ion để loại bỏ muối ra khỏi dung dịch, là một công nghệ khử mặn đang thu hút được nhiều sự quan tâm. Việc sử dụng màng trao đổi ion giúp cải thiện khả năng khử muối cũng như tiết kiệm năng lượng. Trong bài báo này, thông qua việc khảo sát ảnh hưởng của hàm lượng SSA và GA trong màng, cho thấy sự có mặt của SSA trong màng trao đổi cation giúp tăng cường độ dẫn ion của màng. Điều này được chứng minh thông qua các phép phân tích điện hóa như phương pháp quét thế vòng tuần hoàn và phương pháp đo phóng nạp dòng cố định. Hiệu suất khử muối cũng được cải thiện với sự có mặt của SSA và GA. Màng composite PVA/SSA/GA có giá thành thấp và thân thiện với môi trường, thích hợp để dùng làm màng trao đổi cation trong các quá trình khử mặn bằng công nghệ MCDI.

Từ khóa Màng trao đổi cation, điện dung khử ion, polyvinyl alcohol, sulfosuccinic acid, glutaric anhydride