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Nano-structured Materials for Energy Storage Applications-views and Prospects of Rechargeable Li-ion Batteries

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1. INTRODUCTION

Nanocrystalline materials have shown significant promise in industry and technology. This is mainly because the optical, electrical, mechanical, electronic and chemical properties of these materials are a function of their dimensions, which make them superior in various applications compared to their bulk counterparts. The use of nanocrystalline materials will lead to the miniaturization and exploitation of their unique properties. Recently, nanostructured materials have also attracted attention for application in energy storage devices especially for those with high charge / discharge current rates such as lithium ion batteries. The development of next-generation energy storage devices with high power and high energy density is key to the success of electric and hybrid electric vehicles (EVs and HEVs, respectively), which are expected to at least partially replace conventional vehicles and help solve the problems of air pollution and climate change. The renaissance of interest in ionically conducting solids is in part due to the critical role that they play in tackling this greatest threat to humankind in this century, namely global warming. This threat, combined with the finite nature of fossil fuels, makes it imperative that we develop new ways of storing and generating electricity that reduces CO2 emissions. Ionically conducting solids contribute to this in many ways. The energy storage technologies will rely on innovative materials science, i.e. developing electrode materials capable of being charged and discharged at high current rates. Lithium ion rechargeable batteries are one such energy storage devices which are still open to improvements. These batteries consist of a positive electrode (cathode), Li ion-containing electrolyte, and negative electrode (anode) as shown schematically in Fig. 1.

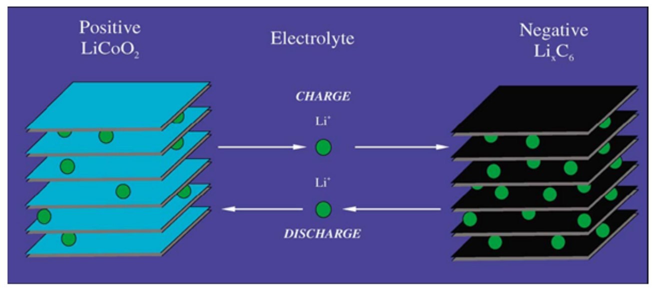

Fig. 1. Schematic representation of a rechargeable lithium-ion battery.

2. ELECTRODES OF LITHIUM ION BATTERIES

The positive and negative electrode materials of the most common, commercial lithium ion batteries are LiCoO2 and graphite, respectively. Both LiCoO2 and graphite are Li ion insertion hosts. During the charging process, Li ions are extracted from the LiCoO2 electrode and simultaneously inserted into the graphitic carbon electrode, coupling with negatively charged electrons to keep overall charge neutrality. During the discharging process, Li ions are reversibly extracted from the negative electrode and simultaneously inserted into the positive electrode. This electrochemical insertion / extraction process is a solid-state redox reaction involving electrochemical charge transfer coupled with insertion / extraction of mobile guest ions into/from the structure of an electronic and ionic conductive solid host. The major structural features of the host are kept after the insertion/extraction of the guests. Although widely used, such cell combination consisting of LiCoO2, graphite electrodes and a lithium ion conducting electrolyte, e.g. a solution of LiPF6 in an ethylene carbonate–dimethylcarbonate, EC–DMC, mixture is not the best and indeed, improvements in energy and power content are warranted to meet the increasing user's demands.

Role of nano technology on electrode improvements

It is usually desirable that the amount of energy stored in a given mass or volume of the lithium ion battery is as high as possible. The terms ‘specific energy density’ (Wh/kg) and ‘energy density’ (Wh/L) are used to compare the energy content of lithium ion batteries, whereas the rate capability is expressed as ‘specific power density’ (W/kg) and ‘power density’ (W/L). For HEVs, it is thought that the required specific energy density and specific power density of lithium ion batteries should be above 50 Wh/kg and 3 kW/kg, respectively. Moreover, much greater values will be necessary for EVs.

Nanostructured electrodes may not only introduce innovative reaction mechanisms but also improve electrochemical properties, such as specific energy storage capacity, high current charge/discharge ability, and cycle stability, over their bulk counterparts. This results from the short diffusion length and high contact area between the active materials and electrolyte. Li ion diffusion is highly dependent on the transport length and accessible sites on the surface of active materials. Those compounds exhibiting low Li ion diffusion coefficients usually show low Li ion storage capacities in bulk form, especially at high current rates.

Graphite is the most common anode material, has a good cycling stability but a relatively low specific capacity, i.e. not exceeding 372 mAh g−1. Thus, if improvement in energy content is desired, new, high capacity alternative electrode materials have to be developed. In this respect, lithium storage metals appears as very appealing candidates. A number of metals, e.g. Al, Si, Sn, are capable of reacting with lithium to reversibly form intermetallic, lithium alloys compounds. These alloys are in principle almost ideal anodes for lithium batteries : they can store and release large amount of lithium, assure high voltages when combined with lithium metal oxide cathodes and provide values of specific capacity exceeding that of graphite by an order of magnitude.

Unfortunately, the accommodation of the large amount of lithium is accompanied by severe volume changes in the host metal. These in turn induce mechanical strains which lead the electrode to crack and, eventually disintegrate with its failure in the round of few cycles. An effective way to improve the cycling stability of the metal alloy electrodes is that of modifying their morphology by reducing their particle size to few nanometers or by designing special nanostructures.

Carbon nanotubes as prospective anode materials

Since their discovery in 1991, CNTs have been synthesized by many processes, such as laser ablation, arc discharge , and supported or unsupported catalytic chemical vapor deposition (CVD), etc. In the CVD, transition metal particles act as seeds of nanotubes so that they strongly influence the structure and quality of the nanotubes. For example, the diameter and chirality of nanotubes can be controlled by size of catalyst, such as Fe, Ni, Co, Mo, and their alloy. Also, it is well known that carbon sources, such as acetylene, benzene, methane, ethylene, and xylene, etc., play an important role in structural properties of CNTs. Tremendous interest and efforts have been devoted to the production, characterization and application of carbon nanotubes. In general, carbon nanotubes can be classified as two categories , e.g. single wall nanotubes (SWNTs) and multiwalled nanotubes (MWNTs). Carbon nanotubes have unique structural, mechanical, electronic and electrical properties; they are attractive system standing for wide range applications such as nanoscale electronic devices, electron field emission sources, etc.

Since various carbonaceous materials can reversibly react with lithium in Li-ion cells, carbon nanotubes have been speculated to the applications as lithium insertion hosts for Li-ion batteries. CNTs demonstrated reversible lithium storage capacity as high as 600 mAhg-1. The electrochemical performance of CNTs strongly depends on their structure, morphology and disorder. Fig.2 depicts CNTs formation and their charge / discharge profile.

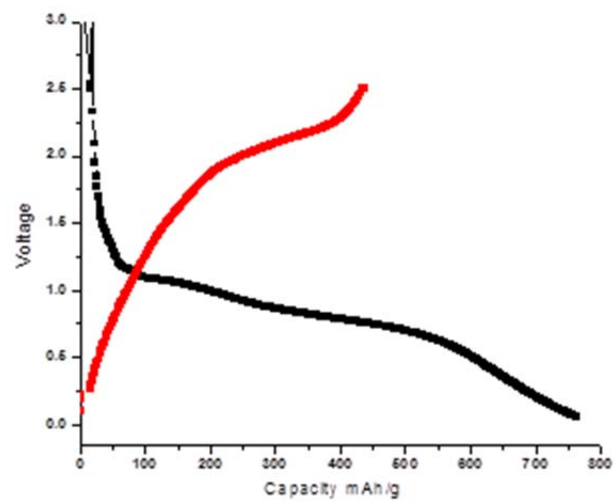

Fig. 2 : Formation of carbon nanotubes and their first cycle charge / discharge profile.

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