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Study on the defective multiwalled carbon nanotubes and their application for Li secondary battery

Owing to the unique structures, together with high stability and high conductivity, carbon nanotubes (CNTs) are considered to be promising materials for energy storage. CNTs were usually regarded to have perfect crystalline structures. Perfect CNTs was defined as "a cylindrical graphene sheets composed only of hexagons having a minimum defects at the tip to form a closed seamless structure." However, more defects may occur in the structure of CNTs, which proved to alter their material properties. Introducing defects into CNTs has been utilized to modify the structure of CNTs and obtain the desired properties. In this work, study of defective multiwalled carbon nanotubes (DMWCNTs) and their application for Li secondary battery are presented.

Defective multiwalled carbon nanotubes (DMWCNTs) have been prepared by using cobalt oxide as the solid-state catalyst. It was confirmed by thermogravimetric analysis study, that using such catalyst, the oxidation temperature of CNTs can be decreased up to 250 ^oC. This demonstrates that the cobalt oxide eased the oxidation of carbon by providing lattice oxygen in promoting the C-O formation to produce CO gas as shown from reactions below:

$$\text{(i) } 6CoO + O_2 \longrightarrow 2Co_3O_4$$
$$\text{(ii) } Co_3O_4 + C \longrightarrow 3CoO + CO$$

To clarify the defect formation, the resulting DMWCNTs were then characterized by various measurement techniques. Increasing the I_D/I_G from the Raman analysis, together with transmission electron microscopy (TEM) images, has proved the presence of defects. From the galvanostatic charge-discharge measurement, DMWCNTs showed the largest storage capacity of 625 $mAhg^{-1}$, which is higher than that of purified and pristine MWCNTs. The defective structures on multiwalled carbon nanotubes (MWCNTs) are not only enhancing the performance of anode material, but also providing a better understanding on Li storage mechanism. From this result, we hinted that extraction at the high potential (1.5-3.0 V) may not be simply related to the extraction of Li bound surface groups as always be considered by many research groups. Eventually, by evaluating the estimated Li capacity derived from the quantization of functional groups on MWCNT samples, it is clear that the amount of O-functionalities itself is too small to explain the large storage capacity of MWCNT based electrodes. Instead of surface functional group, we proposed that the extraction at such high potential might come from the extraction of Li out of in-plane defects.

Attempting to clarify the storage sites of CNTs that extracted at high potential (1.5-3.0 V), a systematic study was conducted by analyzing the MWCNTs, whether containing or absence of functional groups. Considering that slurry-casted working electrodes used in the previous study contain binder material, free-standing MWCNT electrodes were then applied as the working electrode. Free-standing MWCNT electrodes were prepared by simple vacuum filtration of MWCNT suspension, resulting in paper-like CNT material. The use of the MWCNT paper electrode offers the possibility to study the sole characteristic of CNTs, without interrupted by the presence of inactive material (binder). Annealing treatment under Ar atmosphere for 1 hour, at 900 ^{o}C was conducted to remove the functional groups on the surface of MWCNT. Meanwhile, thermal desorption spectroscopy (TDS) analysis was utilized to evaluate the type and content of functional groups on MWCNTs (before and after annealing). It has been confirmed that the annealing treatment at such temperature has removed large fraction of functional groups. It is important to note that after annealing treatment; pristine, purified and DMWCNTs actually contain a comparable low amount of functional groups. Interestingly, they still have different Li storage capacities. Correlating the functional group content and capacity derivation study, we can confirm that the Li extraction at high potential is unlikely related to the presence of functional groups. Two scenarios of trapping sites-explaining the Li extraction at high potential on oxidized MWCNTs have been proposed. Firstly, the in-plane defects as reported in our early work and secondly, solid electrolyte interphase (SEI) as trapping site. Preventing the SEI formation on CNT based anode material and evaluating their storage capacities may be the key to study the role of SEI for trapping the Li ions.

As discussed above, functional groups are likely not giving any effect on Li storage for anode material. Thus, in attempt to utilize the functional groups on the oxidized MWCNTs, we have challenged our MWCNTs as the cathode material for Li ion battery application. Benefiting from the Faradaic reaction between functional groups and Li ions (C=O + Li^+ = C-O-Li), the purified and DMWCNTs were studied for such purpose. In order to study the role of surface functionalities, MWCNTs were annealed at 500 and 900 ^oC under Ar atmosphere to selectively remove the functional groups. TDS was conducted to monitor the type and quantity of O-functionalities, after the annealing processes. From the cyclic voltammetry (CV) analysis in the range of 1.5 to 4.5 V, proceeding the anneal treatment at 500 ^oC, CV curves showed the absence of redox peaks that were attributed to the previous Faradaic reaction. This suggests that such Faradaic reaction may be exclusively come from the reaction between carboxyl groups (low temperature desorbing functional groups) and lithium. Upon heating up to 900 ^oC, the capacitance of MWCNT electrodes further decreased and showing distinctive shapes of CV.