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Fabrication and characterization of a carbon electrode coated with cation-exchange polymer for the membrane capacitive deionization applications

Jae-Sook Kim, Jae-Hwan Choi*

Department of Chemical Engineering, Kongju National University, 275 Budae-dong, Seobuk-gu, Cheonan, Chungnam 331-717, South Korea

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ABSTRACT

A carbon electrode coated with cation-exchange polymer was fabricated in a simple and inexpensive way for applications in membrane capacitive deionization (MCDI). A mixture of poly(vinyl alcohol) (PVA) and sulfosuccinic acid (SSA) was used as a coating solution to introduce negatively charged ion-exchange groups. The PVA/SSA-coated carbon electrodes were fabricated at different crosslinking temperatures and SSA contents. The prepared electrodes were characterized by SEM, FTIR analysis, cyclic voltammetry and electrical impedance spectroscopy. The PVA/SSA coating layer showed high adhesion to the carbon powders. The SSA was effectively introduced as a crosslinking agent and cation-exchange groups, as shown in the FTIR spectra. Cyclic voltammetry analysis indicated that the specific capacitance was increased by coating the carbon electrode with PVA/SSA polymer solution. The specific capacitances of the coated electrode were enhanced by 14.8–30.9% compared with the uncoated one, depending on the crosslinking temperature. The increased capacitance of the coated electrode is attributed to the fixed ion concentration in the PVA/SSA coating layer. The electric resistance and specific capacitance of the coated carbon electrodes were affected strongly by the crosslinking temperature due to the altered degree of crosslinking. The area resistances of the coating layer were in the range of 0.67–1.17 $\Omega\,\mathrm{cm}^2$, depending on the crosslinking temperature and SSA content, which is relatively low when compared with commercial ion-exchange membranes.

1. Introduction

With increasing concerns about energy consumption and the environment, interest in capacitive deionization (CDI) technology has increased significantly as a promising desalination process. It is regarded as an energy-efficient desalination process because it is operated at a lower electrode potential at which no electrolysis reactions occur. In addition, this process is environmentally friendly because it requires no chemicals for the electrode regeneration [1–5].

Since the concept of CDI was first introduced by Murphy and Caudle [6], many researchers have achieved remarkable developments in CDI technology. It is important to increase the ion adsorption capacity of the electrode for higher CDI performance. Thus, many studies have been performed with the goal of increasing the capacitance of a carbon electrode using various carbon materials [7–12].

Another notable development in CDI technology was achieved by Andelman [13,14]. Conventional CDI is known to be energy inefficient because of the dissolved salt present in the pore volume of the carbon electrode. When an electric potential is applied, counter-ions in the pore adsorb onto the electrode, and co-ions (ions with the same polarity as the electrode) are expelled from the electrode. This means that ion adsorption and desorption occur simultaneously in the pore volume in the electrode, seriously reducing the desalination efficiency. To solve this problem, Andelman suggested the placement of a charge barrier adjacent to an electrode of a flow-through capacitor [14], a technique later called membrane capacitive deionization (MCDI).

Recently, many studies have been published about novel MCDI processes [15–19]. Li et al. constructed an MCDI device using carbon nanotube and nanofiber electrodes and ion-exchange membranes. They showed that the salt removal by the MCDI system was about 50% higher than that by the CDI system [16]. Biesheuvel and van der Wal presented pilot-plant experimental data for salt removal in MCDI as a function of influent salt concentration and flow rate [17]. By reversing the cell potential and stopping the flow rate temporarily during the desorption period, they found that the salt concentration ratio between the diluted product and the concentrated salt was as high as 25. From these studies, it was verified that an MCDI system can increase the desalination efficiency and concentration ratio significantly compared to the conventional CDI system.

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* Corresponding author. Tel.: +82 41 521 9362; fax: +82 41 554 2640.
E-mail address: jhchoi@kongju.ac.kr (J.-H. Choi).

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The cation-exchange and anion-exchange membranes used in MCDI are selectively permeable to cations and anions, respectively, and are widely used in electro-membrane processes such as electrodialysis, diffusion dialysis and fuel cells [20]. However, the price of commercial ion-exchange membranes remains prohibitively high for CDI applications. Furthermore, when constructing an MCDI cell, ensuring that the membrane and the electrode are in good contact can be problematic.

To overcome these problems in an MCDI cell, in this study we fabricated a composite carbon electrode directly coated with a cation-exchange polymer. A mixture of poly(vinyl alcohol) and sulfosuccinic acid was used as a cation-exchange polymer. The introduction of negatively charged ion-exchange groups was achieved by chemical modification (crosslinking with SSA). The effects of crosslinking temperature and SSA content on the electrochemical properties of the composite carbon electrode were investigated by cyclic voltammetry and electrical impedance spectroscopy.

2. Experimental

2.1. Materials

Activated carbon powder (P-60, BET surface area = 1260 m^2/g) was purchased from Daedong AC Co., Korea. The ACP was dried in an oven at 80 °C for 24 h and stored in a desiccator before use. Poly(vinylidene fluoride) (PVdF, molecular weight = 530,000), fully hydrolyzed poly(vinyl alcohol) (PVA, molecular weight = 89,000–98,000), di-methylacetamide (DMAc), and sulfosuccinic acid (SSA) were purchased from Aldrich Co. Ltd. Graphite sheets (250 μm, Cat. No. 02511) were supplied by Dongbang Carbon Co., Korea.

2.2. Fabrication of carbon electrode

A carbon electrode was prepared using activated carbon powder. A carbon slurry was prepared as a suspension of activated carbon powder and PVdF in DMAc. The mixture was stirred for 12 h to ensure homogeneity. The slurry was then cast onto a graphite sheet to a thickness of 250 μm. The cast electrode was dried at 50 °C in an oven for 2 h and then in a vacuum oven at 50 °C for 2 h to remove all traces of organic solvent remaining in the micropores of the carbon electrode. The PVdF content of the prepared carbon electrode was 10 wt%.

2.3. Coating of carbon electrode with PVA/SSA solution

Following the work of Rhim et al. [21], we prepared a mixture of PVA and SSA as a cation-exchange polymer solution. The SSA acted as a crosslinking agent and provided cation-exchange functional groups. The reaction mechanism of PVA and SSA has been described in detail by Rhim et al. [21].

Aqueous 10 wt% PVA solutions were prepared by dissolving the preweighed amount of PVA in water at 90 °C for 6 h. The PVA solutions were mixed with various amount of SSA (the mole ratios of SSA to PVA were 5, 10, 15, and 20%), and the mixtures were vigorously stirred at room temperature for 24 h. Then the polymer solution was cast onto the prepared carbon electrode. The cast carbon electrodes were dried at 60 °C in an oven for 1 h and then heated for 1 h in a thermostatic oven at 110 °C to crosslink the PVA and SSA by esterification. To investigate the effect the degree of crosslinking on the electrode properties we fabricated several composite carbon electrodes at different crosslinking temperatures (100, 110, 120, and 130 °C). Detailed preparation conditions of the PVA/SSA-coated carbon electrodes are summarized in Table 1. The prepared composite carbon electrodes were stored in 0.5 M KCl solution for 24 h before electrochemical analysis.

Table 1
The preparation conditions of composite carbon electrodes coated with PVA/SSA.

Electrode codes	SSA/PVA ratio[a] (mol/mol)	Crosslinking temperature (°C)
S/P15_T100	0.15	100
S/P15_T110	0.15	110
S/P15_T120	0.15	120
S/P15_T130	0.15	130
S/P05_T110	0.05	110
S/P10_T110	0.10	110
S/P15_T110	0.15	110
S/P15_T110	0.20	110

[a] The number of moles of PVA was determined by dividing the mass of PVA by the formula weight of the monomer.

2.4. Surface morphology and FTIR analysis

The surface morphologies of the prepared carbon electrodes were investigated using a scanning electron microscope (SEM, MIRA LMH, TESCAN Ltd.). The sample surfaces were covered with gold using ion sputtering, and SEM images were obtained.

To determine the chemical structure of the fabricated composite carbon electrodes, attenuated total reflectance Fourier transform infrared spectroscopy (ATR-FTIR) analysis was conducted. The ATR-FTIR spectra of the coated carbon electrodes were measured by a FTIR spectrophotometer (Nicolet 6700; Thermo Scientific Inc.) in the range of 4000–500 cm^{-1}.

2.5. Electrochemical characterization

To examine the electrochemical properties and electrochemical behaviors of the prepared carbon electrodes, cyclic voltammetry (CV) and electrical impedance spectroscopy (EIS) were measured using a three-electrode system. The carbon electrode specimen was inserted into the specimen holder. A platinum rod coated with carbon and saturated Ag/AgCl electrodes were used as a counter and a reference electrode. The effective surface areas of the working and counter electrode were 1.77 and 3.60 cm^2, respectively. The voltage on the test electrode was controlled by an AutoLab PGST30 potentiostat.

The cyclic voltammetric measurements for the electrodes were made in the potential range of −0.5–0.5 V (vs. Ag/AgCl) at a potential sweep rate of 5 mV/s. To examine the charging resistance and capacitance as a function of frequency, an impedance measurement was performed on the prepared carbon electrodes with an AutoLab FRA impedance analyzer. The impedance spectra were obtained at a potential of 0.0 V in the frequency range of 100 Hz to 20 mHz. An alternating sinusoidal signal of 25 mV peak-to-peak was superimposed on the *dc*-potential.

Electrolyte solutions of 0.5 M KCl were purged with nitrogen before every experiment to remove dissolved oxygen. All experiments were maintained in a water bath at 25 ± 0.1 °C.

3. Results and discussion

3.1. Morphologies of the carbon electrodes

Fig. 1 shows the cross-sectional views of the carbon electrodes, both uncoated (a) and coated with PVA/SSA polymer solution (b). Although the electrode slurry was 250 μm thick as it was cast, the thickness of the dried carbon electrode was about 140 μm; its thickness was reduced by more than half during the drying process.

As seen in Fig. 1(a), the PVdF in the carbon electrode is present as discrete particles and fibrils that interconnect the carbon powders.