



Improved desalination by zinc oxide nanorod induced electric field enhancement in capacitive deionization of brackish water



Karthik Laxman^{a,b}, Myo Tay Zar Myint^a, Rashid Khan^c, Tasneem Pervez^c, Joydeep Dutta^{a,*}

^a Chair in Nanotechnology, Water Research Center, Sultan Qaboos University, PO Box 33, Al-Khoudh, Muscat, 123, Oman

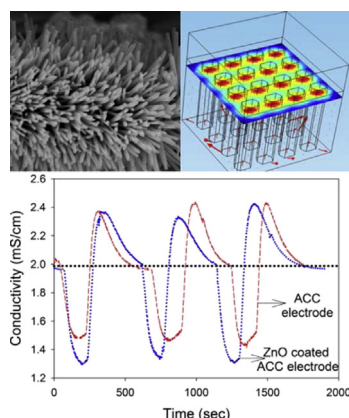
^b Department of Electrical and Computer Engineering, College of Engineering, Sultan Qaboos University, Al-Khoudh, Muscat, 123, Oman

^c Department of Mechanical and Industrial Engineering, College of Engineering, Sultan Qaboos University, Al-Khoudh, Muscat, 123, Oman

HIGHLIGHTS

- Theoretical study of increase in capacitance with metal oxide (ZnO) semiconductor
- Facile growth of ZnO nanorods arrays on CDI electrodes as proof of principle
- Demonstration of the enhancement in ACC capacitance
- Marked reduction in power consumption and improvement in charge efficiency
- 30% higher specific salt adsorption capacity (mg/g) was achieved.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:

Received 1 October 2014

Received in revised form 1 December 2014

Accepted 18 December 2014

Available online xxxx

Keywords:

Electric field

Capacitive deionization

Zinc oxide

Activated carbon cloth

Finite element analysis

ABSTRACT

Ion adsorption in capacitive deionization is a function of the electric field strength present at the electrode surface. We show enhancement in the electric field strength by coating activated carbon cloth (ACC) electrodes with zinc oxide (ZnO) nanorods, where the effective field was shown to vary with respect to the length, diameter and proximity of the coated ZnO nanorods. Deionization of a 17 mM NaCl solution in a single pass experiment using the composite electrodes showed a desalination efficiency of 35%, a 40% improvement as compared to plain ACC electrodes. The composite electrodes also desalinated at a charge efficiency of 78% with a salt uptake of 7.7 mg/g of the electrode. An enhancement in the ion adsorption rate led to a 30% reduction in the energy consumption per mole of salt removed for the desalination process. A theoretical model showing further enhancement in the desalination efficiency by reducing the diameter of the rods is also discussed.

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1. Introduction

In recent years, extensive extraction of groundwater has led to seawater intrusion especially in the arid areas, making the fast depleting freshwater sources brackish and unsuitable for consumption. The use of traditional desalting methods like reverse osmosis (RO) or multi stage

* Corresponding author.

E-mail addresses: dutta@squ.edu.om, nanosqu@gmail.com (J. Dutta).

flash (MSF) is not economically viable for the remote and low salinity nature of these sources, necessitating the need for new portable, low energy desalting techniques, where capacitive deionization (CDI) has shown promise [1–4]. CDI works on the principle of an applied electric potential mediated surface ion adsorption [5–8], where the electrode surface area, point of zero charge of electrode material [9–12], localized pH changes [13], charge and size of the ion [14], salinity of the electrolyte [15], flow rate and applied potential [16] can affect the efficiency of desalination. The magnitude of the applied potential can substantially affect the ion removal capacity, as it is directly proportional to the associated electric field, which is the driving force for surface ion adsorption [17]. From electrostatics, we know that electric field can be expressed as the ratio of force to charge on the electrode. Thus the force available for ion adsorption is directly proportional to the applied potential and the charge stored or capacitance of the electrode. A large capacitance leads to the development of a strong interfacial electric field, which acts to attract/repel ions with opposite/like polarity in its vicinity, desalting the feed water in the process. CDI devices traditionally use carbon based materials due to their inertness, high surface area, conductivity and low fabrication costs [18]. Among them, electrically conducting activated carbon cloth (ACC), which has a high surface area and is easy to handle proves to be ideal for application as electrodes in a CDI cell [19–21], where they have demonstrated to be effective in desalinating domestic waste-water [22]. The drawback of conductive electrodes like ACC is that their low resistance to charge transfer from the electrode to the electrolyte (polarization resistance 'R_p') reduces their capacitance, leading to a reduction in the electric field and hence the salt adsorption capacity of the electrode. A possible way to improve the material 'R_p' which will enhance charge storage and capacitance is by coating it with a dielectric material, which can enhance charge storage through self-polarization. Each charge stored would lead to the creation of an associated electric field, which can be neutralized by attracting ions from the vicinity. This is analogous to increasing the salt adsorption capacity, attributed primarily to an increase in the capacitance and electric field strength due to the addition of a dielectric layer.

Previous studies have shown that coating the ACC electrode surface with high dielectric constant titania nanoparticles can enhance the capacitance and resulting desalination efficiency attributed to localized electric field generation [20]. Another semiconductor which has shown promise is zinc oxide (ZnO), which has been used considerably in solar cells [23–26], photocatalysis [27–29], gas sensing [30], field emission [31] etc. ZnO is a wide band gap semiconductor with a bulk dielectric constant of ~8.5 and is inherently n-type in nature [32]. It can be grown on a variety of surfaces [33–36], thus giving flexibility of the base electrode material to be used. Additionally, ZnO can be grown in various shapes and morphologies like nanorods (NR), nanotubes, nano-needles etc. [37], which can lead to an increase in the effective surface area of the electrode. Finite element models have shown that the electric field can be generated uniformly along a nanorod surface, which can significantly increase the electrode capacitance and efficiency of desalination [31,38].

In this work we coated ACC electrode surface with ZnO nanorods and quantified the capacitance mediated electric field generated at the ZnO nanorod surface with a finite element model. The model is used to predict the field strength for different lengths, diameters and surface coverage ratios. ZnO nanorod coated ACC electrodes were subsequently fabricated and tested for ion adsorption capacity in a flow through CDI cell. The composite electrodes were shown to be more efficient with respect to energy consumption, charge efficiency and desalination efficiency, attributed to the well distributed and enhanced electric field at the nanorod coated ACC electrode surface.

2. Experimental

2.1. Chemicals and substrates

Analytical grade zinc acetate dihydrate (Zn (CH₃COO)₂·2H₂O), sodium hydroxide (NaOH), absolute ethanol (C₂H₅OH) and hydrochloric

acid 34% (HCl) from MERCK, Germany, zinc nitrate hexahydrate (Zn (NO₃)₂·6H₂O) from APS Ajax Finechem, Australia and hexamethylenetetramine ((CH₂)₆N₄) from Aldrich, USA were used as received. Activated woven carbon cloth (Zorflex FM-100) with a specific surface area of about 1100 m²/g [39,40], was cleaned with concentrated 2 M hydrochloric acid (HCl) heated to 115 °C for 12 h. The woven carbon was dried in a vacuum oven at 150 °C for 12 h 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 [41,42]. Briefly, 4 mM sodium hydroxide in absolute ethanol was added in a controlled manner to 4 mM zinc acetate solution (in absolute ethanol) under continuous stirring. The solution mixture was hydrolyzed at 60 °C for 2 h to synthesize ZnO nanoparticles with the diameter of 6–8 nm. Cleaned ACC substrates were dipped in the ZnO nanoparticle colloidal solution for 30 min and dried in an oven at 95 °C for 30 min. This process was repeated two times to get a uniform density of nanoparticle seeds on the ACC surface.

2.3. Hydrothermal growth of ZnO nanorods

ZnO nanorods were grown on the seeded ACC substrates by hydrothermal process at 90 °C for 10 h in an equimolar solution (20 mM) of zinc nitrate hexahydrate and hexamethylenetetramine, which was replenished every 5 h [43]. In order to adjust the initial pH of precursor solution, sodium hydroxide solution (pH ~ 12) was used. Following the hydrothermal growth of ZnO nanorods, the ACC substrates were thoroughly rinsed with deionized water (DI) and annealed in air at 150 °C for 1 h.

2.4. Characterization

The surface morphology of ZnO coated ACC electrodes was characterized by JEOL JSM-6301F field emission scanning electron microscope (FESEM) working at 20 kV. Conductivity measurements were carried out using eDAQ ET916 online conductivity probe with a cell volume of 93 μl. This was coupled to a conductivity isopod (EPU357) with single channel PodVu software for real time recording of the changes in conductivity. Cyclic voltammetry measurement was carried out using 0.5 M NaCl solution in Gamry Interface 1000 electrochemical cell with 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. (3):

$$C_s = \int_{E_1}^{E_2} \frac{i(E)dE}{[2(E_2 - E_1)mv]} \quad (3)$$

where, 'C_s' is the specific capacitance, 'E₁' & 'E₂' are the limits of the applied potential, 'm' is the mass of electrode, 'v' is the scan rate (mV/s) and 'i(E) dE' is the power delivered during the scan.

Active surface area measurements were conducted using NMR relaxation technique in a Xigo Nanotools with water as the solvent. In this system we can probe the spin magnetic moments of hydrogen nuclei in pore fluids in response to a perturbation in the applied static magnetic field. The perturbation changes the total nuclear magnetization, whose relaxation back to equilibrium with respect to time is noted (comprising of longitudinal relaxation time T₁ and the transverse relaxation time T₂). The T₂ relaxation time of the solvent is extracted and analyzed by Acorn area software to interpret the surface area of the electrode (using the specific surface relaxivity of activated carbon κ) in contact with water. Energy requirements were calculated by

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