



Carbon nanotube cloth for electrochemical charge storage in aqueous media

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ARTICLE INFO

Keywords:

Carbon nanotubes
Anodic activation
Supercapacitors

ABSTRACT

We report the study of recharging behavior of CNT cloth material, which allows a large-scale and relatively cheap fabrication, as well as rather simple electrode design. Oxidative chemical purification procedure is applied prior electrode preparation to decrease the content of iron, which served as the catalyst for CNT fabrication. We demonstrate that this procedure, as well as anodic oxidation, results in the increase of CNT specific capacity in both alkaline and acidic aqueous solutions. Recharging rate is less sensitive to oxidation and remains fast enough: at 1 V/s scan rate the capacities in both acidic and alkaline solutions are close to 25 F/g. These characteristics allow to consider CNT cloth as a future stable backbone for materials of aqueous supercapacitors.

1. Introduction

Current supercapacitor research involves a wide variety of conducting oxides and polymers operating mostly on the basis of reversible intercalation of charged species [1]. These materials demonstrate high capacities, but relatively slow recharging rates. Their additional drawbacks are technological complexity and degradation risks. Therefore carbons, with their fast interfacial discharge and availability of numerous highly dispersed modifications, are still the most demanding materials for supercapacitors [2,3].

The efforts of carbon community are concentrated either on the precise design of new (more and more exotic) nanomaterials [2,3], or on advanced electrode architectures [4,5]. Among well-ordered carbon nanomaterials, carbon nanotubes (CNT) play a special role because of a wide variety of available technologies and possibility to design the electrodes with specific CNT alignment. Looking for a highly conductive CNT network with highly accessible specific surface area and optimal pore size distribution, people are inventing complex technologies of CNT immobilization on various supports [4,5], which are surely of great importance for high-tech micro-capacitors. Another strategy applied in this work consists in design of well-structured unsupported CNT-based material and its subsequent technologically simple immobilization. An important advantage of this strategy is higher mechanical stability of CNT-containing electrodes, which typically plays a crucial role in supercapacitor stability.

We report below the study of recharging behavior of the CNT cloth material with satisfactory electrical and unique mechanical properties [6,7]. This material allows a large-scale and relatively cheap fabrication. A simple chemical purification procedure is applied prior electrode preparation to decrease the content of iron catalyst which unavoidably remains in the samples after their synthesis, mostly in encapsulated form. We demonstrate that this procedure, as well as subsequent anodic oxidation treatment, results in the increase of capacity due to formation of the rechargeable O-containing functional groups at the CNT surface.

2. Experimental

The cloth was fabricated as described in Ref. [6]. To delete iron residue and the amorphous carbon, the material was heated in air (440 °C) for 5 h, treated by concentrated HCl for 48 h (25 °C), thoroughly washed, and then twice treated by new portions of concentrated HCl for 2–3 h. After final washing the samples were dried in air (60–80 °C) for 4 h. In what follows we present the data for both as-fabricated (**af**) and purified (**p**) materials.

BET surface areas (Quantachrome NovaWin) were ~200 and ~140 m²/g for **af** and **p** clothes respectively. BET data for the samples after electrochemical treatment were not collected because of too low weight.

Material characterization included also registration of SEM images (JEOL JSM-7600F), XPS (VersaProbeII, ULVAC-PHI), and vibrational

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<https://doi.org/10.1016/j.jelechem.2018.09.004>

Received 5 May 2018; Received in revised form 2 September 2018; Accepted 3 September 2018

Available online 04 September 2018

1572-6657/ © 2018 Published by Elsevier B.V.

spectra. The latter were collected in 100–4000 cm^{-1} interval using Raman (RENISHAW inVia Raman Microscope, up to 270 cm^{-1}) and IR (VERTEX 80v). XPS spectra were interpreted according to approach proposed in Refs [8, 9].

For electrochemical experiments, the cloth sample of 0.15–0.5 mg weight (the thickness up to $\sim 50 \mu\text{m}$, and geometric area $\sim 0.2 \text{cm}^2$) was fixed on the mirror-like polished (1, 0.3 and 0.05 μm alumina particles size) glassy carbon support with a droplet of ionomer solution (Nafion for experiments in acid, AS4 (Tokuyama Corp.) for experiments in alkaline solution). The amount of ionomer was ca. 1 $\mu\text{g}/\text{cm}^2$ of geometric surface area. Samples were weighted with the accuracy of 0.01 mg (GR-202, A&D Co., LTD). At least 3–4 experiments with the samples prepared from each exfoliated layer were performed to check the reproducibility. For the layers thicker than 100 μm , the capacity per mass started to decrease, indicating mass and/or charge transport problems in the thick porous layers.

0.5 M H_2SO_4 solution was prepared from concentrated H_2SO_4 (Merk), and 1 M NaOH solution was prepared from the 50 wt% NaOH (Sigma-Aldrich). All solutions were deaerated by means of bubbling pure argon for 1 h before each electrochemical experiment.

Electrochemical cell with unseparated working and counter electrodes was applied to avoid additional Ohmic loss. Counter electrode was Pt foil, and the reference electrodes were AgCl/Ag (sat) and HgO/Hg for experiments in acidic and alkaline solutions respectively. All potentials were recalculated to RHE scale.

To register cyclic voltammograms at 0.003–1 V/s scan rates in the interval 0.05–1.13 V RHE, Autolab potentiostat was applied. In the majority of experiments we applied the staircase scan mode, which is more close to the multistep recharging modes, but can result in the underestimate of capacity at low scan rates. In addition we tested scan rate dependence using the linear scan mode and confirmed that the data for fast recharging are independent on details of scanning regime.

3. Results and discussion

Typical stabilized cyclic voltammograms of **af** and **p** cloth are presented in Fig. 1. They demonstrate the reversible recharging in a wide range of scan rates, and the capacities per mass are about 2–2.5 times higher for **p** samples, despite of their lower specific surface area. The specific capacities per real surface area are ~ 5 and $\sim 17 \mu\text{F cm}^{-2}$ for **af**

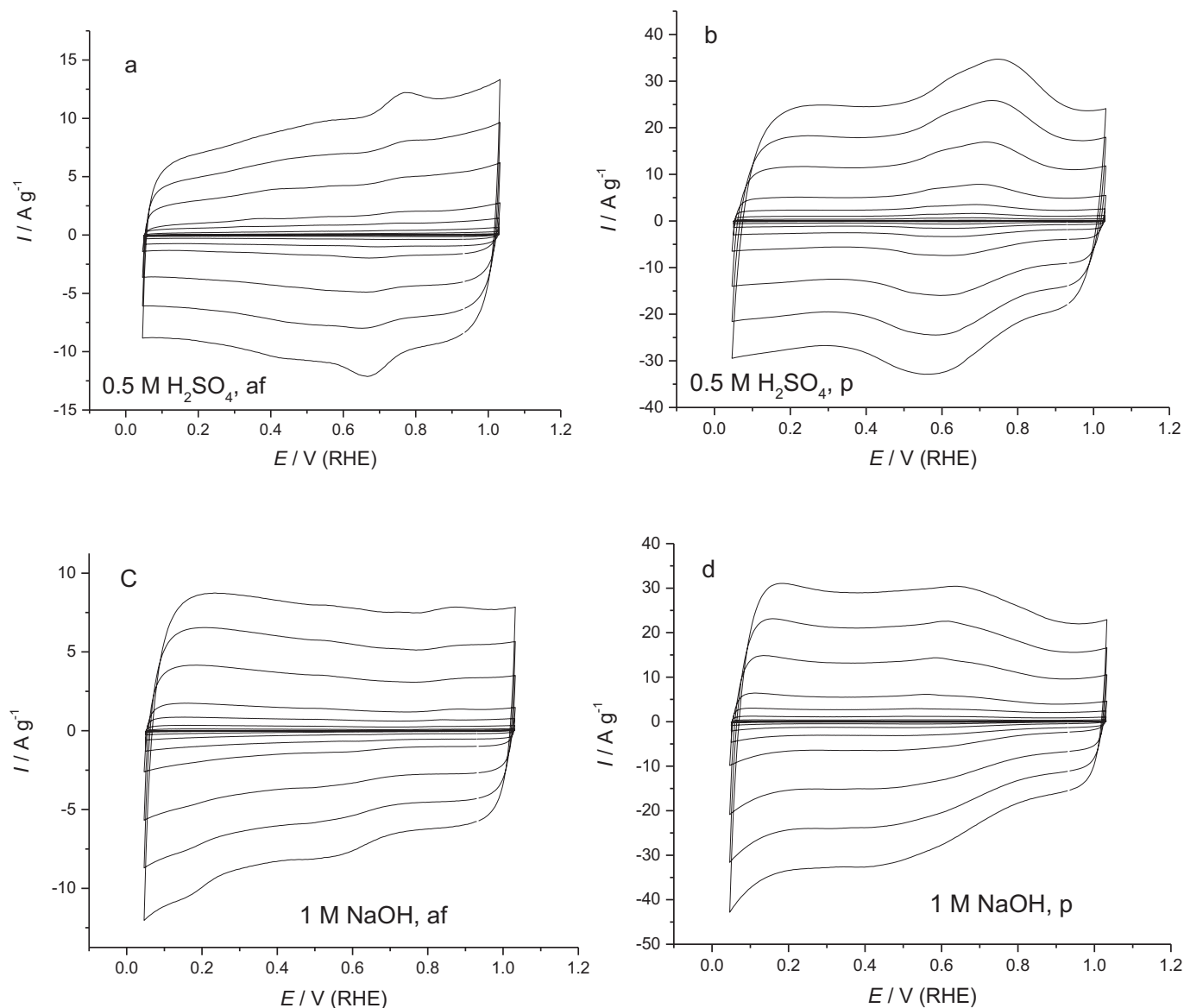


Fig. 1. Stabilized cyclic voltammograms registered in 0.5 M H_2SO_4 (a, b) and 1 M NaOH (c, d) for **af** (a, c) and **p** (b, d) samples with various scan rates (3, 5, 10, 25, 50, 100, 250, 500, 750, 1000 mV/s).

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