



Cation exchange copolymer enhanced electrosorption



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HIGHLIGHTS

- Activated carbon electrodes were coated with sulfonated random copolymers.
- Coating layer resistance did not adversely affect the build up of charge.
- Electrode capacitance was enhanced by polymers with a high ion-exchange capacity.
- Coating thickness influences the resistance of the carbon electrodes.

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ABSTRACT

In this study the effects of cation exchange polymer coatings on activated carbon electrodes for capacitive deionization (CDI) were investigated. Electrodes were fabricated from activated carbon, graphite and PVDF, then coated with sulfonated poly(arylene ether sulfone) random copolymers. Additional resistance was created by the coating layer, however compared with the uncoated electrodes the coatings did not significantly affect the rate of charge build up. Electrochemical impedance spectroscopy (EIS) results indicated that both capacitance and charging resistance are influenced by polymer conductivity, water uptake and the thickness of the coating layer. The results also indicated that in addition to functioning as a superficial charge barrier, copolymer that penetrates into the carbon substrate might offset the loss in capacitance caused by PVDF binder pore blockage.

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1. Introduction

Capacitive deionization (CDI) is a developing desalination technology that can be used for the highly efficient desalination of brackish water, the production of ultra pure water, water softening and the removal of other charged impurities from water streams [1–3]. It is an electrosorption process that relies on the formation of an electrical double layer on a porous, polarizable electrode. This buildup of charge creates a similar buildup of oppositely charged ions from an electrolyte solution at the electrode–solution interface, thereby removing salt ions from solution.

Activated carbon is an attractive material for electrosorption due to its relatively low cost and large specific surface area, typically in the order of 1000–2000 m²/g, and numerous studies have focused on its use for CDI [4–12]. Unfortunately the potential for activated carbon to adsorb salt ions from solution is hindered by its microporous nature, low conductivity, and high electrical and mass transfer resistances [13]. Furthermore, it typically exhibits a randomly arranged pore

network that may hinder ion movement and thus sorption [14]. As such, research efforts to improve its electrosorption capacity and efficiency are ongoing, with techniques such as surface modification and the incorporation of membranes. The modification of the activated carbon surface has been shown to improve electrosorption efficiency by neutralising polar surface charges thereby reducing unwanted physical adsorption. Studies have shown that enhanced performance can be achieved through chemical surface modification of activated carbons with titanium [15,16], titanium dioxide nanoparticles [5], potassium hydroxide and nitric acid [17,18], and zinc oxide nanorods [19].

In addition to the drawbacks of activated carbon, an inherent disadvantage of the CDI process is that during the adsorption of counter-ions, a simultaneous desorption of co-ions occurs. Thus, for each electron passing through the external circuit, less than one salt molecule is adsorbed [20–23]. To restrict this co-ion movement during adsorption, ion exchange membranes may be placed in front of each electrode. This is known as membrane capacitive deionization (MCDI), and was first introduced by Andelman and Walker in 2004 [24]. It has been shown to significantly increase salt adsorption and energy efficiency by improving the efficiency of counter-ion adsorption [25–30]. Ion exchange membranes also allow for the application of a reverse potential

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during the desorption phase, allowing for a greater depletion of ions at the electrode and thus greater adsorption capacity in the following cycles [31].

Commercial cation exchange membranes used for MCDI include Neosepta CM-1 [25] and Neosepta CMX [32–34]. These membranes are poly(vinyl chloride) based with styrene/divinylbenzene copolymers and are designed for desalination purposes with high permselectivity, low electrical resistance, and high mechanical stability [35]. However, the use of flat sheet membranes creates additional resistance between the membrane and the electrode. One alternative approach to reduce this resistance involved the spraying of carbon cloth electrodes with bromomethylated poly(2,6-dimethyl-1,4-phenylene oxide) (BPPO) solution, which was subsequently sulfonated with sulfuric acid to attach functional groups to the polymer [34]. Another approach by Kim et al. [36] saw the coating of carbon electrodes with poly(vinyl alcohol), which was sulfonated and crosslinked by using sulfosuccinic acid. This technique yielded ion-exchange coatings with area specific resistances lower than those of commercial membranes.

The poly(arylene ether sulfone) copolymers used in this study are characterised by having high conductivity and mechanical stability. Similar ion-exchange copolymers have been developed for pressure-driven desalination membranes and for fuel cell applications [37–44], but few studies have focused on their application for CDI [45]. In this work these cation exchange polymers have been applied as thin membrane coatings to activated carbon electrodes in order to enhance electrosorption performance. The characteristics of the coated electrodes are compared to uncoated electrodes, and correlations between the polymer properties and electrode performance are highlighted. In particular, the influence of conductivity and water uptake on resistance and capacitance is discussed.

2. Experimental

2.1. Materials

4,4'-difluorodiphenyl sulfone was purchased from FuMA-Tech GmbH (Germany) and was purified by vacuum distillation. 4,4'-dihydroxydiphenyl sulfone (DHDPHS), N-methyl-2-pyrrolidone (NMP), poly(vinylidene fluoride) (PVDF), activated carbon and graphite powder were purchased from Sigma-Aldrich (Australia). Concentrated sulfuric acid (min. 96%) was obtained from Acros (Belgium). 2,5-diphenylhydroquinone (DPhHQ) was prepared as per the procedure described by Vogel et al. [43].

2.2. Polymer synthesis and sulfonation

Three random copolymers were synthesised by using the silyl-method as per the procedure previously described [43,45]. The ratio of the monomers in the random copolymers was varied such that the monomer ratio of DPhHQ to DHDPHS was 6:4 for RCP 1, 5:5 for RCP 2 and 4:6 for RCP 3. All polymers were sulfonated by using concentrated

sulfuric acid (96–98%). The molecular structure of the random copolymers can be seen in Fig. 1.

2.3. Electrode preparation

Using NMP as a solvent, a slurry consisting of activated charcoal, graphite powder as conductive material and PVDF as a binder was prepared such that the final (dry) content of the electrode was 75 wt.% activated charcoal, 15 wt.% graphite and 10 wt.% PVDF. The slurry was coated onto graphite sheets to a thickness of 200 μm using a doctor blade and dried in a vacuum oven for 24 h at 120° to completely remove the solvent.

Polymer coated electrodes were prepared by first dissolving the sulfonated polymers in NMP such that the concentration was 15 wt.%. The solutions were cast onto the carbon electrodes and dried under vacuum for 2 h at 60 °C, then for a further 24 h at 80 °C. The samples were rinsed with distilled water to remove residual NMP, soaked in 0.5 M NaCl to convert the polymer to the Na⁺ form, then rinsed again with water to remove excess NaCl from the polymer matrix.

2.4. Electrode characterisation

Specific surface area and pore size distribution were measured on a Micrometrics ASAP 2020 Physisorption Analyser using N₂ as the adsorbate at 77 K. FTIR spectra were collected by using a PerkinElmer Spectra 100 to confirm the chemical structure of the cation exchange polymer coatings. Cyclic voltammetry experiments were performed by using a Biologic VSP potentiostat connected to a three-electrode electrochemical cell. The working electrode was the carbon material to be tested with an exposed surface area of 0.785 cm². The reference electrode was a saturated Ag/AgCl KCl electrode, and the counter electrode was a platinum mesh electrode. Electrochemical Impedance Spectroscopy (EIS) was performed by using the same three-electrode cell over the frequency range 10 mHz to 1 MHz, with an applied voltage amplitude of 10 mV.

3. Results & discussion

3.1. Activated carbon surface area & pore size distribution

The isotherm obtained for the activated carbon is shown in Fig. 2. The large increase in adsorbed gas at low relative pressure is a typical Type I isotherm for a microporous solid [46]. The pore size distribution for the activated carbon, also shown in Fig. 2, confirms the microporous nature of the carbon, with a single peak at 0.7–0.8 nm. The gradual uptake from a relative pressure of around 0.2 indicates some mesopores, although as seen in the pore size distribution, these do not contribute greatly to the specific surface area of the carbon.

Due to the microporous nature of the carbon, the BET specific surface area was calculated by using data from the relative pressure range 0–0.08, such that the value $Q(P_0 - P)$ increased with relative pressure P/P_0 (where Q is the volume of gas adsorbed, P is the measured pressure and P_0 is the

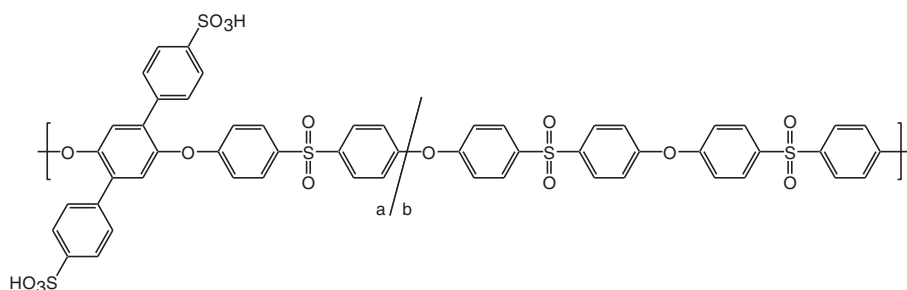


Fig. 1. Repeating unit of the random copolymer. RCP 1: a = 6, b = 4; RCP 2: a = 5, b = 5; RCP 3: a = 4, b = 6.

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