



Low contact resistance carbon thin film modified current collectors for lithium ion batteries



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ARTICLE INFO

Available online 27 August 2014

Keywords:

Chemical vapor deposition
Current collector
Carbon film
Li-ion battery

ABSTRACT

Carbon films have been synthesized by chemical vapor deposition (CVD) on AISI 304 stainless steel (304SS) sheets with various C_2H_2/H_2 flow ratios at 810 °C. The films exhibit three different morphologies and structures: filament, sphere and transition types at different C_2H_2/H_2 flow ratios, as characterized by scanning electron microscopy, X-ray diffraction and Raman spectroscopy. It was found that the degree of graphitization increased with decreasing C_2H_2/H_2 flow ratios. The carbon film modified 304SS sheets were used as cathode current collectors and coated with an active layer containing $LiMn_2O_4$ active materials, conducting additives and binders for lithium ion batteries. The electrochemical properties of these $LiMn_2O_4$ cells with bare and carbon film modified current collectors were investigated. Under high current operation, such as 3000 mA/g, the capacity of the $LiMn_2O_4$ cell with transition type carbon film modified current collector is 55% higher than the cell with bare current collector. The enhanced performances of high current density charge–discharge cycles can be attributed to the reduced contact resistance and improved charge transfer efficiency provided by the transition type carbon film modified current collectors.

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1. Introduction

High operating voltage and high energy density are the characteristics of lithium-ion batteries, which have become the main power sources of consumer electronics in recent years. For the applications in electric vehicles, the lithium ion batteries face the challenge of high current operation. The internal resistance in batteries is one of the factors, which may affect the high current efficiency of lithium-ion batteries. Therefore, developing low resistance electrodes and reducing the contact resistances between electrode materials and current collectors have been of great interest. It was reported that by using porous current collectors high power performances of the lithium ion batteries can be improved [1]. In the study, a three dimensional structure with lower charge-transfer resistance than the conventional aluminum foil current collectors, was used. Current collectors with vacuum grown carbon fibers were also studied, and found to have delivered high energy density [2,3]. Recent study showed that modified metal current collector, such as carbon-coated aluminum foils [4], can reduce charge-transfer resistance and improve adhesion at the active layer/current collector interface, compared with the unmodified current collectors. There have been many known techniques for carbon coating on metals. The accepted mechanism of carbon film deposition was well known and documented as catalytic graphitization since the 1960s [5–8]. Many kinds of metals,

such as Fe, Co, Ni, Zr and Pt, have been used as catalyst in catalytic graphitization [9–11].

In this study, we use AISI304 stainless steel (304SS) sheets as the current collectors and modify them with carbon coatings by chemical vapor deposition (CVD). The carbon film modified and unmodified 304SS sheets as cathode current collectors are characterized and compared. The effects of reduced contact resistance due to carbon film modification and the high-current performances of the resulted lithium cells have been exploited.

2. Experimental details

Carbon films were deposited on 304SS discs (1.33 cm²) in a tube furnace by CVD. The CVD process was carried out at 810 °C for 1 h under acetylene–hydrogen mixed gas with different flow ratios. The 304SS containing elements of Fe (70.2 wt.%), Cr (18.7 wt.%) and Ni (8.1 wt.%) can serve as both current collectors and catalyst for carbon growth. The mixing ratios of C_2H_2/H_2 were 0.15, 0.45 and 1.40. The distinctive morphologies of carbon films deposited under different gas ratios were clearly observed by field emission scanning electron microscope (Hitachi S-4800). As the furnace was heated up to the reaction temperature, only hydrogen flow was introduced into the furnace to avoid carbon deposition at low temperature. At reaction temperature, the acetylene flow was released into the furnace to reach the designated acetylene–hydrogen flow ratios. After deposition, the acetylene–hydrogen flows were stopped and the specimens were

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cooled down to ambient temperature under an argon-containing atmosphere. Crystal structures of the prepared carbon films were identified by grazing incident X-ray diffraction at a grazing angle of 3° (Bruker D8SSS). Interfacial contact resistances (ICRs) were measured with a milliohm-meter (Agilent 4338B) by a sandwich method showed in Fig. 1. Raman spectrometer (Renishaw micro-Raman) with an Ar ion laser emitting at 515 nm was employed to determine the types of carbon structures for the carbon films. The Raman spectra were deconvoluted to analyze the degree of graphitic order.

Slurry of LiMn_2O_4 powder (80 wt.%), polyvinylidene-fluoride (PVDF) binder (10 wt.%), and carbon black (10%) dissolved in N-methylpyrrolidone (NMP) was prepared. To prepare the cathode electrodes, the slurry was then coated by doctor-blade technique on 304SS sheets with and without the CVD deposited carbon films. The electrodes were vacuum dried at 120°C for 12 h. For electrochemical tests, the electrodes were packed in CR2032 coin cells with the LiMn_2O_4 as the working electrodes, lithium metal foils as the counter and reference electrodes. The solution of 1 M LiPF_6 dissolved into a mixture of ethylene carbonate (EC) and ethyl methyl carbonate (EMC) with the volumetric ratio of 1:2 was used as the electrolyte. All cells were assembled in an Ar filled glove box.

The charge–discharge tests were carried out on a multi-channel battery test system (Jiehan 5200) by charging the cells to 4.3 V and discharged to 3.0 V with specific currents (mA/g) ranging from 60 mA/g to 3000 mA/g. The electrochemical impedance spectroscopy (EIS) analysis was carried out on an electrochemical workstation (H13522-50LCR) by applying an AC voltage of 20 mV in a frequency range from 100 kHz to 0.01 Hz. All electrochemical tests were measured at room temperature.

3. Results and discussion

The growth mechanism of different carbon films was discussed in our previous studies by Chung et al. [12,13]. Fig. 2 shows the morphologies of carbon films deposited with different flow ratios of $\text{C}_2\text{H}_2/\text{H}_2$. For $\text{C}_2\text{H}_2/\text{H}_2$ flow ratio of 0.15, carbon filaments, denoted as CF, with a diameter of about $0.2\ \mu\text{m}$ develop. The carbon filaments form random clusters and are not continuous across the surface of the 304SS sheet. EDS results at the spaces (indicated by arrow) between the carbon filament clusters show signals of exposed 304SS sheets. The growth of carbon filaments is not directional. These filaments show axial length of around 8 to $10\ \mu\text{m}$, and diameter of around 100 nm. As the $\text{C}_2\text{H}_2/\text{H}_2$ flow ratio increases to 0.45, the carbon film becomes thicker and the morphology is composed of filaments and spheres, denoted as CT. This carbon film shows more conformal coverage, and no exposed 304SS substrate surface is observed. It indicates that increased C_2H_2 flow promotes the growth of carbon sphere. Under such a condition, the carbon film is in a transition-type growth mode, in which both carbon filaments and spheres can be deposited. As shown in Fig. 2, the filaments in sample CT are shorter

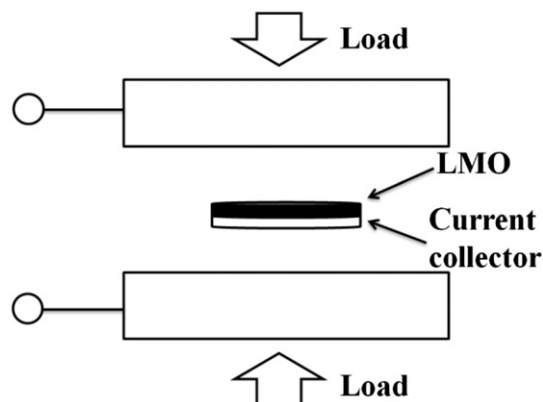


Fig. 1. Schematic representation of the interfacial contact resistance test.

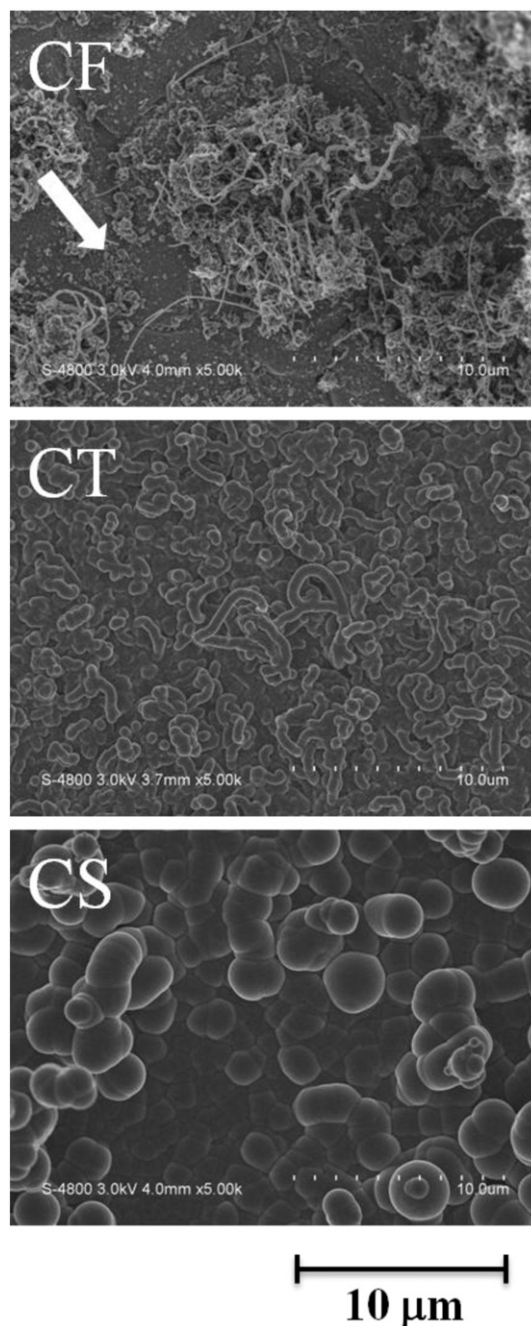


Fig. 2. FE-SEM micrographs of the carbon films prepared under $\text{C}_2\text{H}_2/\text{H}_2$ ratios of ratios 0.15, 0.45 and 1.40, resulting in filament (CF), transition (CT) and sphere (CS) type morphologies.

and thicker with axial length less than $5\ \mu\text{m}$, and diameter of around 500 nm. In-between the filaments, there are granular spheres with sizes of 500 nm to $1\ \mu\text{m}$. For the carbon film deposited under $\text{C}_2\text{H}_2/\text{H}_2$ flow ratio of 1.4, the high flow ratio induces the sphere growth mode, and the film is composed of solely carbon spheres with diameters ranging from about $1\ \mu\text{m}$ to $3\ \mu\text{m}$. This type of samples is denoted as CS.

X-ray diffraction patterns of the specimens grown at different mixing ratio of $\text{C}_2\text{H}_2/\text{H}_2$ are shown in Fig. 3, in which the dash line at $2\theta = 26.4^\circ$ is the (002) diffraction line of Highly Oriented Pyrolytic Graphite (HOPG). XRD results show that the CF has the highest degree of graphitic order with the highest intensity of (002) peak. However, the peaks of precipitate phases from 304SS are also stronger than CT and CS, because the substrate is exposed (Fig. 2, CF). The degree of graphitic order decreases with the increase of $\text{C}_2\text{H}_2/\text{H}_2$ flow ratios.

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