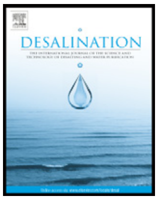
Desalination 286 (2012) 108–114

Contents lists available at SciVerse ScienceDirect

Desalination

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



Preparing MnO_2/PSS/CNTs composite electrodes by layer-by-layer deposition of MnO_2 in the membrane capacitive deionisation

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ARTICLE INFO

Article history:
Received 5 August 2011
Received in revised form 24 October 2011
Accepted 1 November 2011
Available online 25 November 2011

Keywords:
PSS
MnO_2
Layer-by-layer deposition
Composites
MCDI

ABSTRACT

It is of great interest to control the pore structure, conductivity and electrochemical activity properties of electrode materials, as their capacitance in the electrosorption process is determined by these properties. These properties can be modified effectively during the synthesis process. The layer-by-layer deposition approach was employed to prepare a manganese oxide (MnO_2)/carbon nanotubes (CNTs) composite. In this study, Polystyrene Sodium Sulfonate (PSS) facilitated the dispersion of CNTs and even growth of MnO_2. The resulting composite material was used for electrodes in the membrane capacitive deionisation (MCDI) process and a high salt removal efficiency of 96.8% was achieved, with an ion adsorption capacity of 80.4 μmol/g of MnO_2/PSS/CNTs electrode material. Conversely, a MnO_2/CNTs composite that was prepared using a hydrothermal synthesis process did not show such excellent advantages.

1. Introduction

Since the concept of capacitive deionisation (CDI) technology was introduced many decades ago, many studies have been carried out, with results showing that this technology has several advantages over the conventional desalination processes, such as thermal evaporation, reverse osmosis, electrodialysis or ion exchange [1,2]. The basic principle of CDI is similar to the electric double-layer capacitor: the ions are adsorbed and stored in electrical double layers (EDLs) when the electrodes are charged, then the ions are desorbed when the potential voltage is removed. However, the ion adsorption–desorption occurring simultaneously in the electrode pore volumes can result in reduced desalination efficiency [2,3,4]. Therefore, the membrane capacitive deionisation (MCDI) process, in which ion-exchange membranes are used, was introduced to enhance ion selectivity. MCDI has been proven to significantly increase desalination efficiency [2,5,6].

The development of novel and suitable materials for use as electrodes in CDI/MCDI is an important aspect in the advancement of this desalination technology. Recently, carbon materials such as activated carbon (AC) and its composite, activated carbon cloth (ACC), its titania modified material, carbon aerogel and carbon nanotubes (CNTs), and its carbon nanofibre (CNF) composites, ordered mesoporous carbon (OMC), graphene and MnO_2/nanoporous carbon composite [7], have been studied as electrode materials for CDI. In the case of MnO_2/CNT composite, MnO_2's high electrochemical capacitance, low cost and environmentally benign nature combines with the advantage of carbon material, and makes it a popular candidate as high performance electrode material in the application of supercapacitors and Li-ion batteries [8,9,10]. For composite material, there are various ways to hybridise different materials to achieve synergistic properties or functionalities, such as in situ deposition [11,12,13], hydrothermal-assisted deposition [14], ultrasonic assisted wet-chemistry method [15], electro-deposition [16,17,18], wet chemical deposition [12,19] and layer-by-layer (LBL) deposition [20]. The layer-by-layer deposition method is governed by electrostatic interactions between species bearing opposite charges. In term of metal and metal oxide (such as MnO_2, TiO_2) that bear positive charges, anion surfactant polystyrene sodium sulfonate (PSS) with negatively charged functional heads ($-SO_3^-$) was used to provide the electrostatic attraction to bind positive metal ions, as well as to disperse the particle suspensions [21,22,20].

In this study, we compared the performance of MnO_2/CNT composites that were synthesised with and without PSS. Both composites were benefited from the MnO_2's extra capacitance, in addition, the use of PSS can improve the deposition of MnO_2. The layer-by-layer deposition of MnO_2 with PSS enables the homogenous dispersal of substrate CNTs in water solutions, while simultaneously providing negative charges on the surface of the CNTs, so that the positively charged Mn cations (Mn^+) can be effectively attached. The well-dispersed PSS led to uniform dispersion and deposition of MnO_2 on the CNTs. These would maximise the advantageous effect of MnO_2. In contrast, MnO_2/CNTs prepared using the hydrothermal direct deposition process without PSS did not show the above advantage.

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doi:10.1016/j.desal.2011.11.013

This demonstrates that the utilisation of PSS surfactant helped to achieve uniform dispersion of MnO_2 particles on CNTs. This resulted in better connections between MnO_2 and CNTs, thus enhancing the MnO_2's electrochemical activity, as well as the desalination performance.

2. Material and methods

2.1. Material

Double-wall carbon nanotubes (DWCNTs) were purchased from Shenzhen Nanotech Port Co. Ltd (Shenzhen, China). Polystyrene sodium sulfonate (PSS), manganese sulphate and potassium permanganate were procured from Sigma-Aldrich Co. Ltd.(Adelaide, Australia). The cation and anion exchange membranes were obtained from Membrain s.r.o. (Stráž pod Ralskem, Czech Republic). Deionised water was used for all experiments.

2.2. Preparations of MnO_2/CNT with or without PSS

The preparation schematic is illustrated in Fig. 1. 0.1 g DWCNTs were dispersed in 100 mL PSS solution (10 wt.%). The solution was mixed homogenously for one night using a magnetic stirrer, followed by ultrasonic vibration for three hours. These methods allowed sufficient time for the PSS to envelope the DWCNTs and form a negatively charged layer, which stabilised the nanotubes in water through static charge repulsion [20]. 0.57 mL of 0.01 M manganese sulphate ($MnSO_4$) solution was added to the above solution, which was again stirred vigorously for three hours. The well-dispersed, negatively charged PSS layer can attract the Mn^{2+} effectively and facilitate the manganese oxide in spreading uniformly, as well as hindering agglomeration. The resulting powders were obtained by filtering the mixture and heating at 200 °C for six hours. This sample was denoted as C–P–Mn. It was hypothesised that the uniform deposition of manganese oxides on the well-dispersed and negatively functionalised CNT surfaces would contribute to the improvement in the capacitance of the composite materials [20].

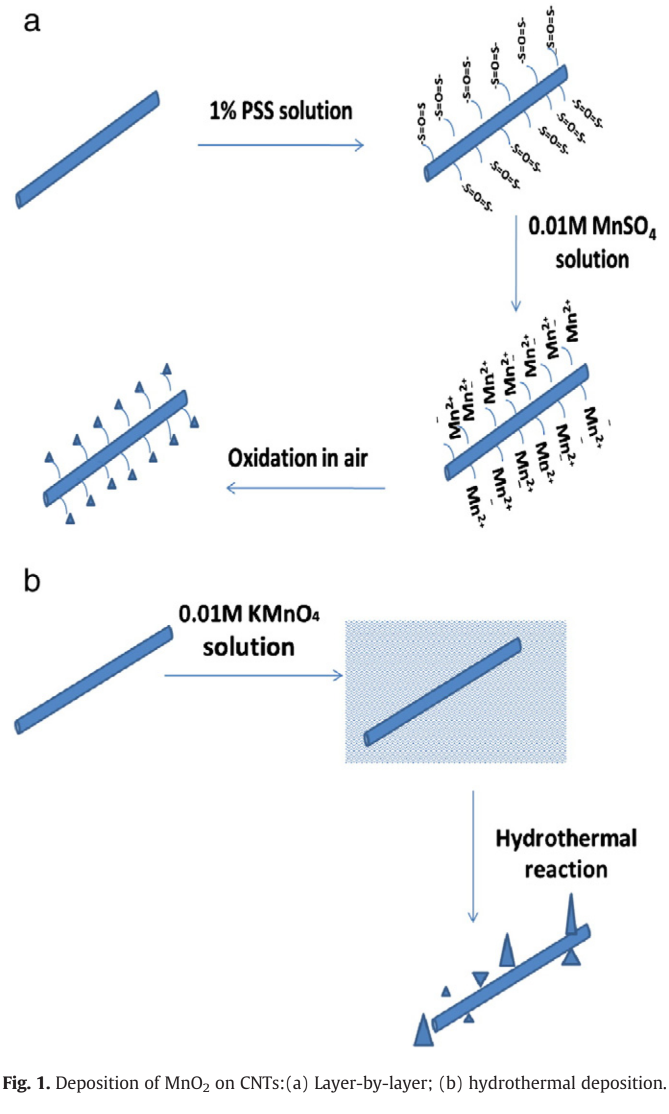

Fig. 1. Deposition of MnO_2 on CNTs:(a) Layer-by-layer; (b) hydrothermal deposition.

Sample C–Mn was prepared without PSS. 0.1 g of DWCNTs was dispersed in 100 mL of water and 0.57 mL of 0.01 M $KMnO_4$ solution was added and mixed homogenously. The whole mixture was poured into the hydrothermal reactor and heated at 200 °C for six hours. The resulting powder was collected after filtering, washing and drying. It was denoted as C–Mn. The DWCNTs were washed with nitric acid before they were used to remove any remaining metal catalyst from synthesis. This was denoted as sample C.

2.3. Material characterisations

Nitrogen adsorption–desorption isotherms were performed on a BELSORP-mini measuring unit (Particle Test Pty Ltd, Japan) at −196 °C (77 K). The specific surface areas (S_{BET}) and pore size distribution were obtained from the Brunauer–Emmett–Teller (BET) and Barrett–Joyner–Halenda (BJH) methods, respectively [23]. Transmission electron microscopic (TEM) images were taken with a Philips CM200. The sample preparation was accomplished by suspending the materials in ethanol and dispersing them on a holey copper grid. X-ray photoelectron spectroscopy (XPS) analysis was performed using a SPECS SAGE XPS with a Phoibos 150 analyser and an MCD-9 detector. The surface atomic concentration of the particles was then determined using CasaXPS software. Fourier transform infrared spectrometry (FTIR, PE, Spectrum 100, Australia) was used to examine the functional groups at various wavelength ranges. Electrical resistance was measured by a four-point probe metre (SX1944, Suzhou Telecommunication Instrument Factory, Suzhou, China).

2.4. The cyclic voltammetry and capacitance measurements

The cyclic voltammetry and capacitance measurements were conducted on an Autolab PGSTAT128N instrument (Metrohm Autolab B.V., France) using a three-electrode cell system. The working electrodes were prepared by pressing a mixture of active material (72 wt.%), graphite (20 wt.%) and polytetrafluoroethylene (PTFE) (8 wt.%) slurry to the graphite paper. The mass loading density was around 6 mg/cm^2. A glassy carbon (GC) and a saturated KCl electrode were used as counter and reference electrodes, respectively. The electrolyte was 1 M NaCl aqueous solution and the sweep potential range was fixed at −0.4 to 0.6 V versus the saturated KCl electrode. The capacitance was calculated from the CV curves by the following equation [13,24]:

$$C = \frac{i * \Delta t}{m * \Delta V} \tag{1}$$

in which C is specific capacitance (F/g), i is the charge–discharge current, Δt is the discharge time, m is the mass of active material and ΔV is the voltage differences.