Carbon Nanomaterials - The Route Toward Applications in Energy

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1. Abstract

This talk will focus on engineering carbon nanomaterials, graphene and carbon nanotubes (CNTs) for high efficiency flexible battery and dye sensitized solar cells. Particularly, engineering the interfaces of graphene-polymer, graphene-substrate and graphene-CNTs will be used to highlight the challenges towards higher efficiency energy applications. Our recent results of a novel binder-free multi-wall carbon nanotube structure as a flexible battery, and a large graphene film for a field emission device and dye sensitized solar cells are presented.

2. Graphene

2-1. Why graphene for energy application?

Graphene is a newly discovered 2D material that exhibits high carrier mobility, good mechanical properties, high transparency and excellent thermal stability. To date, considerable works have been demonstrated in applications of graphene including transistors, supercapacitors, solar cells etc. In particular, application in solar cells with the enhanced efficiency is of great interest, since graphene has exhibited remarkable transparency in the entire solar spectrum including infra-red (IR) region. That is an added advantage of its application in high efficiency solar cell for harvesting more light photons from the solar spectrum. In addition to this, graphene has shown ability to be transferred on any flexible substrates using scalable methods. This versatile transformation property remains a promising opportunity for developing light-weighted flexible electrodes for flexible electronics.

2-2. Graphene electrode

Cu foil was annealed at 1000°C for 1 hr in an inert gas atmosphere followed by cleaning and hot acid treatment. The l foil was then placed inside a thermal CVD system and increased the temperature up to 1000°C. The ambient of CVD furnace was kept at 0.8 atmospheric pressure in the presence of inert gas (Ar) atmosphere and CH_4:H_2 was used as a precursor gas mixture for graphene growth. Electrochemical characterizations of plasma treated graphene electrodes were carried out using GAMRY Reference 6000 potentiostat.

The TiO_2 working photoanodes about ~12 μm thick were prepared on FTO substrate using TiO_2 paste by doctor blade technique and subsequently sintered at 450 °C in ambient atmosphere. The $Ru(dcbpy)_2(NCS)_2$ dye was used to sensitize the TiO_2 photo electrodes dried at room temperature. A sandwich-type configuration was employed to characterize current–voltage behavior of DSSCs.

Data were obtained under 1 sun illumination (AM 1.5G, 100 mW cm^{-2}) with a solar simulator and a Keithley 2400 source meter.The graphene/polymer film shows high quality, flexible transparent conductive structure with unique electrical-mechanical properties; ~88.80 % light transmittance and ~ 100 Ω/sq sheet resistance. The graphene film exhibits excellent structural integrity and uniform electrical properties with large variation of bending radius.

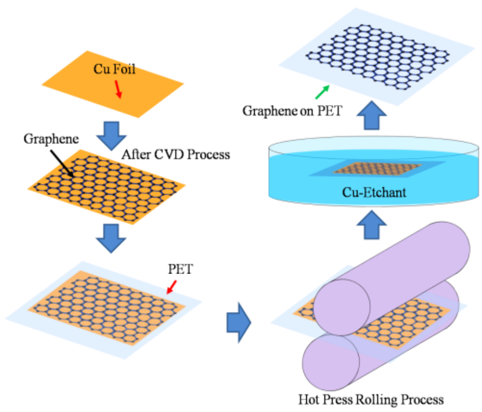

Fig. 1 Process flow for large scale graphene film production.

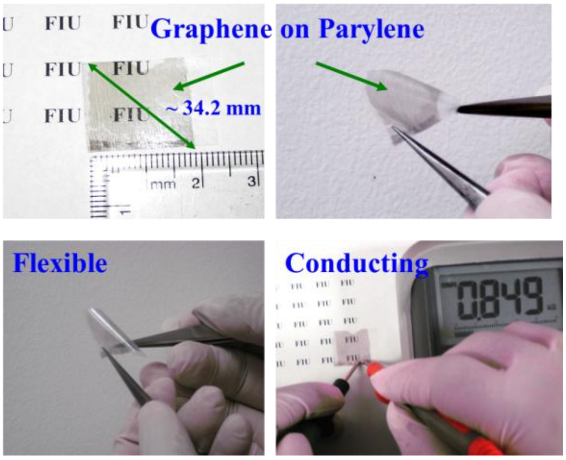

Fig. 2 Fabricated graphene on polymer substrate as transparent conducting electrode.

3. Carbon nanotubes electrode for Li-ion Battery

Recent advances in carbon nanotubes are expected to enhance the power density as well as safety level of future batteries, in addition to imparting the required flexibility. Introduction of carbon nanotubes as electrodes in the Li-ion cells, in place of conventional graphite, are expected to show higher lithiation capability and an overall better performance because of the extremely high surface area of nanomaterials as compared to their bulk counterparts.

The Li-ion battery anode consists of directly grown CNTs on metallic current collectors. For preparation of the electrodes, 50 µm thick pure copper foil was punched in required size and used as substrates to deposit thin films of catalyst, through RF magnetron sputtering system. These coated samples were then inserted in a thermal chemical vapor deposition (CVD) system for direct CNT growth. CVD was performed at a temperature of 973K-1173K, using $H_2 + C_2H_4$ gas mixture as the precursor.

During the initial charging-discharging cycles, the CNT-based electrodes showed very high specific capacity, as compared to conventionally used graphite anodes (theoretical capacity - 372 mAh/g). The anode structure was tested in a half-cell mode at different C-rates and the results are shown in Figure 3. It may be observed from the figure that the reversible specific capacity of the proposed structure is very high. Exceptionally high specific capacity values of this electrode points out to the benefit of using CNT in Li-ion batteries. After a detailed structural analysis, through X-ray diffraction, Raman spectroscopy, SEM and HRTEM, the mechanism of lithiation-delithiation in these electrodes were proposed. During lithiation, Li^+ ions reach individual CNTs, passing easily through the CNT forest structure and attaches with their sidewalls. Very high surface area of the CNTs promotes huge amount of Li^+ ion intercalation. On the other hand, during de-lithiation, most of the ions return back to the opposite electrode. Highly porous nature of the CNT forest structure allows easy transport of the intercalating ions from one electrode to the other.

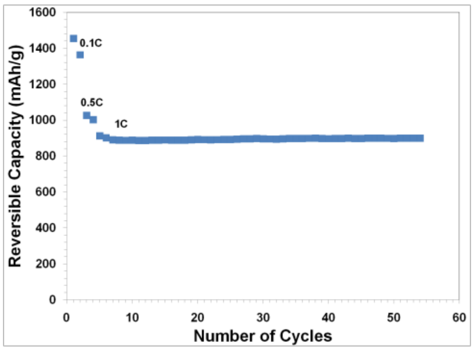

Figure 3: Stability of CNT Li-ion battery: Exceptional stability of the reversible capacity (~ 900 $mAhg^{-1}$) at 1C rate, no capacity degradation was observed in 50 cycles.

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