Hybrid functional carbon electrodes for supercapacitors

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Abstract
Self-standing hybrid electrodes have been fabricated through the systematic combination of low cost capacitive materials, such as activated carbon (AC), with carbon nanotubes (CNTs) which provide high electrical conductivity and a structural matrix in place of heavy metal collectors. The nanotube matrix proved effective to utilize cheap AC as a capacitive material and dispersion should be the key to improve the performance further.

1. Introduction

Enhancing capacity and power performances of batteries and capacitors, while employing low cost materials and fabrication techniques, has been a frequently studied issue for the past decade. Recently, single-wall CNTs (SWCNTs) are extensively researched as an ideal material having high electrical conductivity, large surface area, and outstanding mechanical properties. Excellent capacity and power performances are reported for SWCNTs [1] but its high price of ~1,000 USD/g is a huge barrier for their practical applications. We have developed rapid growth of millimeter-long SWCNTs by chemical vapor deposition (CVD) on flat substrates [2] and continuous production of submillimter-long few-wall CNTs (FWCNTs) by fluidized-bed CVD [3]. By oxidizing these long FWCNTs (Ox.FWCNTs), self-standing electrodes for high-power Li batteries were developed [4]. In this work, we systematically investigate the combination of low cost capacitive materials, such as AC, with CNTs which provide high electrical conductivity and a structural matrix. The dispersion conditions in aqueous surfactant solution and organic solvents, paired with ultrasonication have reported effects over the length and debundling level of CNTs in aqueous solutions [5], but in the case of various types of CNTs mixed with different aspect ratio particles, the dispersion conditions need to be studied in order to keep their length and electrical conductivity as high as possible. This work makes possible to produce flexible electrodes with different performances, able to be used on a case-by-case basis.

2. Experimental

To prepare the electrodes, different amounts of SWCNTs (2 - 4 nm diameter, 500 μm length) [2] and FWCNTs (8 nm diameter, 400 μm length) [6] were mixed with AC, through the ultrasonication of their aqueous (SDBS 1wt% solution) and ethanol dispersions. The electrodes were obtained by vacuum filtration over PTFE membrane filters and extensively rinsed with hot water to remove the surfactant when necessary. Cyclic voltammetry (CV) and electrochemical impedance spectroscopy (EIS) measurements in a three-electrode cell, with 1 M $H_2SO_{4\,aq}$ as electrolyte, were used to measure gravimetric capacitance and redox behavior. Sheet electrical resistance of the CNT films was determined by a four-point probe instrument and the electrodes morphology was studied through scanning electron microscopy.

3. Results and discussion

Figure 1 shows a photo and a SEM image of a typical CNT-AC composite electrode. CNTs form a sponge-like matrix and AC particles are encapsulated inside, yielding a flexible, self-standing film. The two combination electrodes: SWCNT - AC and FWCNT – AC, exhibit the contribution to capacitance from the particulate AC confined in the nanotube matrix. There is a decrease in capacitance with scan rate, which suggests that part of AC became useless at high scan rates. The ethanol dispersed electrodes display higher values than the SDBS ones, probably due to adsorption of surfactant molecules into the pores of AC that leads to a reduction of the available surface area. The specific capacitance of the ethanol dispersed combination electrodes exceeds the one of the pure CNT electrodes for most of the evaluated scan range for FWCNT (Figure 2) and up until 50mV/s for SWCNT. It should be noted that these similar and even higher capacitances were achieved by replacing half of CNTs with AC. Ox.FWCNT showed the largest capacitance owing to the pseudocapacitance, which is seen as a reversible wave in Figure 3. Electrodes containing AC also display redox peaks at different positions while pure CNT electrodes have mostly an electrical double layer capacitance contribution.

References
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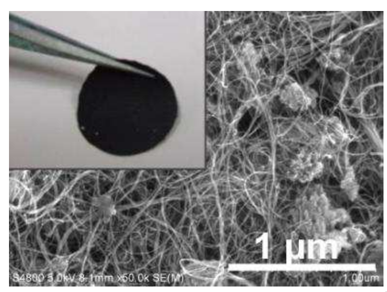

Figure 1. Photo and SEM images of a typical CNT-AC electrode.

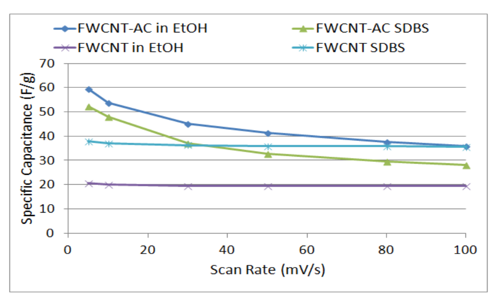

Figure 2. Galvanostatic rate capability of CNT-based self standing electrodes.

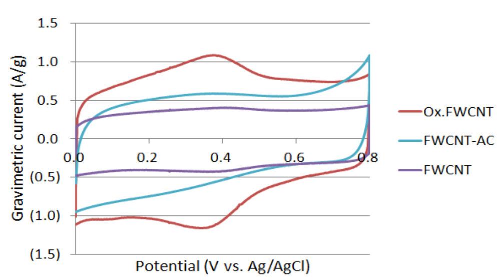

Figure 3. Cyclic voltammogram of FWCNT-based self standing electrodes. Scan rate: 10mV/s.