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Carbon nanotube yarns as strong flexible conductive capacitive electrodes

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ABSTRACT

Carbon nanotube (CNT) yarn, consisting of 23 μm diameter CNT filaments, can be used as capacitive electrodes that are long, flexible, conductive and strong, for applications in energy and electrochemical water treatment. We measure the charge storage capacity as function of salt concentration, and use Gouy–Chapman–Stern theory to describe the data. CNT yarn can also be used as conductive scaffold for the application of a porous activated carbon (AC) layer. We show the potential of CNT yarn for the generation of electrical energy from environmental entropy differences, by coating yarn (both with and without AC coating) with ion-exchange membranes (IEMs) and generating power from the salt concentration difference between river water and seawater. The use of flexible and conductive CNT yarns as capacitive electrodes and electrode scaffolds breaks with the paradigm of planar static electrodes, and opens up a range of alternative designs for electrochemical cells with enhanced performance.

Capacitive electrode processes [1–4] play an important role in diverse applications in science and technology, including electrical double layer (EDL) capacitors [5], electrochemical water treatment [6], desalination by capacitive deionization [7–9], and generation of electrical energy, both from salt water concentration differences by the "CapMix" process [10–13], and from the high CO_2 concentration in power plant off-gases [14,15]. In capacitive electrodes, ionic and electronic charge locally charge-compensate in the EDL at the metal/solution interface. Focusing on porous carbon film electrodes as the electron-conducting material, and water as the electrolyte, the EDLs are formed at the carbon/water interface, often inside microporous (activated) carbon materials [8,9]. To obtain a technologically feasible process, ionic and electronic transport resistances must be low. For the aqueous electrolyte, electrodes must therefore be spaced close together, ideally in a high-conductivity solution. To have good electronic transport (low electrical resistance) a high-conductance "backing plate" or "current collector" must be in firm contact with the carbon film electrode. The current collector can be a graphite ("paper") sheet, or solid rods with a diameter of a few mm made from carbon [7] or titanium [11]. These state-of-the-art materials as current collector are thick or not very strong. This hampers the application of novel electrode designs for capacitive electrode processes. For instance, in CO_2 gradient energy harvesting, it would be highly advantageous to have available very long, flexible and thin electron-conducting wires coated with ion-exchange membranes that can serve as capacitive electrodes to be placed in direct contact with the humid CO_2-rich power plant off-gases.

Recently, Behabtu et al. [16,17] described the fabrication of carbon nanotube (CNT) filaments composed of tightly packed and well-aligned CNTs, produced by wet spinning from the solvent chlorosulfonic acid [18] into water or acetone as coagulant. The spinning solution contains liquid crystalline domains [19] in which the individual CNTs are lined up. By sufficiently fast spinning of the drum that collects the filaments, the CNTs in the filament that forms become well aligned [20]. The CNTs are mainly single-walled and double-walled, have an average diameter of 3.2 nm, and lengths between 1 and 20 μm [16]. The CNT filaments are long, strong, thin (diameter usually 23 μm, but down to 10 μm possible), and highly electron-conductive [16]. In a novel development, tens to hundreds of parallel CNT filaments form "CNT yarn".

In this Communication we report on the use of CNT yarn as capacitive electrodes. First we measure the electrical capacity of CNT yarn in aqueous solutions and next we show that CNT yarn can be directly coated with ion-exchange membranes (IEMs), or, first with an activated carbon layer, and then with an IEM. We will report on the use of CNT yarn for the following three objectives: 1. directly as capacitive electrodes, 2. as scaffold for cylindrical carbon film electrodes, and 3. for use in CapMix applications, where we show the generation of electrical energy from bringing a CNT yarn electrode cell pair (with each electrode coated with an ion-exchange membrane) sequentially into contact with river water and seawater.

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Our results highlight the potential of CNT yarns in capacitive electrode processes, moving away from the paradigm of solid planar electrodes, toward novel innovative electrode designs for applications in energy generation and water treatment with a lower environmental footprint and higher energy efficiency. CNT yarns may also be considered as components in Faradaic (porous) electrodes for electrochemical applications such as batteries and fuel cells.

The CNT yarn used in this study is formed of 370 filaments each of a diameter of 23 μm (mass density of the filament 1.3 g/mL). The yarn has a line mass density of 0.193 g/m, an electrical resistance of 29 μΩ·cm, and a diameter after twisting of ~500 μm (1930 dtex, Teijin Aramid, Arnhem, The Netherlands), see Fig. 1. We apply CNT yarn as a capacitive electrode by itself, or as scaffold for the application of an activated carbon (AC) layer and membrane. Two types of CNT yarn membrane-electrode assemblies were produced (the entire assembly abbreviated from this point onward as "electrode"). The first is a two-component electrode, where the CNT yarn is coated directly with either an anion- or cation-exchange membrane. The second type is a three-component electrode, where CNT yarns are first coated with an AC layer, and next with an ion-exchange membrane.

To form the AC layer, a carbon slurry was prepared by ball-milling an activated carbon (AC) powder and binder solution at 450 rpm for 30 min. Prior to making the slurry, the AC powder (DLC Super 30; Norit, Amersfoort, The Netherlands) was dried in an oven at 105 °C overnight to remove absorbed water. The binder solution was obtained by mixing polyvinylidene fluoride (PVDF; KYNAR HSV 900; Arkema Inc., Philadelphia, PA, USA) and 1-methyl-2-pyrrolidone (NMP; Sigma Aldrich Chemie B.V., Zwijndrecht, The Netherlands). CNT yarn is dipped in the slurry solution for 1 min, taken out and dried at 60 °C in a vacuum oven for 24 h to remove any remaining solvent. The average mass of attached carbon material per unit length of yarn was 1.30 g/m, and the AC layer plus CNT yarn weighs 1.49 g/m. The AC layer contains 10 wt% PVDF binder. The ion exchange membrane layers were applied by dip-coating the CNT yarns and the AC-coated CNT yarns in either anionic (FAS solution, 24 wt% in NMP; Fumatech, Bietigheim-Bissingen, Germany) or cationic ionomer solution (FKS solution, 17 wt% in NMP; Fumatech). After dipping, the electrodes were dried according to the instructions from the manufacturer. The membranes have a thickness of ~30 μm [7].

In the CapMix-experiments, aimed at generating electrical energy from river water and seawater, results of which are reported in Fig. 3, a cell pair is formed of an anion-selective electrode and a cation-selective electrode. These two electrodes are formed by coating CNT yarn (or CNT yarn with an applied AC layer) with an anion-exchange membrane or a cation-exchange membrane. This electrode pair is immersed alternatingly in a dilute (1 g/L) and concentrated NaCl solution (30 g/L), while anode and cathode are connected by an external load (electrical resistance). In all cases, the CNT yarn electrodes are positioned parallel to each other (separation 4 mm for Fig. 3a and 0 mm for Fig. 3b). The cell voltage between the electrodes was logged at 0.1 s intervals by an electrochemical analyzer (IviumStat; Ivium Technologies, Eindhoven, The Netherlands). All experiments were performed at room temperature and were repeated at least three times.

To test the integrity of the membranes that are coated on the CNT yarn, we can measure the open circuit voltage (OCV) of the membrane-coated electrode cell pair. In this procedure, the cell pair is equilibrated in a solution with a certain salt concentration, $c_{\infty,1}$ with the electrical circuit shorted; next, the electrical circuit is opened (and will remain so for the rest of the cycles) and the cell pair is immersed in another solution with salinity $c_{\infty,2}$. The OCV that now develops is twice the membrane potential, and given by $\mathrm{OCV} = 2 \cdot p \cdot V_T \cdot \ln(c_{\infty,2}/c_{\infty,1})$, with p the membrane permselectivity and V_T the thermal voltage, ~25.7 mV. A stable membrane potential (unvarying in time) is crucial for extracting energy in CapMix, and gives evidence that the membrane coating fully covers the underlying carbon material without pinholes.

Scanning Electron Microscopy (SEM) pictures of CNT yarn are shown in Fig. 1. Well visible are the individual filaments of 23 μm diameter that form the CNT yarn. A number of 370 filaments are in each cross-section of the yarn. We measure the capacitance of CNT yarn (with and without an additional AC layer) as function of NaCl salt concentration, by stepping up by distinct values the cell voltage between the CNT yarn electrodes, and measuring the current response. The current is integrated with time to obtain the charge. The values of charge in a charging step (increasing cell voltage) and after discharge

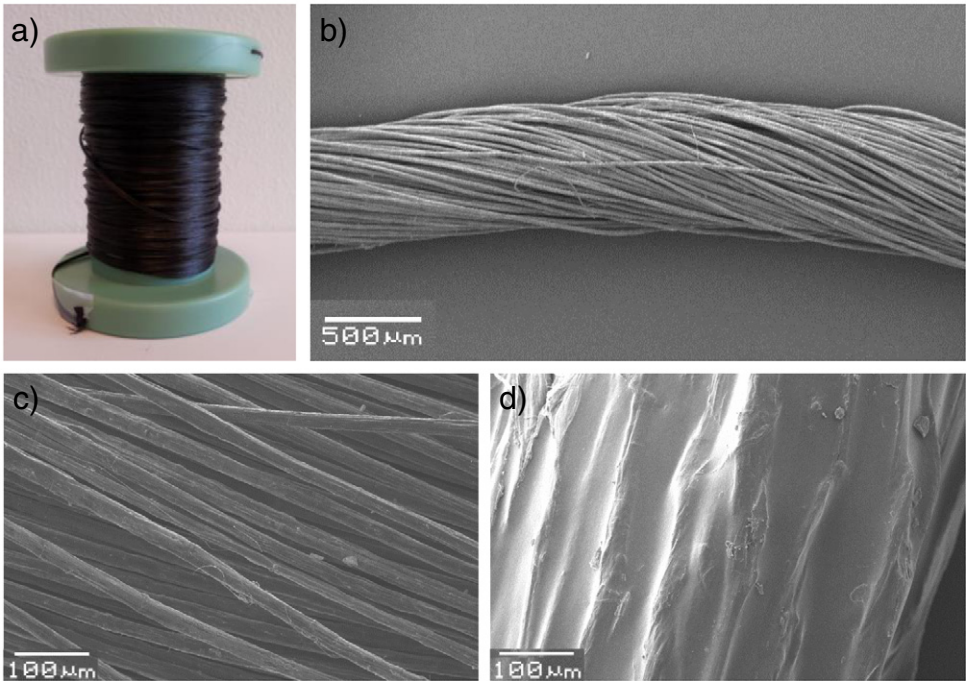

Fig. 1. a) Spool with CNT yarn; SEM images of b) twisted CNT yarn; c) close-up of CNT yarn, showing ~30 filaments; d) CNT yarn covered by cation exchange membrane.