カーボンナノチューブのリチウムイオン電池の電極材料応用

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１．　研究課題

Carbon nanotube (CNT) is an important allotrope of carbon nanomaterials, which can be considered as rolled-up graphene sheet into a seamless cylinder with fullerene caps[1]. CNTs have attracted tremendous attentions due to their unique one-dimensional nanostructure and extraordinary electrical, thermal, mechanical properties and chemical stability, which provide them huge potential applications in composite materials, thermal interface materials and electrode materials. In this project, we mainly focus on the synthesis of CNTs and their application in lithium-ion batteries (LIBs).

In 2004, high purity carbon nanotubes arrays were successfully synthesized by an "super-growth" chemical vapor deposition method[2]. However, the amount of the synthesized CNTs are typically as small as only a few tens grams per square meters. Our group have previously realized semi-continuous production of sub-millimeter-long few-wall CNTs from acetylene at a high carbon yield and short gas residence time. What's more, the production of high purity few-wall CNTs with an average diameter of 6.5 nm are achieved by using an internal heat-exchange reactor, which makes it possible to realize mass production of different types of CNTs in our lab[3,4].

Owing to the lightweight and high electrical conductivities, CNTs with different parameters have been used as conductive additives of electrodes of LIBs because they can provide conductive path for lithium ions. Besides, light weight CNT films have also been prepared and studied as current collectors of LIBs, which have demonstrated improved areal and volumetric capacities by replacing traditional heavy copper or aluminum foils. However, the influences of length and specific surface area of CNTs on LIBs properties have not been systematically investigated yet. Therefore, we first focus on researching the high-yield production of CNTs at lower cost and studying the influences of synthesized CNTs on the performance of LIBs.

[1] S. Ijima, Helical microtubules of graphitic carbon. Nature, 354 (1991), pp. 56-58.
[2] H. Kenji, D.N. Futaba, M. Kohei, N. Tatsunori, Y. Motoo, I. Sumio, Water-Assisted Highly Efficient Synthesis of Impurity-Free Single-Walled Carbon Nanotubes. Science. 306 (2004), pp. 1362-1364.
[3] D.Y. Kim, H. Sugime, K. Hasegawa, T. Osawa, S. Noda, Fluidized-bed synthesis of sub-millimeter-long single walled carbon nanotube arrays. Carbon. 50 (2012), pp. 1538-1545.

[4] Z. Chen, D.Y. Kim, K. Hasegawa, T. Osawa, S. Noda, Over 99.6 wt%-pure, sub-millimeter-long carbon nanotubes realized by fluidized-bed with careful control of the catalyst and carbon feeds. Carbon. 1 (2014), pp. 339-350.

２． 主な研究成果

(1) Deposition of catalysts in fluidized-bed.

According to previous research, achieving the uniform deposition of thin catalyst films on substrates is the key step towards synthesis of high quality CNTs. In this research, $Fe(NO_3)_3$ and $Al(NO_3)_3$ are selected as catalysts due to their low cost. Their nitrates water solutions are atomized by a nebulizer, and the produced catalysts solution mist are introduced into the fluidized-bed by carrier gas and deposited on ZrO_2 beads. During deposition process, temperature and gas flow rate are controlled carefully to prevent the formation of big mist droplets which would cause the aggregation of beads or the drying of the mist particles in advance. SEM images show that catalysts can be deposited uniformly on the surface of ZrO_2 beads at proper deposition condition. After synthesis process in horizontal reactor, CNTs arrays cover the whole surface of beads with a length of 200 μm (Fig. 1).

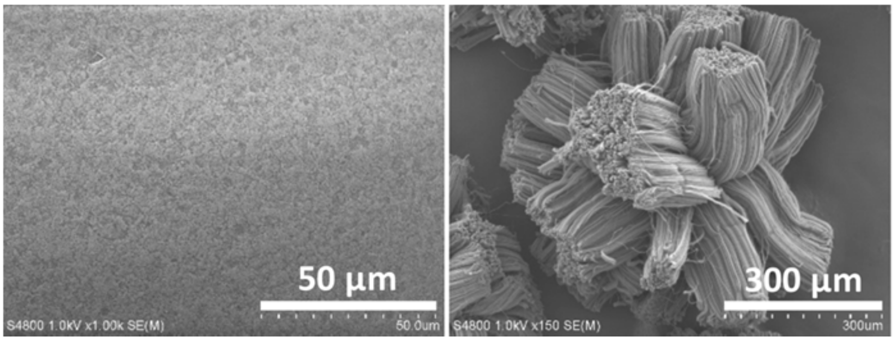

Fig. 1 SEM images of surface of beads after deposition (left) and CNTs on the beads after synthesis (right).

Besides, the thickness of prepared Fe/AlO$_x$ catalysts films are also confirm by X-ray fluorescence spectrometer. Results show that the thickness of catalysts layer is ca. 1-2 nm which is suitable for growth of CNTs arrays.

(2) Synthesis of CNTs by fluidized-bed CVD method.

Sub-millimeter-long few-wall CNTs are synthesized by fluidized-bed CVD method. CNTs with a length of 300 μm and yield of 6.3 mg_{CNT}/g_{beads} are synthesized at the optimized temperature and catalyst ratio. In order to achieve a higher yield of CNTs, bilayer deposition strategy is applied as another thin Fe layer is deposited on the first Fe/AlO$_x$ layer. Surprisingly, the length of CNTs reach ca. 500μm and yield is improved to 16 mg_{CNT}/g_{beads} with a specific surface area of 420 m^2/g, indicating the synthesized CNTs possess average wall number of three (Fig. 2). These excellent results originate from the optimized amount of Al, which is considered to play an important role in suppressing the diffusion and aggregation of Fe atoms.

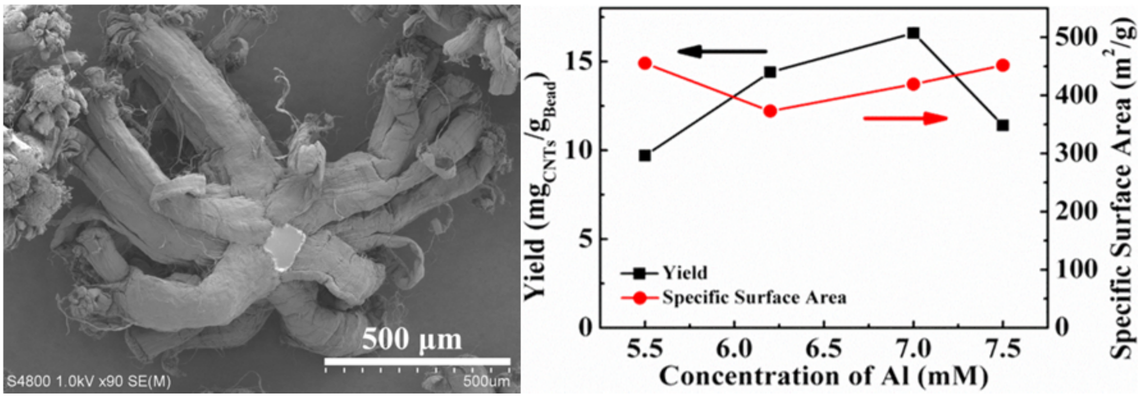

Fig. 2 SEM images of synthesized CNTs (right) and the effect of Al source concentration on the yield and specific surface area of CNTs.

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４．　研究業績

4.1 学術論文　特になし

4.2 総説・著書　特になし

4.3 招待講演　特になし

4.4 受賞・表彰　特になし

4.5 学会および社会的活動

[1] 9th A3 Symposium on Emerging Materials: Nanomaterials for Electronics, Energy and Environment, Kyoto University, Japan, Oct. 30, 2018. Poster presentation.

[2] 1 & 2D Materials International Conference and Exhibition (1 & 2DM), Tokyo Big Sight, Koto-ku, Tokyo, Japan, Jan. 29-30, 2019. Oral Presentation.

５．　研究活動の課題と展望

This research will be mainly conducted in the following two aspects:

(1) Development of high-yield production method of CNTs at low cost

We will still focus on the synthesis of CNTs by fluidized-bed CVD method. Different kinds of catalysts and deposition methods will be applied to promote the formation of nm-sized catalyst particles in order to achieve higher number density and longer life time of catalysts particles.

(2) Application of CNTs as electrode materials of LIBs

By using the CNTs synthesized above, CNTs and other active material composite films will be prepared and used as the electrode materials in lithium ion batteries. The influence of CNT parameters on the performances of LIBs will be investigated. High energy and power densities LIBs with balanced areal and volumetric capacities are expected to be achieved.