Electrochemistry Communications 39 (2014) 22–25

Contents lists available at ScienceDirect

Electrochemistry Communications

journal homepage: www.elsevier.com/locate/elecom

Short communication

Enhancement of charge efficiency for a capacitive deionization cell using carbon xerogel with modified potential of zero charge

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A R T I C L E I N F O

Article history:
Received 4 November 2013
Received in revised form 20 November 2013
Accepted 2 December 2013
Available online 11 December 2013

Keywords:
Carbon xerogel
Capacitive deionization
TEOS-modification
Potential of zero charge
Potential distribution
Charge efficiency

A B S T R A C T

The use of tetraethyl orthosilicate to modify carbon xerogel materials results in the formation of silica oxide and carboxylic functional groups at the carbon's surface. Voltammetric characterization indicates that the potential of zero charge (PZC) of the modified samples was positively shifted to the extent affected by dip-coating repetitions. Cycling tests were performed at 1.2 V for 15 cycles in a flow-through cell with ~4 mM deaerated NaCl. The average charge efficiency of the cell was significantly enhanced from ~60% to ~86% when the modified electrode served as the cathode. This increase in efficiency was mainly attributed to the shifting of the PZC at the cathode towards the cell short-circuit potential, thereby reducing co-ion repulsion at the cathode.

1. Introduction

Sol–gel dip-coating methods using tetraethyl orthosilicate (TEOS) have been reported in literature for the surface modification of carbon fibers [1] and activated carbons [2,3] for capacitive deionization (CDI) applications. These modified carbons coated with a thin SiO_2 film exhibited an improved capacity for ion adsorption, which was accounted for by the enhancement of surface polarization characteristics, surface area, and wettability of the modified substrates [1–3].

The potential of zero charge (PZC) is the electrode potential for which the interfacial tension between the electrode and electrolyte is maximized, and the charge stored at the electrode is correspondingly minimized [4]. In literature, the region of the PZC for CX [5], carbon aerogel [6], and activated carbon [7] has been observed in voltammograms when low scan rates and diluted salt solution were used. Additionally, the PZC formation mechanism depends on surface properties of the carbons [4,6,8]. Since SiO_2 has a negative zeta potential in neutral solutions [1,9,10], TEOS-modification is expected to affect the carbon xerogel's (CX's) surface polarity. As a consequence, a change in the PZC for the modified CX will be reflected in voltammograms.

Charge efficiency is one of the important performance terms for a CDI cell, which is given by the ratio of the equivalent charge of salt adsorbed to the charge passed during the adsorption step. This efficiency value can be increased by variations in the applied voltage to the cell and the salt concentration [11], and the use of the membrane assisted electrodes [12,13]. Beyond these physical variations/modifications, charge efficiency also can be alternatively elevated by chemically modifying the PZC of carbons. Recent articles report that if the electrode's PZC is located in the electrode's working domain, a charge inefficiency will occur due to co-ion repulsion [14–16]. Thus, to minimize this effect, we investigated the effect of TEOS-modification on the PZC of CX relative to the electrodes' working domain. To the best of our knowledge, we demonstrate here for the first time TEOS-modification of CX for CDI applications by modifying the CX's PZC.

2. Experimental

The preparation of CX sheets has been previously reported in detail by our group [17]. Following the CX fabrication, the sheets (with dimensions of ~$9 \times 5 \times 0.04$ cm^3) were modified by the following steps: TEOS (Sigma-Aldrich, >99%), ethanol (Pharmco-Aaper, 200 proof) and HNO_3 (Acros, 68–70%) were vigorously mixed with a volumetric ratio of 1:20:1 for 1 h. The CX sheets were dipped into the mixture for 3 min, and dried in an oven at 100 °C for 30 min. The samples were further heated at 300 °C in the oven for another 12 h. The CX sheets were dipped repetitively into the TEOS mixture to vary the amount of SiO_2 deposited [1], and the samples are denoted CX-Si-X, where X is the number of repetitions. A scanning electron microscope (SEM) (Hitachi 4800), a surface area and porosity analyzer (Micrometrics ASAP2020), a Fourier transform infrared (FTIR) spectrometer (Nicolet 6700), and a potentiostat (Princeton Applied Research 273A) were used for surface morphology, pore structure, surface species, and potential-current characterizations, respectively.

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http://dx.doi.org/10.1016/j.elecom.2013.12.004

Cycling tests were performed in a flow-through cell with the CX electrodes adjacent to titanium current collectors. The CX electrodes were separated by a 1.5 mm thick silicon rubber spacer. Adsorption–desorption cycles were performed at 1.2 V and the short-circuit potential for a total of 15 combined cycles. The CX electrodes had a total mass of ~0.8 g (~42 cm^2). During system operation, 500 ml of ~4 mM NaCl was continuously purged with wetted N_2 in the reservoir and circulated using a peristaltic pump (Masterflex) at 27.2 ml min^{-1}. A conductivity meter (Cole-Parmer 19500-45) at the cell outlet was installed to calculate the electrosorption capacity (Γ).

$$\Gamma = (\Delta\sigma M_w V)/(mc) \tag{1}$$

where Δσ is the conductivity difference between the adsorption–desorption steps at steady state (i.e., last 100 s), M_w is the molar mass of NaCl, V is the volume of the NaCl solution, m is the mass of the CX used, and c equals 112.77 determined from the slope of conductivity as a function of NaCl concentration. The charge efficiency (Λ) is the ratio of Γ (converted to equivalent charge using Faraday constant (F)) to the charge passed during the adsorption step (Q_{ad}).

$$\Lambda = (\Gamma F/M_w)/(Q_{ad}) \times 100\% \tag{2}$$

After the cycling tests, the used cathodes and anodes were resized to ~0.35 cm^2, spaced 1.5 mm apart, and placed in ~4 mM deaerated NaCl along with a reference electrode and a counter electrode. This four-electrode setup was employed to define the potential distribution using a power supply, and then locate each electrode's PZC using a potentiostat. In detail, by shorting the cathode and anode the short-circuit potential versus the reference electrode was measured using a multimeter, and by applying a voltage of 1.2 V with the power supply across the cathode and anode, the potential drop across each electrode versus the same reference electrode was measured again with the use of the multimeter. Subsequently, each used cathode (and anode) was individually characterized at 1 mV s^{-1} via a conventional three-electrode connection using the potentiostat and a counter electrode.

3. Results and discussion

Fig. 1(a) shows that the CX has void spaces surrounded by carbon networks. This surface morphology is maintained after mild modification (CX-Si-1, Fig. 1(b)), and changes slightly as the number of dip-coatings increases (CX-Si-5, Fig. 1(c)). Additionally, typical SiO_2 aggregation was observed in some areas of this sample. As the number of dip-coatings further increases, the carbon network becomes less distinguishable (CX-Si-10, Fig. 1(d)). Instead, a 'flake-like' area appears that could be a SiO_2 layer due to repetitive coatings. The surface areas measured by N_2 gas adsorption for each sample were 196 m^2 g^{-1} (CX), 176 m^2 g^{-1} (CX-Si-1), 175 m^2 g^{-1} (CX-Si-5), and 212 m^2 g^{-1} (CX-Si-10). The decrease in the surface area could be due to occlusion of the carbon pores by a thin SiO_2 film, as the magnitude of d(V) / dlog(w) for CX-Si-1 and 5 decreased whereas the pore structure is maintained (Fig. 1(e)). In contrast, the increase in the surface area for CX-Si-10 implies that the SiO_2 layer has nano-porous characteristics, which enhanced the d(V) / dlog(w) value at ~3.5 nm (Fig. 1(e)).

Since no distinct silica characteristic can be found for CX-Si-1 using microscopy, FTIR spectroscopy examined the chemical species at the CX surface (Fig. 1(f)). New bands at ~1730, ~1430 and ~1100 cm^{-1} corresponding to C=O stretching, Si–C_6H_5 stretching, and Si–O–C stretching, respectively were found [18]. This assignment indicates that the modification resulted not only in a thin-film containing Si, but also in the attachment of –COOH functional groups to the carbon surface [18]. It is known that SiO_2 has a negative zeta potential in neutral solution, and $-COO^-$ from the hydrolysis of –COOH carries a negative charge [1,5]. Therefore, the CX's surface with these species is negatively polarized, consequently enhancing cation (Na^+) adsorption but reducing anion adsorption (Cl^-). This expectation is consistent with the voltammetric characterization of the freshly-prepared sample of CX, CX-Si-1 and 5 in Fig. 1(g). It was also found that the voltammogram for CX-Si-10 shrank, which could be due to the thick non-conductive SiO_2 layer formed at the carbon's surface [2] or clogging of the carbon pores by a thick SiO_2 layer (see the decrease in d(V) / dlog(w) value for CX-Si-10 in Fig. 1(e)). In contrast, the area under the voltammograms for the other samples is still comparable, which indicates no

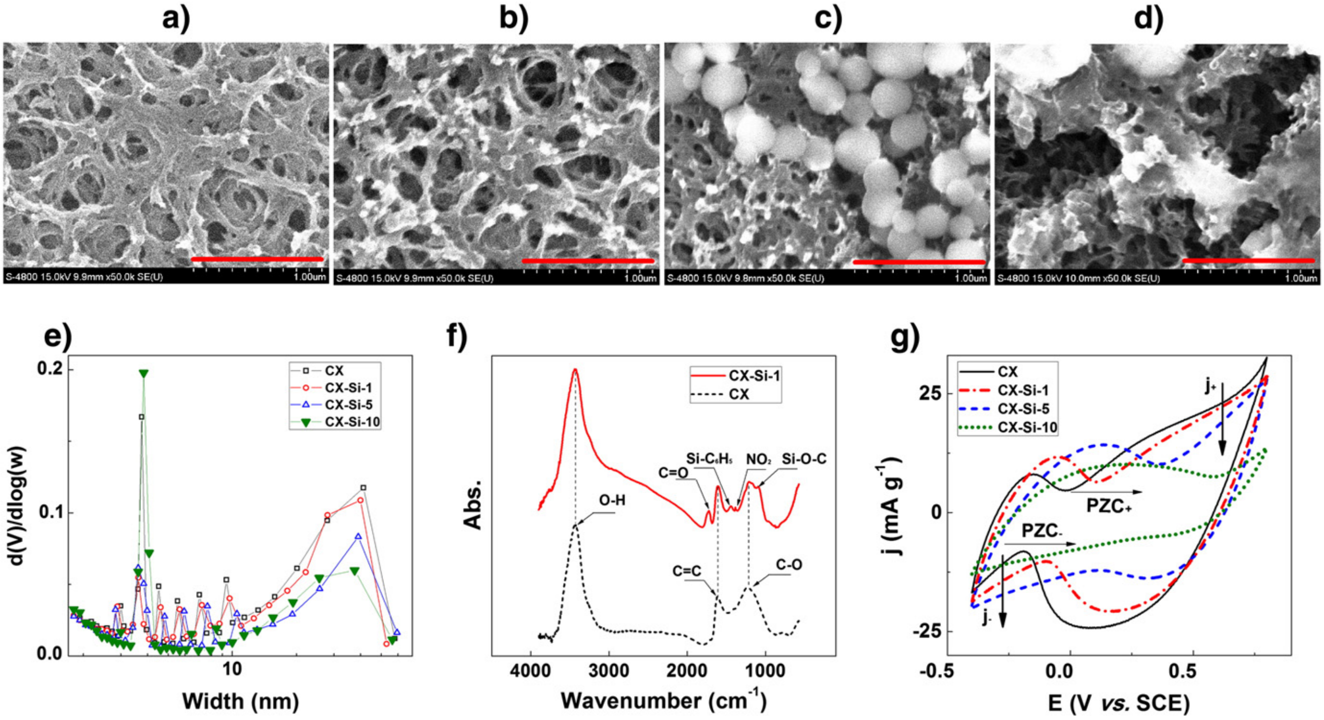

Fig. 1. Surface morphologies of (a) CX, (b) CX-Si-1, (c) CX-Si-5 and (d) CX-Si-10. Size bar is 1 μm. (e) Pore size distributions. (f) FTIR spectra of CX and CX-Si-1. (g) Cyclic voltammogram at 1 mV s^{-1} in ~4 mM deaerated NaCl.