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Nanostructured carbon cloth electrode for desalination from aqueous solutions

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Abstract

The electrochemical properties on capacitive deionization (CDI) of carbon cloth in NaCl solution have been investigated. For KOH etched carbon cloth, hydroxyl and carbonyl functional groups have increased significantly, while carboxyl functional group has changed little with etching time. For HNO_3 treated carbon surface, carboxyl, carbonyl, and hydroxyl functional groups were produced considerably, and then slightly formed with etching time. From the evaluations of CDI process the carbon cloth electrodes etched in KOH or HNO_3 for 3 h represent higher kinetic constants than that for the non-treated carbon cloth.

Keywords: XPS; Activated carbon cloth; Capacitive deionization; Cyclic voltammetry

1. Introduction

To separate the inorganic ions from seawater and wastewater, capacitive deionization (CDI) is an efficient and economical new process. For high efficiency of CDI process activated nanostructured carbon cloths provide important opportunity as electrodes for desalination from salty solutions. The surface of carbon cloths represents the nanoporous structure with high specific surface area, which can provide the major advantages for electrochemical reaction in aqueous solution. Because the ion-adsorption efficiency of the carbon electrode can be strongly dependent on the microstructure [1–5] and chemical functional groups formed during the chemical surface modification, activated carbon cloths were chemically surface-modified by etching in alkaline or acidic solution with various etching time in order to improve the efficiency of capacitive deionization from aqueous solution. After chemical surface modifications, the varieties of surface functional group were analyzed by X-ray photoelectron spectroscopy (XPS), and the electrochemical properties and the efficiency of desalination rate of activated carbon cloths have been investigated by cyclic voltammetry and capacitive deionization results.

2. Experimental

In an effort to investigate the properties of desalination for removal of inorganic species from salty solutions, activated carbon cloth (Kuraray, Japan) as the electrode was prepared. For the purpose of chemical modification of activated carbon surface, carbon cloths were etched in 1M KOH and HNO_3 solution at 90–100 °C for 3, 6, and 12 h. The electrochemical experiment employed a commercial electrochemical analyzer (IM6, Zahner, Germany). The potentials are referenced to saturated calomel electrode (SCE), and a platinum sheet was used for the counter electrode. For test of capacitive deionization, CDI unit was specially prepared. The change in the concentration of NaCl solution was monitored using an ion conductivity meter (YSI 3200, Yellow Springs, OH). For

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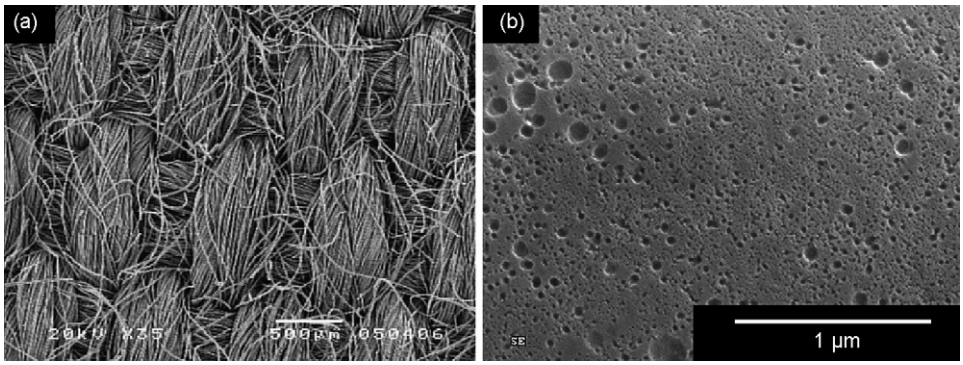

Fig. 1. Scanning electron micrographs for surface morphologies of activated carbon cloth (a), and surface pore structures of non-treated carbon fiber (b).

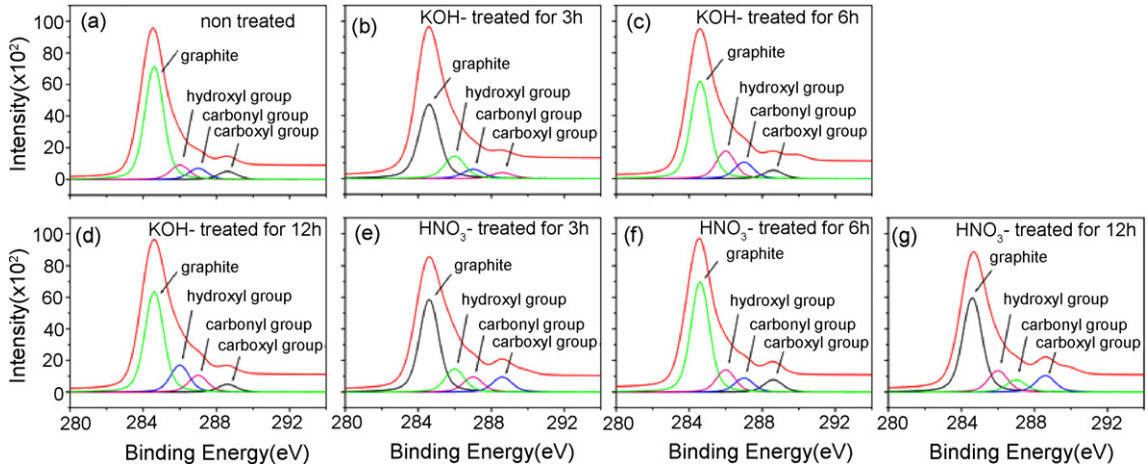

Fig. 2. C 1s XPS spectra of non-treated carbon cloth (a), chemically modified carbon cloth in 1M KOH for 3 h (b), 6 h (c), 12 h (d), and 1M HNO_3 for 3 h (e), 6 h (f), 12 h (g).

evaluation of surface functional groups on carbon cloth, XPS analysis was carried out by electron spectroscopy for chemical analysis (ESCA) 2000 (VG microtech).

3. Results and discussion

3.1. Activated carbon cloth electrodes

The surface microstructures of activated carbon cloth used in this study are presented in Fig. 1. The activated carbon cloth is made from bundles of carbon fibers that are woven into a cloth, and exhibits surface microstructures of carbon fiber with various pore size. XPS analysis was performed for evaluations of the changes in the surface concentration of functional groups formed after chemical surface modification. The C 1s spectrum has been deconvoluted into four components with chemical shifts corresponding to graphite type (284.6 eV) [6,7], hydroxyl or phenol (286 eV), carbonyl (287 eV), and carboxyl (288.6 eV) groups [8]. From these spectra shown in Fig. 2, the area ratios of graphitic carbon to carbon bonded to different functional groups were calculated, and are shown in Table 1.

For KOH treated carbon cloth in Table 1, hydroxyl functional group increased over two-fold after oxidation for 3 h, and then gradually decreased with etching time. But content of carbonyl group increased with etching time, while carboxyl functional group remains more or less unchanged. On etching for 3 h in

Table 1
Relative contents of the surface functional groups determined by C 1s spectra from XPS for non-treated, KOH treated, and HNO_3 treated carbon cloths with etching time

	Graphite (%)	Carboxyl groups (%)	Carbonyl groups (%)	Hydroxyl groups (%)
Non-treated	77.20	5.44	7.52	9.84
KOH treated for 3 h	66.39	5.28	8.23	20.10
KOH treated for 6 h	65.04	5.53	10.96	18.47
KOH treated for 12 h	66.23	4.98	11.06	17.73
HNO_3 treated for 3 h	63.49	10.28	10.35	15.88
HNO_3 treated for 6 h	69.49	7.69	8.80	14.02
HNO_3 treated for 12 h	65.41	10.16	8.36	14.77

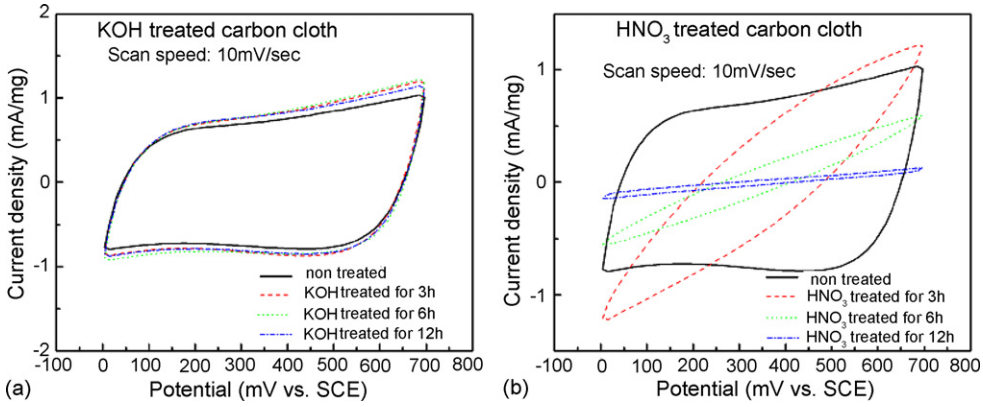

Fig. 3. Cyclic voltammograms for KOH (a), and HNO_3 (b) treated nano-carbon cloths in 0.5 M NaCl at 10 mV/s.

HNO_3, carboxyl, carbonyl, and hydroxyl (phenol) functional groups were produced significantly, but these functional groups do not increase further when etched for more than 3 h.

3.2. Electrochemical characterization

The carbon cloths used for electrochemical analysis were chemically modified in 1.0 M KOH and HNO_3 for 3, 6, and 12 h. The CV current-response behavior for KOH treated electrode in Fig. 3a exhibits a small increase in cathodic and anodic currents than that for non-treated carbon cloth electrode, but no significant changes were observed with chemical etching time. The CV behaviors obtained from HNO_3 treated electrodes were very different compared to KOH treated electrode, and the deviations from rectangular shape of voltammograms were observed due to Faradaic reaction, which disturbs the current reaching a truly horizontal value in cyclic voltammetric test, as shown in Fig. 3b. Furthermore, anodic and cathodic currents decreased prominently with etching time. This also demonstrates that electrochemical behaviors of carbon cloth etched in HNO_3 are not entirely dependent on the electric double layer process. It is also expected from Fig. 3b that higher capacitance can be found only for carbon cloth electrode etched in HNO_3 for 3 h.

Fig. 4 shows the current response curves of carbon cloth electrodes with non-treated, KOH treated for 3 h, and HNO_3 treated for 3h at various sweep rates. For current response behaviors of carbon cloths with non-treated and KOH treated for 3 h, as shown in Fig. 4a and b, nearly rectangular voltammograms were observed, and at increasing sweep rates, anodic and cathodic charging currents proportionally increased. From these linear relationships the double layer capacitance, C_{dl}, of the electrodes can be estimated by Eq. (1)

$$C_{dl} = \frac{i}{s}, \tag{1}$$

where i is the current response at sweep rates, s.

Fig. 4a and b also represent that ions are adsorbed on the electrode surface by forming an electric double layer due to Coulombic interaction rather than electro chemical reaction. However, for HNO_3 treated carbon cloth in Fig. 4c, the delay for the current to reach a horizontal value and the increase of slope in the horizontal region were significant with the sweep rate, which also indicate a noticeable decreasing capacitance (C_{dl}) with increasing sweep rate, s.

For further understanding of the reaction mechanism a potential step method was used. The pulses with anodic and cathodic steps of 300 mV were applied during 60 s in 0.5 M NaCl solution, and the resulting chronoamperograms are shown in Fig. 5. The rate of decay of the current was clearly lower on the HNO_3 treated carbon cloth than that for other carbon electrodes when electric field was applied. Thus, the current responses of Fig. 5 indicate that the reactions on the carbon cloth etched in HNO_3 solution are dependent strongly on Faradaic reaction compared to that for others. However, only for carbon cloth electrode treated in HNO_3 for 3 h, as shown in Fig. 5c and d, after a short period of time the higher current flow was observed, indicating that it reacts continuously on the electrode surface, and in such case relatively high CDI efficiency can be expected.

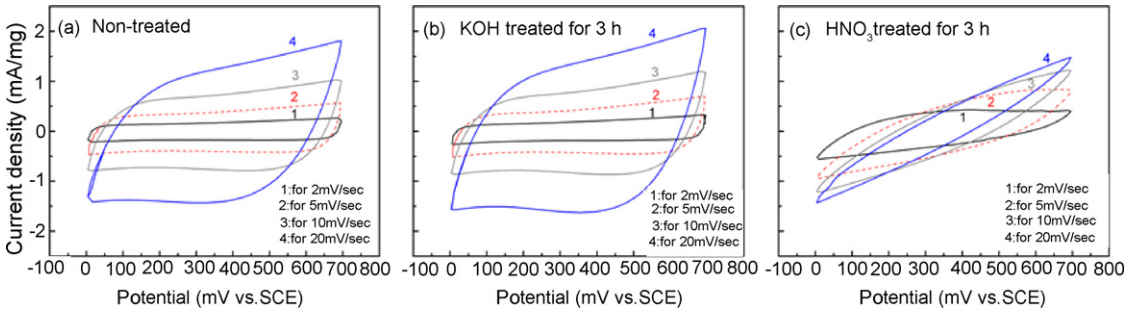

Fig. 4. Cyclic voltammograms for non-treated (a), KOH treated (b), and HNO_3 treated carbon cloth (c) in 0.5 M NaCl at various sweep rates.

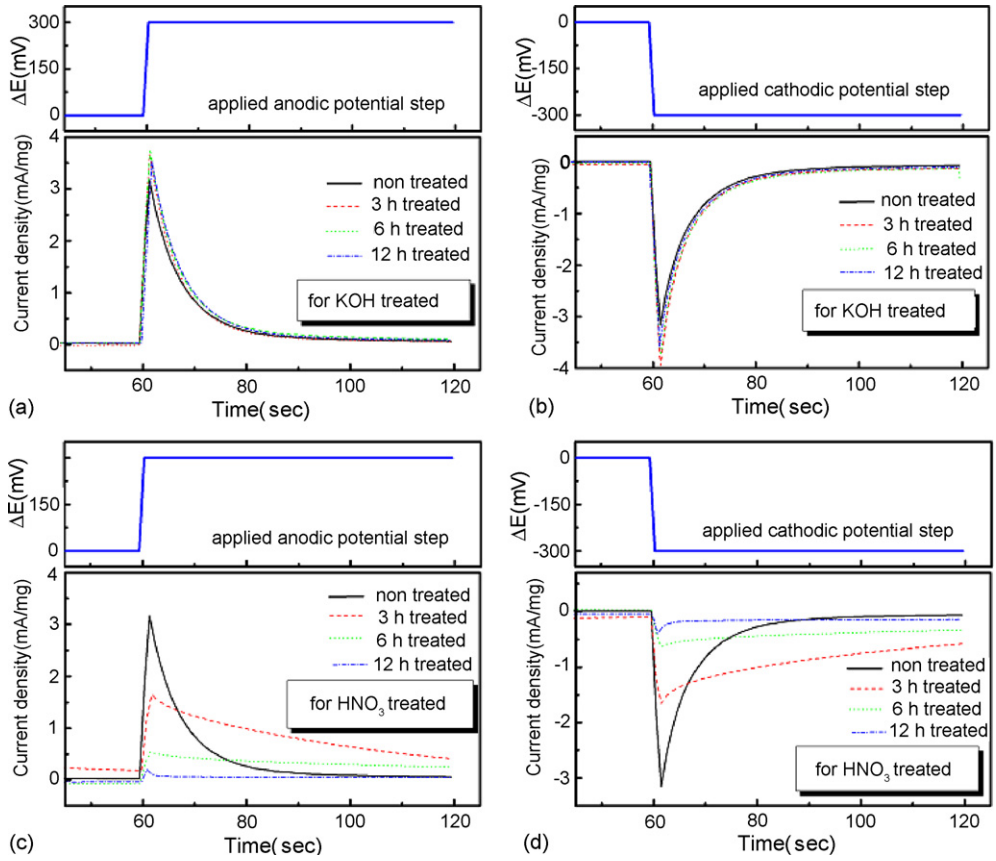

Fig. 5. The current–time response curves obtained from KOH treated electrode with anodic (a) and cathodic (b) potential steps, and HNO_3 treated carbon cloths with anodic (c), and cathodic (d) potential steps in 0.5 M NaCl solution.

3.3. Capacitive deionization (CDI) measurement

For measurements of electrosorption, CDI cell was specially prepared, and the activated carbon cloths with 160 mm × 160 mm were used as an electrode for CDI unit. Aqueous solution was pumped in by a peristaltic pump from the bottom, and drained from the top of the unit. In this experiment, the potential of 1.5 V and flow rate of 25 ml/min were applied.

Fig. 6 shows capacitive deionization of carbon cloths in NaCl solution with 2000 and 6000 μs/cm at the applied voltages of 1.5 V. For a conductance of 2000 μs/cm in NaCl solution after 240 s, the maximum desalination rates observed were 22.5% for non-treated carbon cloth, 44.2% for carbon cloth etched in KOH for 3 h (as shown in Fig. 6a) and 36.7% for carbon electrode etched in HNO_3 for 3 h (as shown in Fig. 6c). In case of experiment using a conductance value of 6000 μs/cm after 180 s the maximum desalination rate comes to 12% for non-treated carbon cloth, 22.7% for carbon cloth etched in KOH for 3 h, and 14.9% for carbon electrode etched in HNO_3 for 3 h (as shown in Fig. 6b and c). The results from Fig. 6 indicate that in case of carbon electrode etched in KOH for 3 h, the removal efficiency of inorganic salts is excellent compared with that for others.

The kinetic constants during desalination can be calculated by first order reaction rate Eq. (2)

$$\ln\left(\frac{\lambda_t}{\lambda_0}\right) = -k_1 t + \text{constant} \quad (2)$$

where λ_o and λ_t are the initial (inlet) and resultant (outlet) conductivity, respectively.

The kinetic constants for CDI process in NaCl solution with conductance of 2000 and 6000 μs/cm at 1.5 V are shown in Table 2. From the evaluations of kinetic constants in Table 2, the constants for the carbon cloth electrodes etched in KOH and HNO_3 for 3 h are higher than that for the non-treated carbon cloth.

These CDI properties can be explained in terms of characteristics of surface functional groups. For chemically etched carbon cloth for 3 h in KOH, electrode surface exhibits a significant amount of hydroxyl group (20%) as shown in Table 1. It can be assumed that this hydroxyl and carboxyl groups promote the adsorption of inorganic ion in solution by

Table 2
The kinetic constants for CDI process at the applied potential of 1.5 V in NaCl solution

Condition of chemical modification	NaCl solution with 2000 μs/cm	NaCl solution with 6000 μs/cm
Non-treated	$1.70 \times 10^{-3}\ s^{-1}$	$0.96 \times 10^{-3}\ s^{-1}$
KOH treated for 3 h	$4.18 \times 10^{-3}\ s^{-1}$	$2.12 \times 10^{-3}\ s^{-1}$
KOH treated for 6 h	$3.04 \times 10^{-3}\ s^{-1}$	$2.05 \times 10^{-3}\ s^{-1}$
KOH treated for 12 h	$3.55 \times 10^{-3}\ s^{-1}$	$1.90 \times 10^{-3}\ s^{-1}$
HNO_3 treated for 3 h	$2.53 \times 10^{-3}\ s^{-1}$	$1.26 \times 10^{-3}\ s^{-1}$
HNO_3 treated for 6 h	$2.31 \times 10^{-3}\ s^{-1}$	$0.69 \times 10^{-3}\ s^{-1}$
HNO_3 treated for 12 h	$1.13 \times 10^{-3}\ s^{-1}$	$0.29 \times 10^{-3}\ s^{-1}$

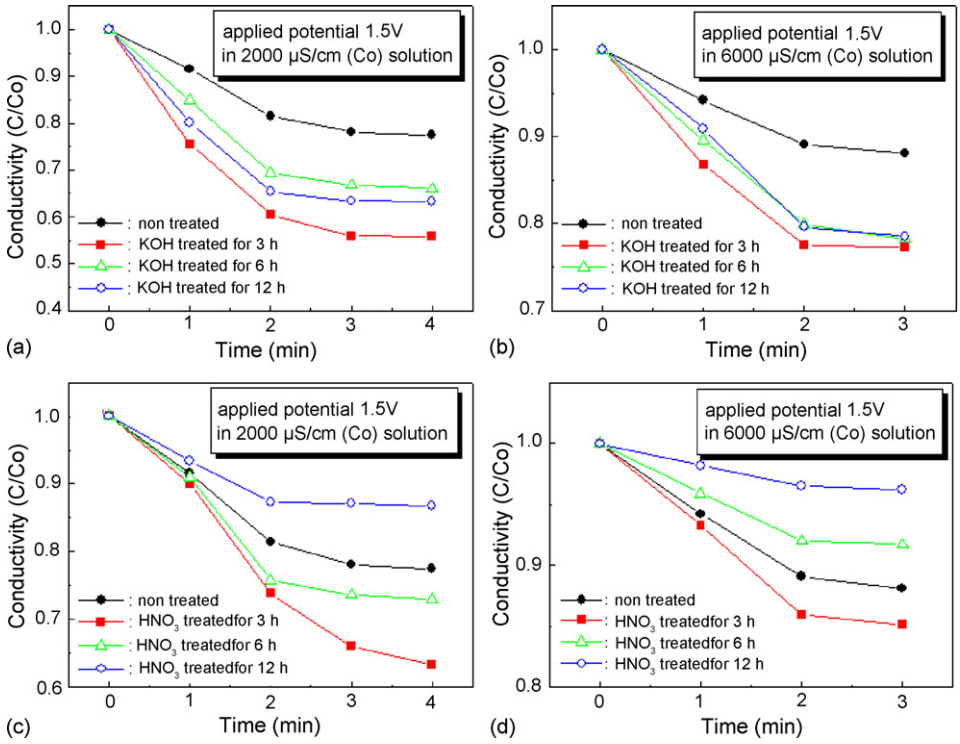

Fig. 6. Deionization efficiencies of chemically etched carbon cloths in NaCl solution at the applied voltage of 1.5 V. The experiments were conducted using initial conductivity of approximately 2000 μs/cm (a), 6000 μs/cm (b) for KOH treated carbon cloths, 2000 μs/cm (c), and 6000 μs/cm (d) for HNO_3 treated electrodes.

ion-exchange reaction as hydrophilic compounds. In case of chemically modified carbon cloth in HNO_3 for 3 h, the electrode surface contains an adequate amount of carboxyl (10.3%) and hydroxyl group (15.9%) to support the ion-exchange reaction, and carbonyl group (10.4%) to accelerate electron transfer by Faradaic reaction [9]. These facilitate the CDI efficiency due to not only ion adsorption by an electric double layer, but also electron transfer by Faradaic reaction.

4. Conclusions

In order to investigate the properties of desalination for removal of inorganic species from salt solution, activated carbon cloth were chemically etched in 1M KOH and HNO_3 solutions for 3, 6, and 12 h. During the chemical modification of carbon cloth in KOH solution, hydroxyl and carbonyl functional groups increased significantly, while carboxyl functional group showed almost little tendency of changing with etching time. For HNO_3 treated carbon surface, carboxyl, carbonyl, and hydroxyl functional groups increase considerably at initial stage. The electrochemical behaviors are affected by the surface oxide functional groups created during chemical surface modifications in acid or alkaline solution. For CV current–response behaviors of KOH treated electrode, no significant changes were observed with chemical etching time, while the CV behaviors obtained from HNO_3 treated electrodes display the deviations from rectangular shape of voltammograms due to Faradaic reaction. From the evaluations of CDI process the carbon cloth electrodes etched in KOH or HNO_3 for 3 h represent the higher kinetic constants than that for the non-treated carbon cloth, especially in case of etched in KOH for 3 h, and the removal efficiency of inorganic salts is most effective among all the specimens.

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