Template synthesis and electro-chemical study of carbon nanotube array electrodes

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Template Synthesis for preparation of micro- and nano-scale materials has attracted great interests in recent years[1]. The preliminary results of fabrication of nano-structured spinel $LiMn_2O_4$ and carbon nanotube array electrodes for Li-ion batteries using template technique have been reported[2] from this lab. In this presentation, the electrochemical intercalation of Li^+ ions into Mutilwalled Carbon Nanotubes (MWNTs) has been investigated by using carbon nanotubes array electrode system, and some useful information has also been obtained by using Cyclic-voltammetry (CV), Electrochemical Impendence Spectrum (EIS) and Raman Spectroscopic methods. Although some attempts were performed to explore the application of MWNTs in lithium battery[4], MWNTs array electrode system can provide significant information because of its artificially confined structure.

The MWNTs array was prepared within the porous aluminum template membrane (the pore diameter is about 50 nanometer in the report here) by Catalytic Vapor Deposition (CVD)[3], and then the membrane surface opposite barrier-type part is covered with a sheet of platinum by vacuum sputtering. After that, the barrier-type part of the alumni membrane is removed by 5% phosphoric acid in 30°C, so the MWNT top end will expose to atmosphere.

Fig.1 is a SEM image of the cylindrical MWNTs and it indicates that the upper ends bend over like the bristles of a brush, and cross-section image(Fig.2) shows that most part of the MWNTs immerse in the template and actually form the tabular array. First order micro-Raman spectrum of the pristine MWNTs were also recorded too, as shown in Fig.3. The main Raman peaks observed at 1325cm^{-1} and 1590cm^{-1} respectively, and the peak centered around 1325 cm^{-1} attribute to defects in the graphene sheet, tube ends and staging disorder[5]. The 1590 cm^{-1} band correspond to the G mode vibration of the carbon atoms in the graphene. Cyclic-voltammetric results (Fig.4) shows that big difference between redox peaks for Li^+ ion intercalation/ de-intercalation reaction, it correlated well with the charge/discharge curves with these MWNTs materials. In addition, since limited part of the tubes in the array electrodes were exposed to the electrolytes, higher current was focused on the exposed small area, thus these array may be expected to tolerate high current density and may be utilized in future micro-battery system.

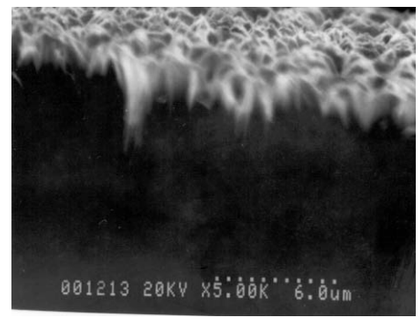

Figure 1 A SEM (×5000) graph of the protuding MWNTs on the array electrode surface

Figure2 SEM graph of the cross-section of the array electrode (×5000)

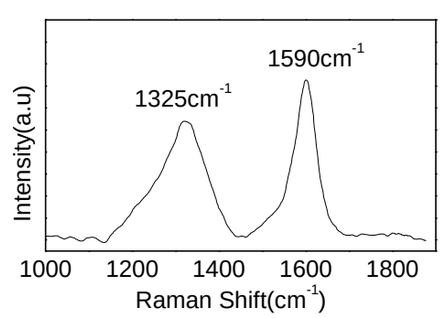

Figure.3 Raman Spectrum of the MWNTs

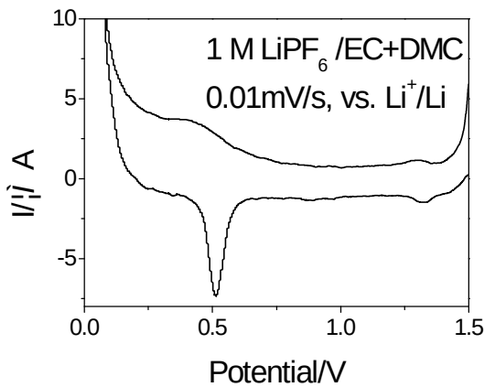

Figure 4 A CV graph of the array electrode in 1 M $LiPF_6$ / EC+DMC, scan rate is 0.01mV/s, The potential is vs. Li^+\Li

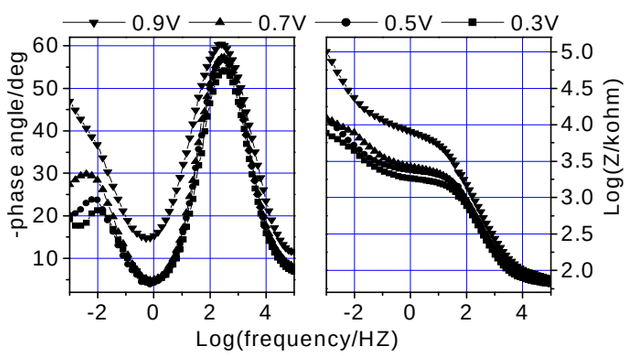

Figure 5 Bode graph of the EIS in 1 M $LiPF_6$ / EC+DMC

At the same time, the electrochemical impendence of the array electrode has been investigated and the Bode graph is shown in Fig.5. The results demonstrate that the values of phase angle and impedance Z change distinctly with change of potential in low frequency, and charge transfer resistance is smaller at 0.5 V .

The array electrodes where MWNTs have different diameter have also been prepared and investigated in the lab, and it seems that the diameter of MWNTs also affect the Li^+ intercalation reaction to some extent. Due to the limited space, those investigations is left out and will be presented in the meeting.

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