Desalination and Water Treatment
www.deswater.com

doi: 10.1080/19443994.2015.1087882

57 (2016) 17731–17737
August

Taylor & Francis
Taylor & Francis Group

Carbon electrode modified by KOH solution to improve performance of capacitive desalination

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Received 21 January 2015; Accepted 23 August 2015

ABSTRACT

A carbon electrode was modified by different concentrations of KOH solution to enhance its capacitive deionization performance. The hydrophilicity and electrochemical properties of the carbon electrode were characterized by FTIR analysis, contact angle test, cyclic voltammetry, and impedance spectroscopy analysis. The results show that contact angles of the carbon electrode decrease from 115° to 62° with an increase in the concentrations of KOH, indicating an increase in the hydrophilicity. The specific capacitance of carbon electrode achieves the maximum of 108.8 Fg^{-1} when modified by 5% KOH solution. Furthermore, desalination experiments were carried out in a lab-scale experimental system. The salt-removal efficiency of the modified carbon electrode increases by 23% under the conditions of 2.5 V applied voltage, initial concentration of 1,500 μs/cm, and flow rate of 20 ml/min. Thus, the capacitive deionization performance of the carbon electrode is significantly improved by the modification with KOH. This enhanced performance can be attributed to the hydroxyl functional groups introduced on to the surface of the carbon electrode and an increased wettability of the surface. Our results indicate that the KOH-modified carbon electrode will have great potential in the capacitive deionization technology.

Keywords: Capacitive deionization; Carbon electrode; Desalination; KOH

1. Introduction

Capacitive deionization (CDI) technology is an efficient desalination technique with the advantages of low energy consumption, high removal efficiency, and negligible secondary pollution [1]. It is a promising technology that can overcome the drawbacks of conventional desalination technologies such as reverse osmosis, ion exchange, and distillation. In the CDI process, ions are electrosorbed at the electrode surface during the desalination process and the adsorbed ions are quickly released back into the bulk solution when the potential is removed. One of the main advantages of CDI technology is that there is no secondary pollution because no acids, bases, or salts are required to regenerate the electrode surface in the process [2–5]. The CDI operation is also an energy-efficient process as it is operated at a low electrode potential.

Activated carbon electrodes are widely used in the CDI process due to their high specific surface area, conductivity, and excellent electric-adsorption performance [6–9]. The carbon electrode can also overcome the disadvantages of the metal electrode such as low elution of metal ions. The hydrophilicity of carbon

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electrode is a significant factor that determines the capacitive deionization performance. Some researchers have attempted to improve the hydrophilicity of carbon electrodes by various methods. Lappan et. al. [10], Choi et. al. [11] and Park et. al. [12] prepared a carbon electrode by mixing activated carbon powder (ACP) and polyvinylidene fluoride (PVDF) in a N,N-dimethylacetamide solution, which was coated on the surface of current collector for the CDI process. Lee et al. [13] and Kim et al. [14] prepared carbon electrodes by mixing ACP and ion-exchange resin to improve the hydrophilicity and the conductivity of AC electrode. Other researchers have tried to improve the deionization performance by adding special materials such as conductive carbon black, graphene, and nanoparticles [15–19]. However, these previous reports involve complicated procedures and the results are not satisfactory. Thus, it is necessary to find a simple and efficient method to improve the capacitive deionization performance of carbon electrodes. Ji et al. [20] reported that activated charcoal particles modified by the solution of KOH had higher surface area and more hydrophilic functional groups on the surface compared with that of unmodified AC particles. However, there is a report to date on carbon electrodes modified by KOH solution for the process of capacitive deionization.

This work attempts to improve the capacitive deionization performance of the carbon electrode through modification with KOH. The effects of different mass concentrations of KOH on the hydrophilicity, electrochemical properties, and desalination performance of the carbon electrode were examined to develop the optimized KOH modification conditions.

2. Experimental

2.1. Material and chemicals

ACP (P-60, BET surface area of 2,325 m^2/g) was purchased from the Shanghai Colloid Chemical Plant. ACP was dried in an oven at 105℃ for 12 h and stored in a desiccator before being used. KOH, HCl, and other chemicals were of analytical grade and used without further purification.

2.2. Preparation of carbon electrode

The carbon electrode was fabricated by pouring ACP into a tubular mold and compressing it at the pressure of 68 Mpa. The carbon particles fuse together under the pressure, and result in carbon tubes with good mechanical properties. The carbon tubes were calcined for 2 h in a vacuum oven at 250℃ under N_2 atmosphere.

The prepared carbon tube was 30 cm in length, with an internal diameter of 4 mm and external diameter of 10 mm. All the prepared carbon tubes were immersed into 5,000 ml KOH solution in a stainless steel container and heated for 1 h at 100℃. The mass concentrations of KOH solutions were 0, 3, 5, 8, and 10%. It was necessary to add 3 ml of ethyl alcohol into KOH solutions in order to ensure that the carbon tube would have sufficient contact with the KOH solution. The prepared carbon tubes were then processed by ultrasound in 2,000 ml of 0.1 M HCl solution for 2 h, and washed with boiling water until the pH value of water was neutral. All the modified carbon tubes were dried in a vacuum oven at 105℃ for 24 h and cooled down for 24 h at room temperature. Finally, graphite powder was added throughout the pore space of the electrode. A wire of copper was injected into graphite powder and then both ends of the tube were sealed by ethoxyline resin. Thus, graphite powder and the copper wire were fixed into the carbon tube as electrodes.

2.3. Physical and electrochemical characteristics

Fourier transform infrared spectroscopy (FTIR) analysis of the carbon electrodes was performed by a FTIR spectrophotometer (FTIR-7600). The contact angles on the surface of tubular carbon electrodes were tested by the sessile drop method with densitometer and contact angle meter (JW2000).

Cyclic voltammetry (CV) measurement of the carbon electrode was performed on an electrochemical workstation (CHI 600 D) with a three-electrode system. The carbon electrode, a Pt wire electrode, and an Ag/AgCl electrode were used as the working electrode, counter electrode, and reference electrode, respectively. The electrolyte was 0.5 M KNO_3 aqueous solution and the sweep potential range was adjusted from −1 to 1 V (vs. Ag/AgCl electrode) at a potential sweep rate of 5 to 15mv/s. The impedance spectra were obtained at an initial potential of 0 V in the frequency range of 1 to 10000 Hz. All experiments were conducted in a water bath at 25 ± 0.1℃.

2.4. Desalination experiment

KNO_3 solution was used to test the desalting performance avoiding the corrosion of special ions. The desalination experiment of KNO_3 solution was tested as shown in Fig. 1. The operating conditions were as follows: initial conductivity of KNO_3 of

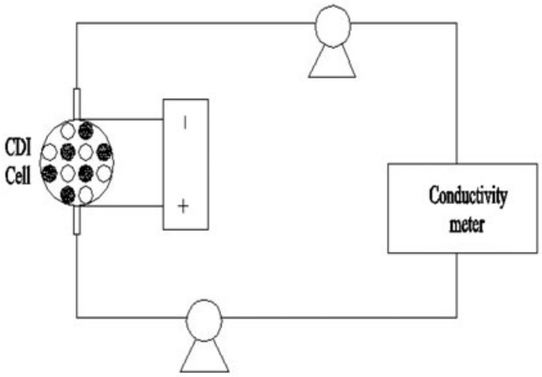

Fig. 1. Diagram of capacitive deionization experiment. (●-positive electrode; ○-negative electrode.)

1,500 μs/cm, electrode spacing of 1 cm, flow rate of 10–30 ml/min, and voltage of 1.0–2.5 V. The desalting efficiency was defined as below, where C_0 and C_t (μs/cm) represent the initial and final concentrations of KNO_3, respectively.

$$\text{Desalting efficiency} = (C_0 - C_t)/C_0 \times 100\% \tag{1}$$

3. Results and discussion

3.1. Hydrophilicity of carbon electrode

Hydrophilicity is an important factor affecting the capacitive deionization performance of the carbon electrode. The wettability of carbon electrode increases with an increase in the hydrophilicity; thus, the carbon electrode with excellent hydrophilicity can maintain sufficient contact with the solution to enhance the capacitive deionization performance. Fig. 2 shows the images of a water droplet on the surface of the unmodified and modified electrodes.

The contact angle of the unmodified carbon electrode was 115°. The contact angles of the carbon electrodes modified by the increasing concentrations of KOH solution were 90°, 75°, 66°, and 62°, respectively. The carbon electrode is wettable when the contact angle is less than 90°, and the hydrophilicity increases as the contact angle decreases [21]. The experimental results confirmed that the carbon electrodes showed a good hydrophilicity due to KOH modification, and the hydrophilicity increased with an increase in the concentrations of KOH solution. The enhanced hydrophilicity of the carbon electrode was attributed to the introduction of hydrophilic groups on the surface of carbon electrodes [22]. During the carbon electrode preparation process, all the carbon electrodes were boiled in KOH solution and then ultrasonically cleaned in HCl solution in order to introduce the hydrophilic hydroxyl groups. The FTIR spectra of the carbon electrode are shown in Fig. 3. It can be seen that there are no hydroxyl absorption peaks in the spectrum of the unmodified carbon electrode. However, the FTIR spectra of KOH modified carbon electrodes show the characteristic hydroxyl absorption band at 3,500 cm^{-1} [23,24]. The above results confirm that hydroxyl functional groups were successfully introduced on the surface of carbon electrodes, resulting in a significant increase in the hydrophilicity of the carbon electrode.

3.2. Electrochemical property

The electrochemical impedance spectroscopy measurement was performed to analyze the charging resistance and specific capacitances (C). Radius of the curves on the Nyquist plots represents the mass transfer resistance of ion, and radius of the curves is inversely proportional to resistance. As shown in Fig. 4, it was evident that the carbon electrode had a better conductivity after it was modified by KOH solution. The radius of impedance curve of the carbon electrodes decreased with an increase in the KOH concentrations, which demonstrated that the ionic resistance in the electrodes decreased with an increase in the KOH concentrations. This is attributed to the pore expansion on the electrode surface caused by potassium ions (K^+) to reduce mass transfer resistance [25–27].

However, the high concentrations of KOH will reduce the specific surface area of carbon electrodes in order to lower the specific capacitances [28]. Fig. 5 shows the SEM images of the carbon electrodes which have been modified by KOH solution. The concentration of KOH was directly related to the surface structure of carbon electrodes. As shown in Fig. 5, the surface of the carbon electrode modified by low concentration of KOH was smooth. Also, there are many pores present in the surface of the carbon electrode modified by the low concentration of KOH. This indicates that an appropriate concentration of KOH should be selected for the modification of the carbon electrode.

Specific capacitance can be derived from the imaginary part (Z'') of the impedance spectra according to the following equation, where ω denotes the angular frequency.

$$C = |1/\omega Z''| \tag{2}$$

The corresponding plots of capacitance as a function of frequency are shown in Fig. 6. The specific

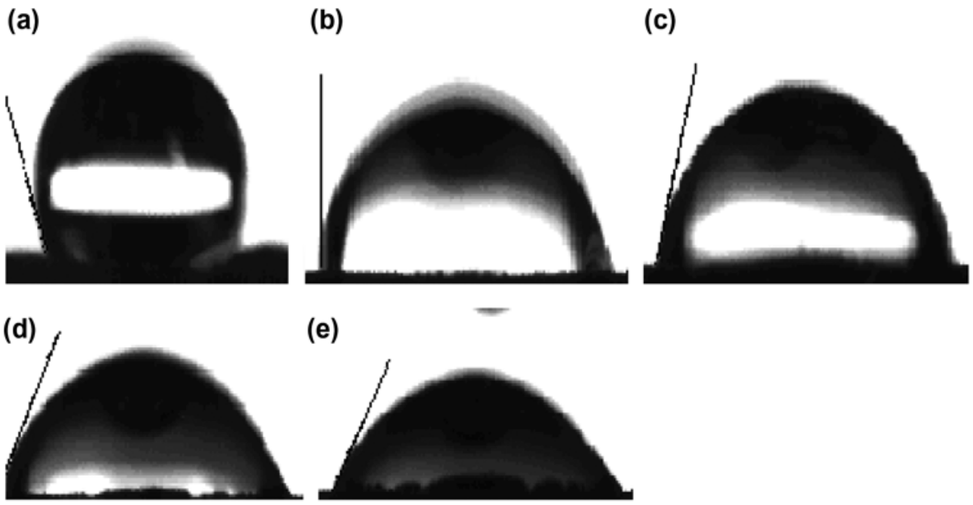

Fig. 2. Contact angle images of water droplet on electrodes modified by different concentrations of KOH solution. ((a) 0, (b) 3%, (c) 5%, (d) 8%, (e) 10%).

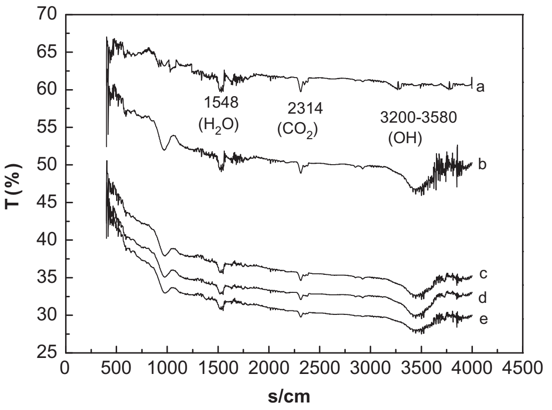

Fig. 3. FTIR spectra of electrodes modified by different concentrations of KOH solution. ((a) 0, (b) 3%, (c) 5%, (d) 8%, (e) 10%).

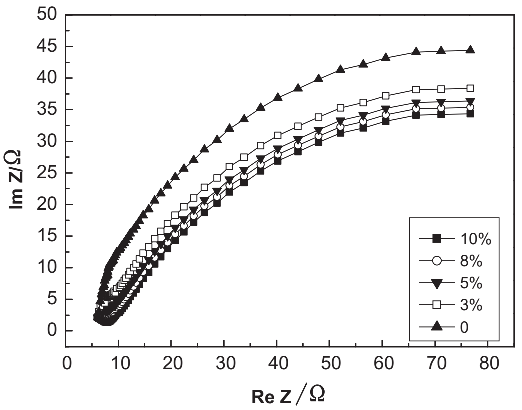

Fig. 4. Nyquist plots for the impedance response of the carbon electrodes modified by different concentrations of KOH solution.

capacitance of the unmodified carbon electrodes was higher than that of carbon electrodes modified by KOH solution. The capacitances of the carbon electrodes increased with a decrease in the mass concentrations of KOH (<5%) and decreased with an increase in the mass concentrations of KOH (>5%). This phenomenon indicated that K^+ ions will significantly reduce the electrode specific surface area at high concentrations of KOH, resulting in decreased capacitances. This showed that the optimal concentration of KOH for modifying the carbon electrode was 5%.

Another important characteristic property of the carbon electrode is reversibility, which represents the desalination and regeneration performance of the carbon electrode. The cyclic voltammograms were obtained in order to measure the reversibility. The voltammograms were symmetric within the applied potential, which means that ions were effectively adsorbed or desorbed according to the applied potential within the electric double layer at the electrode surface. Fig. 7 shows the cyclic voltammograms for carbon electrode modified by KOH of 5% at different scan rates (5–15 mv/s) from −1 to 1 V. The cyclic voltammograms were composed of charge current and discharge current curve. The charge current curve and discharge current curve were symmetric and there was almost no deviation from the shape of the cyclic voltammogram. Thus, it was confirmed that the reversibility as well as the desalination and

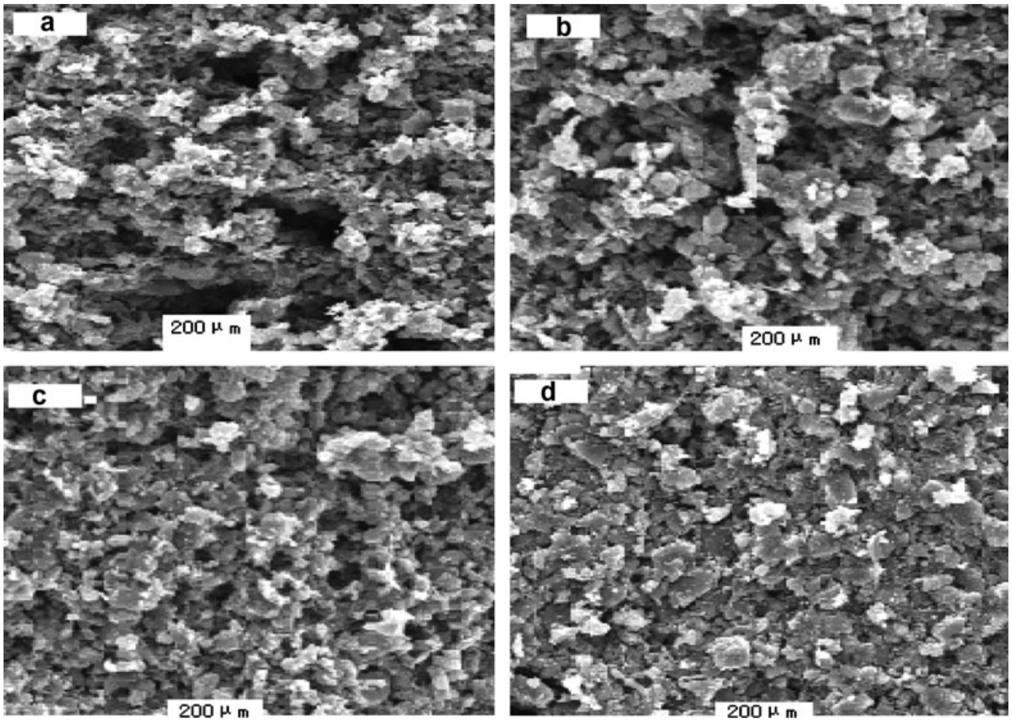

Fig. 5. SEM images of carbon electrodes modified by different concentrations of KOH solution. ((a) 10%, (b) 8%, (c) 5%, (d) 3%).

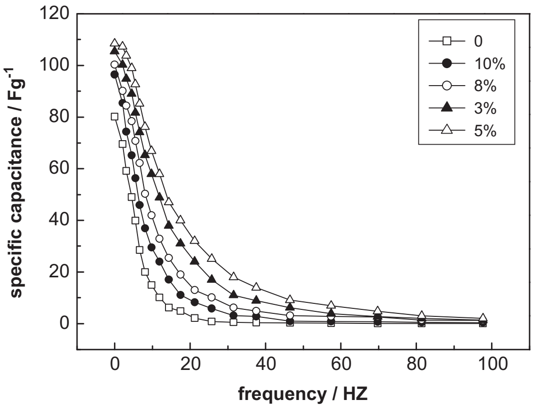

Fig. 6. Specific capacitances of the carbon electrodes derived from impedance data as a function of frequency.

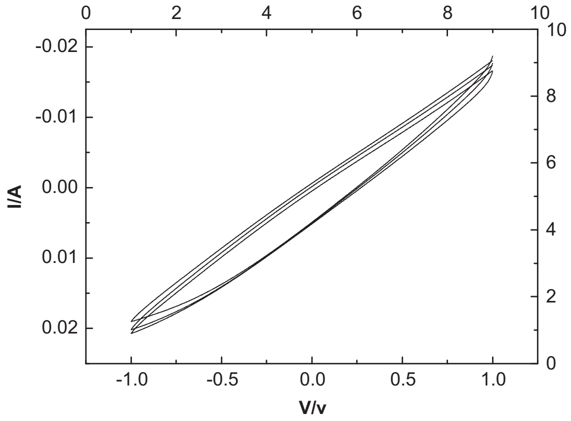

Fig. 7. Cyclic voltammograms of electrode at different sweep rates.

regeneration performances were excellent for the carbon electrode [29,30].

3.3. Desalination performances

In the desalination experiment, unmodified carbon electrode and that modified by KOH solution of 5% concentration were used to remove ions in the KNO_3 solution with the concentration of 1,500 μs/cm. The CDI process is directly related to electrical voltage and flow rate [31–33]; thus, the desalination performance of the carbon electrodes was evaluated at different electrical voltages and flow rates, as shown in Figs. 8 and 9.

The salt-removal efficiency increased with an increase in the voltages and decreased with an increase in the flow rates. The optimal voltage and flow rate are determined to be 2.5 V and 20 ml/min,

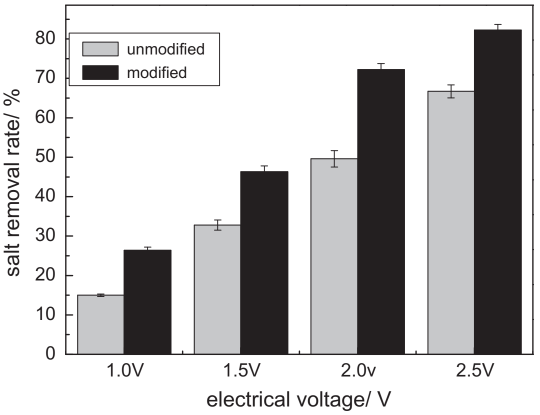

Fig. 8. Electrosorption of KNO_3 for electrode at different voltages.

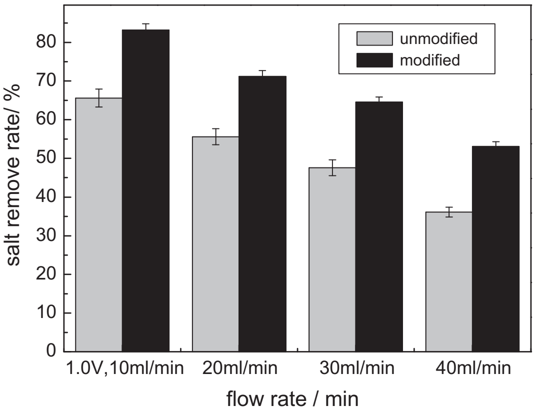

Fig. 9. Electrosorption of KNO_3 for electrode at different flow rates.

respectively. The salt-removal efficiencies of the unmodified and modified carbon electrodes were in the range of 67 to 72.3% and 72.7 to 82%, respectively, which indicated 13–20% increase in the salt-removal efficiency of the modified carbon electrode.

4. Conclusions

The carbon electrode modified by KOH solutions showed excellent hydrophilicity, which increased with an increase in the KOH concentrations. The optimum concentration of KOH solution for the modification of the carbon electrode was found to be 5%. The specific capacitance of the carbon electrode was significantly improved by modification with KOH. The modified carbon electrode exhibited excellent desalination performance, and the salt-removal rate increased by 23% compared to the unmodified carbon electrode. This improved performance is attributed to the increased number of hydroxyl groups on the surface of the electrode after modification with KOH. There was no significant decrease in the salt-removal rate after three cycles, indicating good reversibility for the modified carbon electrode.

Acknowledgments

This work is supported by the National Natural Science Foundation of China (No. 50978067), the 11th five-year specific events of water (2008ZX07421-002, 2009ZX07424-005, 2009ZX07424-006) and the Science and Technology Development Program of Jilin Province (20116022) and Jilin City Science and Technology (Project no. 2013625011).

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