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RAPID COMMUNICATION

Tunable self-discharge process of carbon nanotube based supercapacitors

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Abstract
Self-discharge tuning of supercapacitors is critical in prolonging their energy retention, which would significantly benefit their applications in energy storage if the self-discharge process can be controlled. This report on self-discharge mechanisms of supercapacitors built with single-walled carbon nanotubes (SWNTs) demonstrates the effects of surface chemistry on self-discharge by interfering in the electrostatic interaction between electrolytic ions and the SWNT surface and also explores the tunability of the self-discharge process. Experimental results give decent correlation between the self-discharge performance and the concentration of functional groups attached to the electrode surface. The time the self-discharge process takes to reach half of the charged voltage is extended by ~5 times with functional group decreasing by ~13%. Tuning of the self-discharge rate is therefore feasible for the SWNT supercapacitors by simply trimming the surface chemistry of the nanotubes.

Introduction

Energy storage has permeated our daily life for the last few decades and has become an indispensable part of our daily routine. Though current techniques in energy storage devices such as batteries and supercapacitors (SCs) seem acceptable for daily demands, many improvements are still needed. As an example, electric vehicles (EVs) or plug-in hybrid EVs favor energy-storage devices with high power input/output [1,2], high energy density, and long service lifespan to compete with traditional gasoline cars. On the other hand, current rechargeable batteries have either low power or poor cyclability, not to mention the weighty metal-based electrode materials used [2-4]. Extensive research has been carried out on batteries in order to modify and overcome these drawbacks, but have attained few applicable or effective results.

The capacity fading in lithium-ion batteries is intrinsic and unavoidable as a result of the non-reversibility of lithiation/delithiation [3]. SCs based on electrostatic interaction [5] rather than chemical reaction may solve the cyclability issues of batteries for good, which provide us

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with a possible option to circumvent stability issues facing the development of lithium-ion batteries. Additionally, agreeable energy density of SCs [6-8] ensures adequate energy output. However, the challenge of utilizing SCs as an alternative power source other than batteries lies in their poor energy retention as a result of their fast self-discharge rate [9-11]. There are two fundamental types of self-discharge mechanisms in double-layer SCs [9,10,12,13]. One is with the driving force of an ionic concentration gradient $\partial c/\partial x$ (c is the ionic concentration, varying with the distance x from the electrode/electrolyte interface), and the other is driven by potential field $\Delta U = V$ (V is the voltage held by the SCs). Each energy fading process is named after its driving force, hence, diffusion control self-discharge and potential driving self-discharge. In the diffusion control self-discharge, $V = V_{initial} - m \times t^{1/2}$. In the potential driving self-discharge, $V = V_{intial} \times e^{-t/\tau}$ (m is the diffusion parameter, and τ is the time constant of the self-discharge process; both m and τ indicate the self-discharge rate, and mainly determined by the ionic mobility). Superior energy retention has been attained by the SCs built with activated carbon and 1 M $TEABF_4$(PC), in which the voltage could stay above 1 V for 36 h [9], suggesting feasibility of SCs to replace lithium-ion batteries in certain daily charged applications that require fast charging. In addition to plausible long-term energy retention, it is of the utmost importance to realize tunable self-discharge for SCs that accommodate different requirements for various applications.

For the SWNT-$TEABF_4$ double layer SCs' self-discharge [10], the divided potential driving (DPD) model

$$V \propto V_f e^{-t/\tau_f} + V_s e^{-t/\tau_s} \quad (1)$$

has been proposed and demonstrated its reliability in fitting and characterizing this type self-discharge process, where potential field is the dominating driving force. The causes leading to the DPD self-discharge model instead of a single exponential decay

$$V \propto V e^{-t/\tau} \quad (2)$$

is yet unclear but is predicted to be related to the functional groups attached to the SWNT surface, as the heterogeneity on the surface chemistry would create two types of interactions between ions and electrode at the electrode/electrolyte interface.

In electrochemistry, carbon materials are one of the most common materials under exploitation for rechargeable batteries and for SCs [6,14-17]. Many properties of carbon materials are decisively influenced by chemisorbed oxygen, in the form of various functional groups [18]. By altering the quantities and species of the attached functional groups, properties of carbon materials such as hydrophilicity [19] or electro-conductivity [20,21] can be maneuvered, subsequently manipulating the materials' performance in various areas such as electrocatalysts [22], gas adsorption [23], gas sensing [24,25], thermal sensing, composite strengthening [26-28], and electrochemical performance [14,29].

In this paper, the chemical vapor deposition (CVD) synthesized single-walled carbon nanotubes (SWNTs) are treated to different levels of functionalization, as demonstrated with Raman, X-ray photoelectron spectroscopy (XPS) and thermal gravimetric analysis (TGA). Tracing their self-discharge performance with varied functional groups allows us to gain insight into the triggering effects of surface functional groups on the DPD self-discharge performance and most importantly, to tune the self-discharge process by the means of surface chemistry modification. The functional group-dependent self-discharge indicates the tunability on the self-discharge process of SCs built with differently functionalized single-walled carbon nanotubes (SWNTs).

Materials and methods

CVD synthesis of SWNT macrofilm electrodes

The free-standing SWNT macrofilms were fabricated using a facile chemical vapor deposition (CVD) method [30]. Ferrocene and sulfur were mixed at an atomic ratio of Fe:S=10:1 and served as precursor/catalyst. The reaction took (30-50) min at 1140 °C under a mixture gas flow of argon and hydrogen. To get rid of the impurities such as amorphous carbon and the catalytic iron particles, the SWNT films as collected were then first treated in air at 420 °C for 30 min and then rinsed with hydrochloric acid and copious DI water. After air-drying, the obtained samples were referred as SWNT. The purification process would introduce certain amount of the functional groups on the SWNT films. To obtain the other two film samples with varied contents of functional groups, post-treatments are applied. Heat treatment (400 °C in argon) is applied to reduce functional groups since functional groups tend to decompose at elevated temperatures [14,18,31] and the obtained SWNT film samples are referred to as *r*-SWNT. On the other hand, to increase the number of functional groups, the SWNT films were soaked in the $KMnO_4$ solution [32,33] (0.1 g $KMnO_4$ in 20 mL concentrated sulfuric acid) for 10 min, then followed with hydrochloric acid rinsing and copious DI water wash. The as-treated sample after air-drying was referred as *o*-SWNT. Both reduction and oxidation procedures are carried out in a gentle manner in order to preserves the entangled structures of the SWNT films as an entity (Figure 1).

Characterizations

The SEM images were taken using a JEOL JSM-7400F scanning electron microscope. For XPS, monochromatic aluminum Ka X-rays (1486.6 eV) was applied to excite photoelectrons from the carbon nanotube surface. All spectra were calibrated by setting the C 1s photoemission peak for sp^2-hybridized carbons to 284.5 eV, and were fitted after a Shirley type background subtraction. Raman spectra were collected using a laser with an excitation wavelength of 532 nm. Thermal gravimetric analysis was designed from room temperature to 1000 °C at a heating rate of 2° C min^{-1} under nitrogen protection (60 mL min^{-1}).

Supercapacitor assembly and electrochemical tests

To study the self-discharge, SCs were built with each of the SWNT, *r*-SWNT and *o*-SWNT films as electrodes, which are