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Review

Carbon nanotubes in Li-ion batteries: A review

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ABSTRACT

Portable-electronics epitomizing technological breakthrough in history of mankind, are universal reality thanks to rechargeable batteries. LIBs, lithium-ion batteries, owing to high-reversible capacity, high-power capability, good-safety, long-life and zero-memory effects are at the heart of this revolution. Nonetheless, longer-battery-life, higher-current- and power-density, better-safety, and flexibility, crucial for portables and hybrid-electric-vehicles further fuel the research to better their electrochemistry. Electrode materials are vital for performance of batteries. Recent developments in nanoscience and nanotechnology offer potential prospects to devise novel-nanostructured electrode materials for next-generation better-performing LIBs. Nanostructured materials are pivotal to these progresses due to their manageable surface-area, stunted mass and charge-diffusion span, and volume change acclimatization during charging/discharging. CNTs, carbon-nanotubes, with distinct 1D-tubular structure, excellent electrical and thermal conductivities, mechanical flexibility and significantly large surface-area, are considered ideal additives to enrich electrodes' chemistry. Here, we observe contemporary developments in synthesis and characterization of CNTs and CNTs-based nanostructured composite-electrodes for utilization in LIBs.

Contents

Abbreviations: 1-,2-,3-D, one-, two-, three-dimensional; CNT(s), carbon nanotube(s); CVD, chemical vapor deposition; DWCNT(s), double-walled carbon nanotube(s); EVs, electric vehicles; HEVs, hybrid electric vehicles; LIB, lithium-ion battery; MWCNT(s), multi-walled carbon nanotube(s); SEI, solid electrolyte interphase; SWCNT(s), single-walled carbon nanotube(s).

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1. Introduction

Being part of energy hungry civilizations humans have been inexorably exploring the nature for the available energy resources. Be it renewable or non renewable, almost all the possible alternatives have been considered and exploited. Among these 'alternatives' we come across both 'clean' and 'not-so-clean or polluting' sources. With the ascend of industrialization by leaps and bounds the corresponding energy requirements have also soared up, forcing rapid depletion of the non renewable resources. This has necessitated the need for devising new sources and improving efficiencies of the existing systems. Also the unbridled use of unclean resources has imposed a new threat in the form of environmental pollution. While there has been a new-found attention in the areas of renewable and clean sources of energy, storage of this energy has also surfaced as the contemporary thrust area [1–5].

Battery is the system to store energy when it is available in plenty and can act as energy source when required. Depending upon reusability, batteries are available in two variants – primary or disposable and secondary or rechargeable. Though the primary batteries can only be used once as their electrolyte changes irreversibly during discharging; secondary batteries can be discharged and recharged multiple times. The ubiquitous use of portable electronic devices has further pressed the call for high energy density batteries or fuel cells. Since they were first commercialized in 1990s by Sony Corporation, Li-ion batteries (LIBs) have become the leading batteries in this category owing to their high power and energy density. In spite of their dominance in the consumer market, further research is currently going on to develop flexible, ultrathin and soft batteries for the modern pliable portables [2–7]. Flexible batteries are a necessity not only for the portable electronics but there is objective to fix them in empty spaces of the body parts of future generation hybrid vehicles. The aim is to improve charging rate, energy density, operating temperature, power density, safety, durability and sufficient electrochemical cycling characteristics. Of all the factors responsible for battery's performance, electrodes play a significant role. Hence there is a necessity to improve the electrode materials for realizing the highest capacity and superior electrochemical characteristics while maintaining the desired flexible and ultrathin nature of the electrode. Extensive research efforts are overtaken in the past, leading to considerable improvements in materials and chemistries to boost the battery technologies for next generation applications [1–15].

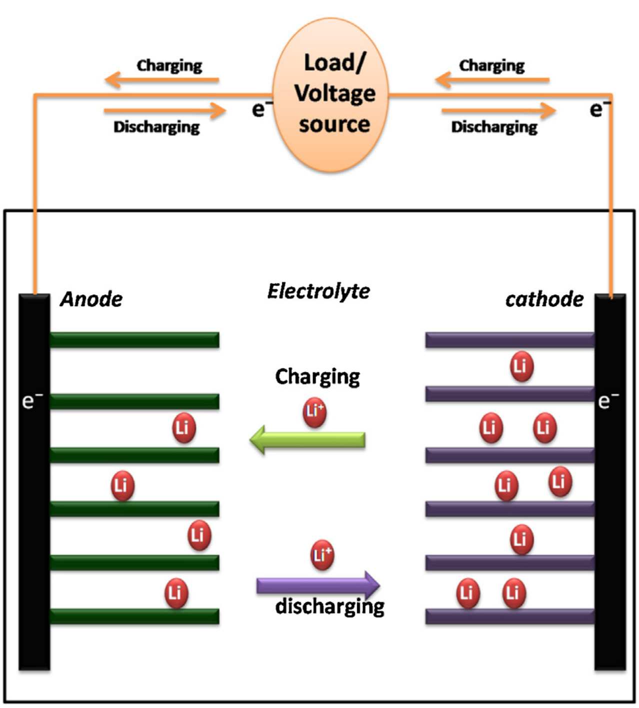

Fig. 1. Working principle of a typical Li-ion cell. The cell operates on the principle of cyclic transfer of Li ions between the anode and cathode.

A typical Li-ion cell consists of three parts, namely – anode, cathode and a conducting electrolyte. Energy is stored in the electrodes in the form of Li-intercalation compounds. Fig. 1 outlines rough schematics of a typical Li-ion cell. Cathode, generally made up of a lithium metal oxide, acts as positive terminal and anode, commercially composed of graphitic carbon, is the negative terminal of the cell. Electrolyte is usually a lithium salt such as $LiPF_6$ (Lithium hexafluorophosphate) or LiBOB (Lithium bis(oxalato)borate) dissolved in an organic solvent (ethylene carbonate or dimethyl carbonate for example). In an ideal Li-ion battery the lithium ion transfer number should be unity in the electrolyte.

The following half-reaction takes place at cathode:

$$LiMO_2 \leftrightarrow Li_{1-x}MO_2 + xLi^+ + xe^- \quad (1)$$

And the anode half-reaction is:

$$xLi^+ + xe^- + 6C \leftrightarrow Li_xC_6 \quad (2)$$

Eqs. (1) and (2) are in units of moles, x is the coefficient ordinarily one for a complete reaction, and M represents the metal with which lithium metal oxide is formed.

During charging, voltage applied across the electrodes derives the half reactions in the forward direction (i.e. from cathode to anode). Metal in the lithium metal oxide (cathode) is reduced to form lithium ions which are released into the electrolyte. These ions diffuse through the electrolyte and get inserted into the carbon/graphite anode. During the ion formation free electrons are also produced to maintain the charge neutrality. However, the electrolyte does not facilitate the conduction of free electrons through it. These electrons are subsequently driven across a wire connecting the two electrodes to provide the necessary electrons required for the insertion of Li ions into the anode. The voltage required to complete this process depends upon three parameters, namely – type of metal used in the lithium metal oxide; the material of the anode; and also the type of the electrolyte used. During discharging, the reaction takes place in the reverse direction (i.e. from anode to cathode) and the potential difference across the two electrodes drives the external load. So the electrons move from anode to cathode during the discharge cycle which causes positive current to originate from the cathode, making cathode to act as positive terminal of the cell/battery [1–3].