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Effect of a semiconductor dielectric coating on the salt adsorption capacity of a porous electrode in a capacitive deionization cell

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ABSTRACT

A theoretical model was developed to study the effect of an additional dielectric coating on the conducting electrodes in a capacitive deionization cell. The electric field generated at the electrode surface and its distribution was quantitatively investigated for coating materials with different dielectric properties. The model shows that a nanostructured low dielectric and intrinsically polar material like zinc oxide (ZnO) is well suited to enhance the efficiency of capacitive desalination. Electrodes formed by ZnO nanorods coated on conducting electrodes of activated carbon cloth (ACC) were subsequently fabricated and its desalination parameters were studied using a 17 mM (1000 ppm) NaCl solution as the feed at an applied potential of 1.6 V DC. The composite ZnO nanorod coated electrodes improved salt removal efficiency by 40%, and adsorbed 35% of the salt in a single pass experiment, at a charge efficiency of 80% and an electrosorptive capacity of 8.1 mg/g of the electrode. A simultaneous increase in the ion adsorption rate led to a ~40% reduction in the energy consumption as compared to an uncoated ACC electrode.

1. Introduction

Renewed interest in capacitive deionization (CDI) has been recently observed both from academia as well as the corporate sectors [1–5]. Low power consumption [3], small footprint and easy portability make capacitive desalination an ideal technology for the removal of salt from remote low salinity brackish water sources [6]. Ideally, a CDI cell comprises of two large surface area conducting electrodes like activated carbons, separated by a small gap through which saline water flows. A DC potential of generally < 2.0 V is applied between the two electrodes, generating an effective localized electric field at each electrode that serves as the driving force for assisted ion adsorption [7]. The electrode with the positive potential attracts anions while the electrode with negative or reference potential attracts the cations, leading to the adsorption of the ions on electrode surfaces and its depletion from the source water. To increase the ion adsorption efficiency of an electrode, researchers have mainly focused on new materials [8–11], increased electrode surface area [12–16], surface energy [17,18], addition of ion exchange membranes [19,20] and water flow regimes [21,22] etc. However, an important aspect which has not been given substantial attention is the electric field (e-field) enhancement, especially considering that it is the driving force for ion adsorption and determines the capacitance of the CDI devices [7]. A possible way to increase the e-field at a given applied potential is by the addition of a dielectric material on the activated carbon electrodes. The internal polarization in the dielectric materials enables charge storage as dipoles distributed within the material core and on its surface [7,23]. Each stored charge generates an associated e-field around it and a combination of such charges lead to the magnification of the effective field attracting the ions in the vicinity. The dielectric materials used are generally semiconductor oxide materials [24–31] whose relative permittivity plays a vital role on its charge storage and hence e-field generation capacity. Since the relative permittivity of a material can change with its dimension, especially in the nanoscopic regime [32], morphology and size effects are important considerations. Typical materials

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which have been used as oxide coatings on activated carbons are manganese oxide (MnO_2), titanium dioxide (TiO_2), zinc oxide (ZnO), silicon dioxide (SiO_2), zirconium dioxide (ZrO_2) etc. [27,28,33], but not all lead to an increase in the desalination efficiency [33], suggesting that material chemistry, crystal structure and permittivity can contribute to the polarization. Generally an increase in desalination efficiency with an oxide coating has been attributed to increase in surface area of the electrode [24,25,34] or change in surface zeta potential [31], which are valid, but not the sole reasons for the observed improvement. Ryoo et. al stated a possible increase in localized electric field due to TiO_2 coating on activated carbon cloth (ACC) electrodes [23,33], but to our knowledge a comprehensive study of the effect of different dielectric materials, morphologies and quantitative mapping of the generated field has not been reported.

In this work, we theoretically model the effect of coating activated carbon cloth electrodes with thin films of different oxide materials (TiO_2, ZrO_2, ZnO and SiO_2) based on their dielectric constants. The effect of the coating thickness, morphology and crystal structure on the e-field magnitude and distribution is quantified using a finite element model. Based on the theoretical results, ZnO nanorods (ZnO NR) were used as the dielectric material and ACC electrodes coated with ZnO nanorods were used for desalinating a 17 mM sodium chloride salt solution. The composite ACC-ZnO NR electrodes are shown to be more efficient in terms of desalination efficiency and power consumption, primarily attributed to the increased electric field strength.

2. EXPERIMENTAL SECTION

2.1. Chemicals and substrates

Analytical grade zinc acetate dihydrate ($Zn(CH_3COO)_2{\cdot}2H_2O$), sodium hydroxide (NaOH), absolute ethanol (C_2H_5OH) and hydrochloric acid 34 % (HCl) from MERCK, Germany, Zinc nitrate hexahydrate ($Zn(NO_3)_2{\cdot}6H_2O$) from APS Ajax Finechem, Australia and hexamethylenetetramine ($(CH_2)_6N_4$) from Aldrich, USA were used as received. Activated woven carbon cloth (Zorflex FM-100) with a specific surface area of about 1100 m^2/g [35,36], was cleaned with boiling 2 M hydrochloric acid (HCl) for 12 hours. The woven carbon was dried in a vacuum oven at 150 °C for 12 hours prior to the growth of zinc oxide nanorods on its surface to be used as composite electrodes for desalination.

2.2. Preparation of ZnO nanoparticles and seeding of activated carbon cloth (ACC)

ZnO nanoparticle colloid was prepared by following a previously described method [37,38]. In brief, 4 mM sodium hydroxide was dissolved in absolute ethanol and subsequently added to 4 mM zinc acetate solution (in absolute ethanol) in a controlled manner under continuous stirring. The mixture was hydrolyzed at 60 °C for 2 hours to form ZnO nanoparticles having a diameter of ~8–10 nm. ACC substrates were subsequently dipped into the nanoparticle colloid for 30 minutes, after which they were dried in an oven at 95 °C for a further 30 minutes. The above steps were repeated twice to get a uniform density of nanoparticle seeds on the ACC surface.

2.3. Hydrothermal growth of ZnO nanorods

ZnO nanorods were hydrothermally grown from the seeded ACC substrates at 90 °C for 10 hours in a 20 mM equimolar solution of zinc nitrate hexahydrate and hexamethylenetetramine, replenished every 5 hours.[39] Sodium hydroxide solution was added to adjust the initial pH of the growth solution to 6.8. After nanorod growth, ACC substrates were thoroughly rinsed with deionized water (DI) and annealed at 150 °C for 1 hour in air.

2.4. Characterization

Morphology of ZnO coated ACC electrodes were characterized by JEOL JSM-6301F field emission scanning electron microscope (FESEM) working at 20 kV. Conductivity profile during the desalination experiments were measured using eDAQ ET916 online conductivity probe with a cell volume of 93 μl. The conductivity probe was coupled to an online single channel conductivity isopod (EPU357) incorporated with PodVu software for real time conductivity recording. Cyclic voltammetry and electrochemical impedance spectroscopy (EIS) measurements were carried out in Gamry Interface 1000 electrochemical system. The electrolyte used was 0.5 M NaCl solution filled into a three-electrode system: Platinum wire as counter electrode, Ag/AgCl as reference electrode and ZnO nanorods coated ACC as working electrode. Specific capacitances of the electrodes were calculated by integrating the area under the cyclic voltammetry (CV) curves as shown in Eq. (1).

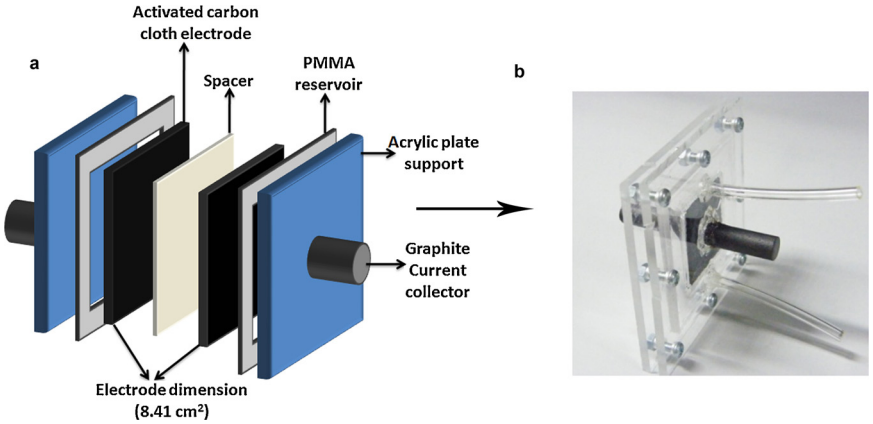

Fig. 1. (a) Schematic representation of the CDI cell comprising the PMMA reservoir and activated carbon cloth electrodes and (b) image of fabricated CDI cell.