

Capacitive deionization (CDI) for desalination using carbon aerogel electrodes

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(Manuscript Received on July, 2016, Manuscript Revised on September, 2016)

ABSTRACT

Capacitive deionization (CDI) is an electrochemical water treatment process that holds the promise of not only being a commercially viable alternative for treating water but for saving energy as well. Carbon aerogel electrodes for CDI process with high specific surface area (779.04 m²/g) and nanopore (2-90 nm) have been prepared via pyrolyzing RF organic aerogel at 800oC in nitrogen atmosphere. The CDI characteristics of

Keywords: *Capacitive deionization, carbon aerogel, aerogel electrodes, desalination, electrosorption.*

carbon aerogel electrodes were investigated for the NaCl absorption into a CDI cell at variation conditions. Experiments data showed that the maximum NaCl removal capacity was 21.41 mg/g in 500 mg/L NaCl solution, higher than for other carbon-based materials in the literature. It was evaluated that the CDI process using carbon aerogel electrodes promising to be an effective technology for desalination.

1. INTRODUCTION

Capacitive deionization (CDI) is a technology for removing ionic materials from aqueous solution using an electrostatic adsorption reaction on the electric double layer (EDL) created on the electrode surface interface when a potential is applied on porous carbon electrodes [1, 2]. The technique is mainly applicable for brackish water and offers advantage of easy regeneration, low voltage, and ambient operational conditions. Salty water is

passed through the electrode surface with an applied charge. Cations and anions are drawn toward the cathode and anode, respectively. Salts from water are removed by the electrosorption of ions on the porous surface of electrodes [3]. After the electrode becomes saturated, it can easily be regenerated by cancelling or changing the electrical potential of the electrodes, the regeneration of the electrode is not only very simple, but is also recognized as an environmentally friendly process [4, 5].

Many studies have applied various porous carbon materials for CDI process including activated carbon [6, 7], activated carbon fibers [8, 9], ordered mesoporous carbons [10], carbon aerogel [11, 12], carbon nanotube and graphene [13, 14]. Carbon aerogels, a porous material that features high specific surface area, low density, good electrical conductivity and high chemical stability, seem to be a promising porous materials for CDI technology. In the early 1990's, Farmer et al. developed carbon aerogel materials, with specific surface area of 600-800 m²/g, using in a capacitive deionization process for removing mixed ionic solutions [3, 15]. The electrosorption of several cations and anions (Na⁺, K⁺, Mg²⁺, Rb⁺, Br⁻, Cl⁻, SO₄²⁻, NO₃⁻) from natural river water was studied in the research of Gabelich et al. [16] for carbon aerogel electrodes with a specific surface area of 400-590 m²/g and average pore sizes in range of 4-9 nm. It was found that monovalent ions with a smaller (hydrated) ion size were preferentially electrosorbed by CA electrodes. Xu et al. have used carbon aerogel electrodes to show the successful deionization of brackish wastewater [4]. Considering the low mechanical stability of CA as a result of the very low density and large porosity, paste rolling of CA with silica gel was studied by Yang et al. [17] as a method to improve the mechanical properties. Variation of carbon to silica mass ratios were investigated and slight effect on performance of the CDI process was observed when adding the silica gel. Kohli et al. [18] were also studied the electrodes synthesized using mesoporous carbon aerogel, microporous-activated carbon, and different combinations of the two for capacitive deionization application. The experiments data indicated composite electrodes showed fast

absorption and desorption and higher salt removal efficiency.

In this work, carbon aerogels were generally synthesized by pyrolysis of resorcinol-formaldehyde organic aerogel obtained from ambient drying. Carbon aerogel electrodes for CDI process were developed by a coating method using polyvinyl alcohol (PVA) as a binder and evaluated their properties. The CDI experiments using carbon aerogel electrodes were fabricated and their CDI characteristics on NaCl solution were examined. The operational conditions of CDI systems were investigated for maximizing ion absorption.

2. EXPERIMENTAL

2.1. Fabrication of carbon aerogel electrodes

2.1.1 Preparation of carbon aerogels

Carbon aerogel (CA) was derived from pyrolysis of a resorcinol-formaldehyde (RF) aerogel [19]. The molar ratio of formaldehyde (F) to resorcinol (R) was held at a constant value of 2. They were dissolved in distilled water with Na₂CO₃ as a base catalyst, the mass percentage of the reactants in solution was set at RF = 40%, and the molar ratio of resorcinol to catalyst (C) was set at R/C = 1000. Sol-gel polymerization of the mixture was carried out in plastic moulds by holding the mixture at room temperature for 24 h, at 50°C for 24 h, and at 80°C for 72 h to obtain RF wet gels. The aqueous gels were then exchanged with acetone for 3 days. Subsequently, RF organic aerogels were prepared by directly drying RF wet gels at ambient temperature and pressure for 5 days. Carbon aerogels for the CDI process were synthesized via pyrolyzing RF organic aerogels at 800°C in a continuous nitrogen atmosphere, flowing at a rate of 400 mL/min for 3 h. Carbon

aerogels were further activated at 800°C for 2 h in a flow of CO₂ to remove residual organics and promote its properties.

2.1.2 Prepare of carbon aerogel electrodes

Carbon aerogel electrodes for CDI process were prepared by a coating method as follows. Carbon aerogel was grinded into powder and it was cast into electrode using polyvinyl alcohol (PVA) as a binder. The amount of polymer binder was controlled to achieve a solid content of 15% after drying. Carbon aerogel and PVA were mixed in distilled water, and the mixture was then pressed onto an Al foil (as a current collector). The carbon coated Al foil was then dried under ambient conditions for 48 h, and punched in required size as electrodes. The apparent surface area of the electrodes was 81 cm² and the thickness was about 2 mm.

2.2. Characterization methods

In order to investigate the microstructure of carbon aerogels, the pristine samples were characterized by scanning electron microscopy using a HITACHI S-4800 microscope and X-ray diffraction using a Bruker D8 Advance diffractometer with Cu-K α radiation ($\lambda=1.54060$ Å) operated at the voltage and current values of 40 kV and 40 mA respectively for the 2θ values in the range 5–70° at a scan speed of 1.2°/min. Specific surface area and pore-size distribution of samples were characterized by analysis of nitrogen absorption-desorption isotherms measured by ASAP 2020 analyzer (Micrometrics Instruments Corp.). Brunauer-Emmett-Teller (BET) method was used for total surface area measurements, and t-plot method was used for estimating mesopore surface area. Pore-size distribution was obtained by the Barret-Joyner-Halenda

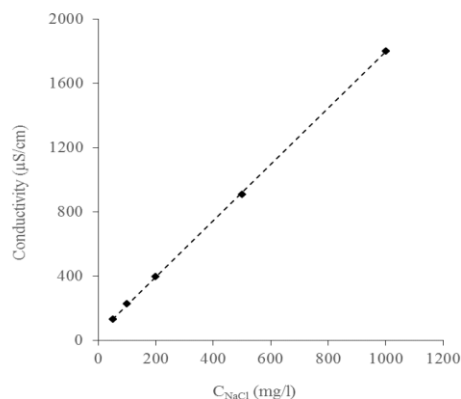


Figure 1. Calibration curve for ionic conductivity versus NaCl concentration.

(BJH) method from desorption branch of the isotherms. Total pore-volume was calculated from the adsorbed volume of nitrogen at $P/P_0=0.99$ (saturation pressure).

2.3. Capacitive deionization experiments

Measurement the adsorption of ions on electrodes, single-pass experiments were conducted in a cell with a dimension of 100 mm (long)×6 mm (width)×100 mm (high). The electrodes were placed face to face at both sides of a spacer with 2 mm and connected with a DC power supply. Water was fed from a storage vessel and the salinity (conductivity) of the water leaving the cell was measured directly at the exit of the cell. The change in the conductivity of NaCl solution was monitored online using an ion conductivity meter (type EC500, EXTECH). Electrosorption capacity of the carbon was determined from the change in conductivity of the salt solution using a calibration curve (Figure 1), and salt uptake was then divided by the total carbon electrode mass. Total carbon used in each experiment with a pair of carbon electrodes was 4.00 grams.

Using this calibration curve, we have (1):

$$\text{Cond.} = 46.683 + 1.7529C_{\text{NaCl}} \quad (1)$$

where Cond. is the conductivity, and C_{NaCl} is the NaCl concentration.

3. RESULTS AND DISCUSSION

3.1. Physical characteristics

Figure 2 showed the morphology of carbon aerogel samples with and without activation. The morphologies of CA particles were found to be nearly spherical in shape. CA particles were randomly crosslinked with each other, forming a continuous three-dimensional web structure with nano-sized primary particles more or less fused. The particles size of the CA was in the range of about 40–50 nm, similar to the nano-structures of monolithic CA reported by Wu et al. [20]. The CA prepared in this work have the nano-particle structures typical of the samples prepared with the CO₂ supercritical drying technique in the studies of Al-Muhtaseb et al. and Qin et al. [21, 22]. Additionally, the particles size of the CA was hardly affected by activation under CO₂ flow; Figure 2b indicated that the particles size was decreased into 20–30 nm because of the reaction of CO₂ with carbon network and the abrasion of carbon structure during activation.

The XRD diagram of the synthesized CA samples were shown in Figure 3. It presented two large peaks at about $2\theta = 24^\circ$ and 44° , similar to the diffraction peaks of C(002) and C(101) and it was in agreement with the literature data [23].

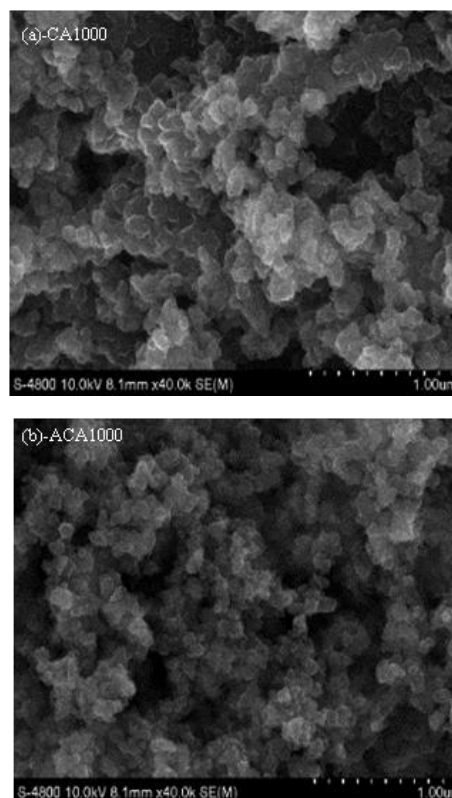


Figure 2. SEM photographs of aerogel samples. (a) carbon aerogel (CA1000) and (b) activated carbon aerogel (ACA1000).

The first peak indicated that CA samples contained a proportion of highly disordered materials in the form of amorphous carbon. In addition, the samples also contained some graphite-like structures (crystalline carbon) indicated by the presence of a clear (002) band at $\sim 24^\circ$ and (101) weak band at $\sim 44^\circ$. These observations suggested that the crystallites in all the CA samples have intermediate structures between graphite and amorphous state called turbostratic structure or random layer lattice structure. For CDI electrode materials, the specific surface area and pore size distribution were two important determinants for absorption capacity. Larger specific surface area means

more absorption sites, leading to higher removal capacity. In our study, the pore structure of carbon aerogel and carbon aerogel electrode were characterized by nitrogen adsorption at 77K. Figure 4, along with the main textural parameters summarized in Table 1, showed the nitrogen adsorption-desorption isotherm and pore size distribution of CA and CA-PVA15 electrode. The isotherm of CA and CA-PVA15 electrode has been observed to be of Type IIb following the IUPAC classification, indicating multilayer absorption on the surface of the electrode. This type of isotherm was characteristic of microporous and macroporous adsorbents. The BET specific surface area of carbon aerogel and electrode were calculated to be 779.06 and 399.41 m^2/g , respectively. The pore-diameter was distributed in range of 7–28 Å for both carbon aerogel and CA-PVA15 electrode, similar to the study of Seo et al. and Yang et al. [24, 25]. There were several peaks of pore size distribution indicated the macropores in the CA-PVA15 electrode, which diameter was in range of 30-90 nm, leading to decrease specific surface area of prepared electrode.

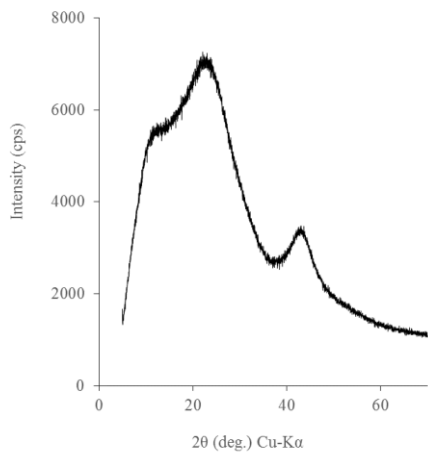
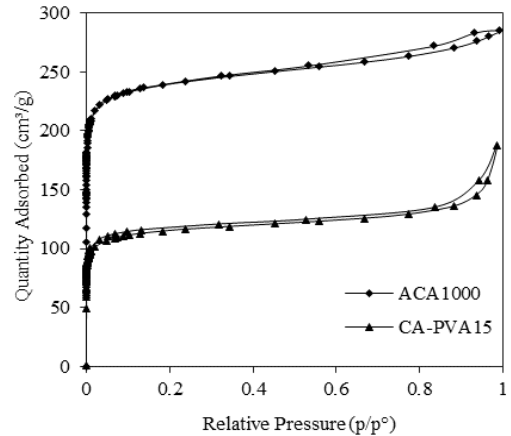
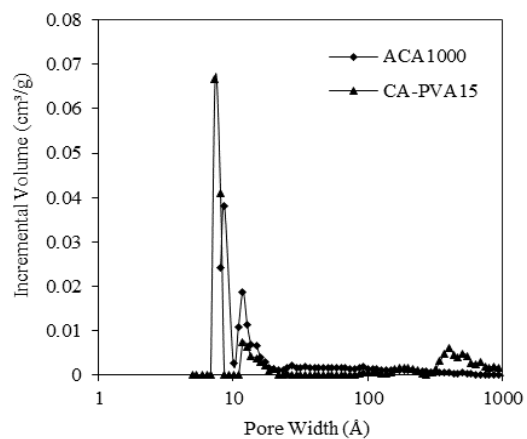


Figure 3. X-Ray diffraction pattern of carbon aerogel (CA1000).

The results of nitrogen absorption showed that surface area of carbon aerogel electrodes could be sufficiently used for CDI process.



(a)



(b)

Figure 4. Nitrogen adsorption-desorption isotherm (a) and pore size distribution (b) of CA and CA-PVA15 electrode.

Table 1. Porous properties of carbon aerogels and carbon aerogel electrodes.

Properties	Carbon aerogel	Carbon aerogel electrode
Density (g/cm ³)	0.150–0.510	0.238-0.256
S _{BET} (m ² /g)	779.06	399.41
Average pore size (Å)	22.24	24.42
Median pore width (Å)	6.11	9.47
Average particle size (Å)	77.02	150.22
V _{total} (cm ³ /g)	0.4408	0.2896
V _{mic} (cm ³ /g)	0.3173	0.1371
V _{mes} (cm ³ /g)	0.0547	0.0453
V _{mac} (cm ³ /g)	0.0688	0.1072
V _{mic} (%)	71.98	47.34
V _{mes} (%)	12.40	15.64
V _{mac} (%)	15.62	37.02

3.2. Capacitive deionization characteristics

The CDI performance of carbon aerogel was carried out to maximize the NaCl removal capacity by changing the NaCl concentration (100–1000 mg/L) and the volume flow rate (25–100 mL/min). The effect of initial NaCl concentration was performed at a volume flow rate of 50 mL/min through a CDI unit cell with 4.0 g of carbon aerogels solution under 1.5 V of the applied voltage. The range of the NaCl concentration (C_o) was changed from 100 mg/L to 1000 mg/L. Figure 5 showed the conductivity drop of CDI process with carbon aerogel electrodes on various NaCl concentration. Table 2 showed the ion removal characteristics of carbon aerogel electrodes on CDI process at different conditions. The results showed that NaCl absorption on carbon aerogel electrodes increased in the range of 100-500 mg/L of NaCl concentration. The NaCl absorption on carbon aerogel electrodes was saturated about 21.41 mg NaCl per 1 g of carbon aerogel over 500 mg/L. When the initial NaCl concentration increased to

1000 mg/L, the removal capacity of carbon aerogel electrode was decreased to 8.23 mg NaCl per 1 g carbon aerogel. In the solution, Na⁺ (1.16 Å) and Cl⁻ (1.67 Å) ions were existed at hydrated ions with hydrated radius of Na⁺ and Cl⁻ ions were 3.58 Å and 3.31 Å, respectively. The hydrated ions radius affected on the electrical double layers (EDLs) of carbon aerogel electrodes, which were direct influence on the ions absorption of electrodes. At high NaCl concentration in solution, 1000 mg/L, hydrated ions densities on surface of electrodes were high and formed the thickness EDLs. Additionally, small pore size of carbon aerogel led to EDL overlapping effect and the surface area of these pores cannot be used to adsorb ions [25], which was also the main reason for the small removal capacity of porous materials with high specific surface area at high concentration.

Table 2. Ions removal characteristics of carbon aerogel electrodes.

Initial NaCl con. (mg/l)	NaCl adsorption (mg/g)	Flow rate (ml/min)	NaCl adsorption (mg/g)
100	2.11	25	3.26
200	5.87	50	8.23
500	21.41	75	16.05
1000	8.23	100	14.63

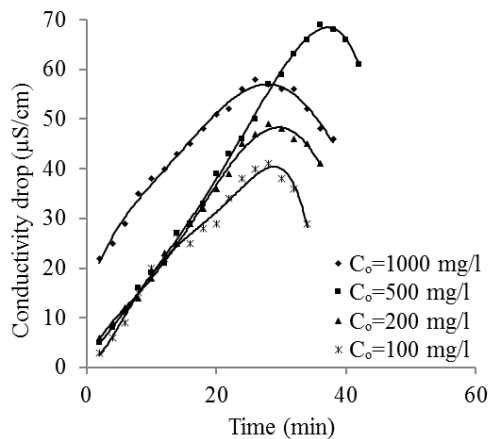


Figure 5. Effect of initial NaCl concentration on conductivity drop of CDI process.

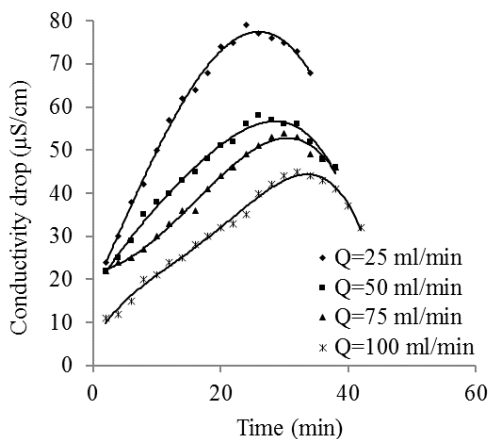


Figure 6. Effect of volume flow rate on conductivity drop of CDI process.

Figure 6 showed the effect of volume flow rate on NaCl removal capacity in CDI cell via the conductivity drop versus time. All experiments were performed with 1000 mg/L NaCl solution under 1.5 V of the applied voltage. The range of the volume flow rate through a CDI unit cell was changed from 25 mL/min to 100 mL/min. It indicated that the removal capacity with volume flow rate at 75 mL/min showed the highest result of conductivity decrease. The NaCl removal characteristics were summarized on Table 2. The NaCl removal capacity increased as volume flow rate went up to 75 ml/min, after that slight reduction while flow rate climbed to 100 ml/min. The NaCl adsorption on carbon aerogel electrodes was reached about 16.05 and 14.63 mg NaCl per 1 g carbon aerogel over 75 and 100 mL/min, respectively. The adsorption of carbon aerogel electrodes increased along with the flow rate because of the corresponding increase in the linear velocity of the influent water passing through the electrode surface. It was therefore necessary to raise the adsorption rate of the electrode to enhance the processing volume with a given electrode area. An increase in the adsorption rate of ions on the electrode was required to elevate the NaCl removal capacity. In case of increase the flow rate to 100 mL/min, the adsorption capacity on carbon aerogel electrodes was desorbed by effect of the flow. Therefore, it was deemed necessary to reduce the time constant, which is defined as the product of the resistance of the carbon electrode and the capacitance.

4. CONCLUSIONS

Carbon aerogels were synthesized and used as electrodes for CDI of NaCl solution. Their monolithic continuous flexible framework,

crystalline microstructure together with preferred macro- and micropores size distribution, result in larger effective surface area. The properties of developed carbon aerogel were $S_{\text{BET}} = 779.06 \text{ m}^2/\text{g}$ and pore size diameter in range of 7–28 Å. Fabricated carbon aerogel electrode increased macropores, with pore size of 300–900 Å, lead to carbon aerogel electrode was sufficiently used for CDI process. The absorption tests with a CDI unit cell containing the fabricated electrode and 500 mg/L NaCl solution indicated the maximum

adsorption capacity was 21.41 mg/g, higher than for other carbon-based materials in the literature, which makes it a promising material for capacitive deionization. However, further experiments need to be conducted to investigate the thermal dynamics and stability of carbon aerogel for practical applications in capacitive deionization.

Acknowledgment: This research is funded by Academy of Military Science and Technology, Vietnam.

Khử mặn bằng công nghệ điện dung khử ion sử dụng điện cực carbon aerogel

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TÓM TẮT

Điện dung khử ion là phương pháp điện hóa xử lý nước hiện đại với những ưu điểm về kinh tế và năng lượng. Điện cực carbon aerogel sử dụng trong công nghệ điện dung khử ion với diện tích bề mặt riêng cao $779.04 \text{ m}^2/\text{g}$ và kích thước lỗ xốp nano 2 – 90 nm được chế tạo bằng phương pháp nhiệt phân RF aerogel hữu cơ ở 800°C trong điều kiện khí nitrogen. Các tính chất của quá trình điện dung khử ion bằng điện cực carbon aerogel được khảo sát và đánh giá ở

những điều kiện khác nhau. Kết quả thực nghiệm công nghệ điện dung khử ion cho thấy khả năng hấp phụ NaCl của điện cực carbon aerogel đạt 21.41 mg/g với nồng độ NaCl 500 mg/L, cao hơn các vật liệu điện cực khác ở những nghiên cứu trước. Thực nghiệm cho thấy công nghệ điện dung khử ion sử dụng điện cực carbon aerogel có nhiều triển vọng trong công nghệ khử mặn.

Từ khóa: Điện dung khử ion, carbon aerogel, điện cực aerogel, khử mặn, hấp phụ điện hóa.

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