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Short communication

Charging and discharging of the electrochemically swelled, aligned carbon nanotube fibers

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ABSTRACT

Aligned carbon nanotube fibers are macroscopic materials with remarkable properties, such as high specific strength, stiffness, extreme flexibility as well as electrical and thermal conductivity. It is demonstrated that when subjected to negative potentials, these structures undergo the process of swelling in which the increase of their external dimension is observed. Swelling is believed to be caused by cation insertion in the process similar to intercalation. The efficiency of swelling was determined both in organic and aqueous solutions of different pH. Chronocoulometry was used as the technique to monitor the charging-discharging processes of swollen ACNT fibers in a presence of different electrolytes, i.e. LiCl, NaCl and KCl. The possibility of performing the charging-discharging cycles multiple times indicates that the swollen ACNT fibers can be considered as an advantageous material for electrodes in ion batteries and supercapacitors.

1. Introduction

The development of aligned carbon nanotubes, ACNTs, allows one to expand the scope of their application beyond the nanoscale into the macroscale [1]. ACNTs have characteristic structure in which CNTs are locally roughly aligned in bundles. Since each CNT travels between different bundles, the material is entangled. Synthesis-induced alignment technologies enable a formation of the ACNT fibers of tailored length, fiber density, structure and nanotube alignment [2–3]. Continuous ACNT fibers exhibit remarkable properties, such as high specific strength, stiffness, extreme flexibility as well as electrical and thermal conductivity, making them a useful standalone macroscopic material [4]. The high-performance ACNT fibers have been successfully applied as wires in electrical transformers [5–8] or yarn supercapacitors in textiles and microdevices [9].

Due to their filamentous morphology, CNTs are characterized by high surface area and porosity. This suggests that they can be used as alternative material for graphite in lithium-ion batteries [10]. The most essential process occurring in Li ion battery is the intercalation of lithium into graphite electrode [11–12]. CNTs have been already demonstrated to be able to accumulate high Li^+ concentrations, especially in a form of composite materials, e.g. CNT/Sn_2Sb nanocomposites [13] or nitrogen-rich CNT/amorphous carbon composite [14].

In this paper, it is shown that during the application of sufficiently negative potential, the ACNT fibers undergo the process of swelling. Together with the increase in their external dimensions, the active surface area is expanded and sensing parameters of ACNTs are improved. The process of swelling of ACNT fibers has already been observed by our group [15], however, it is the first preliminary report in which its origin has been analyzed. Since KOH and HCl are known as activating agents for carbon materials [16–18], these electrolytes have been chosen to verify the influence of pH on the efficiency of swelling. Chronocoulometry was used to monitor charging–discharging processes of swollen ACNT fibers in the presence of different electrolytes, i.e. LiCl, NaCl and KCl.

2. Experimental

Potassium chloride (Sigma, 99%), lithium chloride (Sigma, 99%), sodium chloride (Sigma, 99%), hydrochloric acid (Avantor, 0.1 M standard solution), potassium hydroxide (Avantor, 0.1 M standard solution), potassium hexacyanoferrate(II) trihydrate (Sigma, 98.5%), tetrabutylammoniumhexafluorophosphate (Aldrich, 98%), and ferrocene (Acros Organics,98%), were used as received. Type 1 (R > 18 M Ω cm^{-1}) deionized water and acetonitrile (Aldrich, 99.8%) were employed as solvent.

Aligned multi-walled CNTs were obtained by direct-spinning in the chemical vapor deposition (CVD) reactor. Hydrocarbon feed (CH_4) was decomposed in the presence of catalyst (ferrocene) and promoter (thiophene) at 1200 °C under hydrogen atmosphere. As-formed CNTs were collected in the form of ACNT films onto PET sheets as published elsewhere [2–3]. Aligned CNT films supported by PET foil were cut

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into rectangular shapes (16 × 10 mm), PET support was removed and the resulting ACNT self-standing films were wetted with acetonitrile. This procedure led to the formation of the ACNT fibers with a diameter of 0.15 mm.

The electrochemical cell was equipped with the ACNT fiber working electrode, glassy carbon rod auxiliary electrode and Ag/AgCl (in aqueous media) or Ag wire (in organic medium) reference electrode. One end of ACNT fiber was held by a copper foil clip, which was connected with a crocodile clip to the potentiostat. The electrochemically induced swelling of the ACNT fiber was realized by application of constant potential (Solartron Analytical 1287 Electrochemical Interface) in 0.1 M electrolyte solution (KCl, LiCl, NaCl, $LiClO_4$ or Bu_4NPF_6, respectively). SEM images (Phenom X Scanning Electron Microscope) were acquired before and after the process of swelling. The quantitative description of swelling effect was reached through the cyclic voltammetry with swollen CNT fibers as working electrodes in 1 mg/ml potassium hexacyanoferrate(II) aqueous solution or 0.1 mg/ml ferrocene acetonitrile solution. Charging and discharging of swollen ACNT fibers were realized by means of chronocoulometry (CH Instruments 620 Electrochemical Workstation) in 0.1 M electrolyte solution (KCl, LiCl, NaCl, $LiClO_4$ or Bu_4NPF_6, respectively).

3. Results and discussion

In aqueous environment, the application of sufficiently low negative potential of an electrode results in water electrolysis and an associated gas bubble evolution. When the tight ACNT fiber is used as working electrode, after a specific time of potential application, the part of fiber immersed in water starts swelling, which results in the expansion of its radial dimension and external surface area several times (Fig. 1a). That new, swollen form of the ACNT fiber appears to be stable, thus no collapse is observed when the material is removed from the solution and dried. For the comparison, porous carbon fibers have been subjected to the same procedure as ACNT fibers. During the process no changes

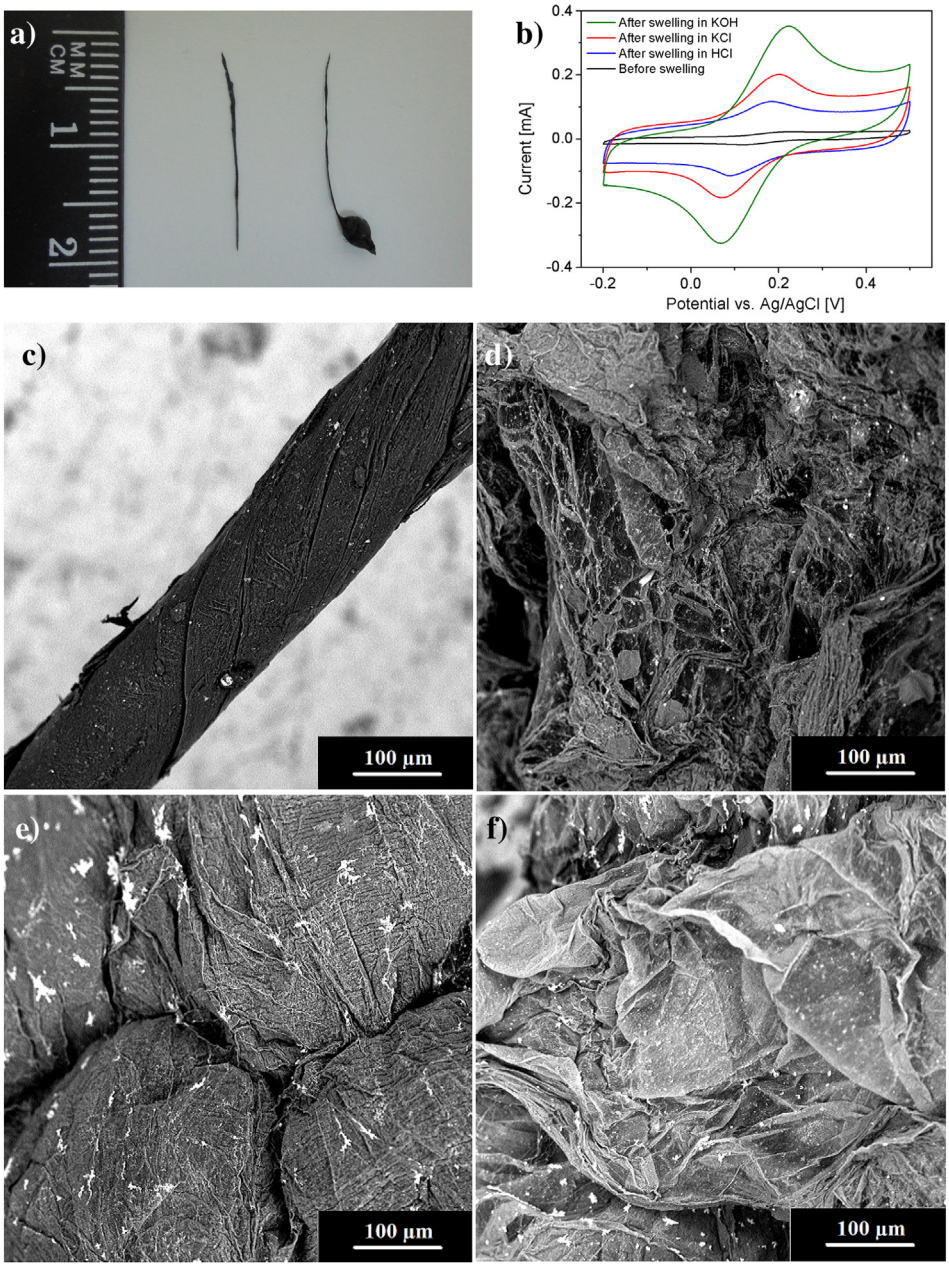

Fig. 1. Photos of unswollen ACNT fibers and fiber swelled in 0.1 M KCl solution for 10 min at −2.0 V vs. Ag/AgCl (a), CVs of $K_4[Fe(CN)_6]$ (b) and SEM images collected for the ACNT fiber working electrode before (c) and after the process of swelling in HCl (d), KCl (e) and KOH (f).