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Electrochemical impedance study of Li-ion insertion into the raw acid-oxidized carbon nanotubes

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Abstract

Electrochemical impedance spectroscopy (EIS) was applied for the raw acid-oxidized multiwall carbon nanotubes during Li-ion insertion with the electrolyte of 1M $LiPF_6$ in EC and DMC. Impedance spectroscopy consists of two separated arcs in the high and intermediate range frequency. The high frequency arc is attributed to Li migration within the surface films and the medium frequency arc is associated with the charge transfer. Obtained spectra were analyzed with an equivalent circuit model. Kinetic parameters such as the charge transfer resistance, film resistance, diffusion coefficient and exchange current were evaluated. The contribution of the film to the measured impedance response is discussed.

Keywords: Carbon nanotubes; Lithium batteries; Impedance; Oxidation; Resistance; Diffusion coefficient

1. Introduction

Long-life, environmentally friendly, low-cost reliable batteries are today urgently required to meet some crucial demands of our modern society. Recent developments in rechargeable Li-ion battery [1] technology include the use of lithium-carbon compounds in place of metallic lithium anodes for improved safety. Current production is dominated by carbons [2–6]. However, there is still an important search for new or optimized carbons, especially with well-controlled nano-structure and surface functionality, in order to improve the storage capacity and the cycleability of the power supply, carbon nanotubes [7–13], have been carefully considered for all these applications, where their unique morphology (e. g. Helical fishbone arrangement of graphitic layers, presence of a central canal) is expected to be profitable for getting improved performance. We [14–18] have already reported the electrochemical intercalation of lithium into the carbon nanotubes and their by-product; these results are of valuable information for carbon nanotube electrodes used in Li-ion batteries. In order to increase the capacity of the carbon nanotubes, we [19] try to use the acid-oxidation multiwall carbon nanotubes as anode of lithium battery. In Ref. [19] the electrochemical intercalation of lithium into the raw acid-oxidation multiwall carbon nanotubes was characterized by charge–discharges tests, cyclic voltammetry, X-ray diffraction, transmission electronic microscopy, FTIR spectra. However, the mechanism of the influences of film on the discharge performances has not been clarified for that system. It is quite important for us to understand the effects of the film structure and behavior on the discharge processes. In this work, we first discuss the reaction between the carbon nanotubes and the mixture of acid, and then the impedance profiles are analyzed using possible equivalent circuit models, as functions of the open circuit potentials. The aim of this work is to give a rational explanation of the fact that the impedance of the acid-oxidation multiwall carbon nanotubes depended on the open circuit potentials.

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2. Experimental

Raw multiwall nanotubes were prepared by the carbon arc method described by Ajayan et al. [20]. A dc arc plasma was formed between a 50 mm graphite negative electrode and an 8 mm positive electrode in 500 Torr of helium. The hard deposit rod formed on the negative electrode was mounted in epoxy resin and dissected. As reported earlier, the rod consisted of a hard outer shell and an inner core. The inner core consisting of sections of a dull black soft matrix was collected and sonicated in 2-propanol. The colloidal suspension was pipetted off, leaving a residual precipitate. Transmission electron microscopy showed that both fractions were predominantly nanotubes and nanoparticles [15]. Therefore, the fractions were combined and used in the following studies.

The raw multiwall carbon nanotubes were oxidized in a mixed solution of concentrated HNO_3 and H_2SO_4 (1:3 by volume) at 130 °C for 10 min., followed by filtering onto a glass filter and washing with distilled water, then the black product was heated at 300 °C for 2 h.

A three-electrode system was applied to use in this study. Lithium sheets were used as reference and counter electrodes. The raw acid-oxidized multiwall carbon nanotubes were used as working electrodes. The carbon nanotube electrodes were made by dispersing 85 wt.% carbon nanotube powders, 10 wt.% carbon black and 5 wt.% polyvinylidene fluoride (PVDF) binder in dimethyl phthalate solvent to form a slurry, which was then pasted onto a nickel net. The electrode has a geometric area about 1.0 cm^2 and total weight of 15~20 mg. The electrode thickness was approximately 0.1 mm. The electrolyte used was a 1 M solution of $LiPF_6$ dissolved in a 50:50 mixture by volume of ethylene carbonate (EC) and dimethyl carbonate (DMC). The cell assembly was carried out under an argon atmosphere in a glove box (UNIlab). The Ar atmosphere was continuously circulated through a purification train containing molecular sieves and the copper metal to remove trace oxygen and water vapor.

The impedance studies were carried out using a PAR model 398 impedance measurement system that was comprised of a Model 5210 lock-in analyzer, a Model 273 potentiostat and an IBM computer. This allowed for the automated measurement of the electrochemical impedance of the cell over the frequency range 100 kHz to 0.01 Hz. The ac amplitude was 5 mV peak to peak and the sampling rate of five samples per decade was used. Equilibrium is considered to be reached when open-circuit voltage remains stable (about 1 mV over 10 h.). In the present work, a constant phase element (CPE) is used for equivalent circuits except for resistor, R. The general expression for the admittance of the CPE is

$$Y_{CPE} = Y_c\omega^n \cos(n\pi/2) + jY_c\omega^n \sin(n\pi/2) \quad (1)$$

where ω is the angular frequency, which is $2\pi f$ with f being frequency and $j=(-1)^{1/2}$. Y_c is the CPE factor and n is the CPE exponent, depending on the n value, the CPE can have a variety of responses, if n=0, it represents a resistance with $R=Y_c^{-1}$; if n=1, a capacitance with $C=Y_c$, and if n=0.5, a Warburg response[21]. The EIS spectra were analyzed using the nonlinear least-squares fitting program EQIVCRT developed by Boukamp [22]. The fitting program generates a Chi-square value within the range of 10^{-4} level. The relative standard deviations for each parameter obtained by the fitting program do not

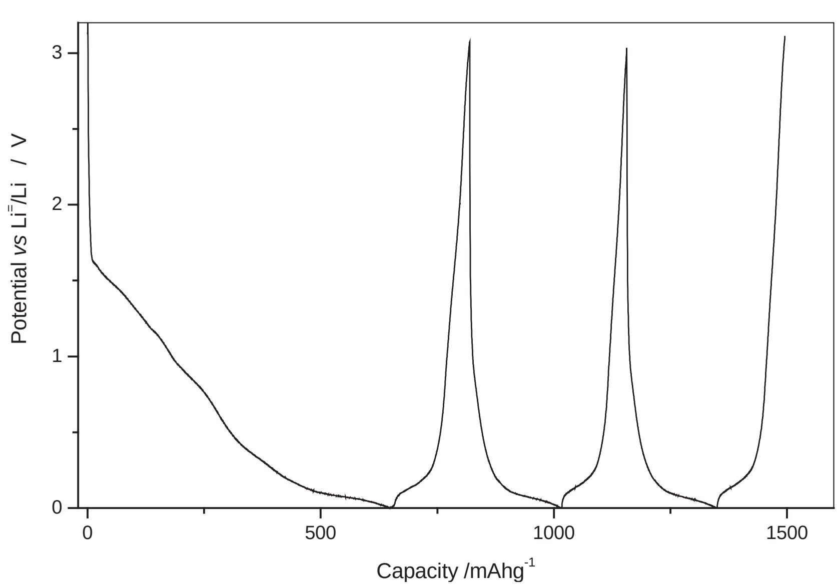

Fig. 1. The discharge–charge behavior of the raw acid-oxidized carbon nanotubes.