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Systematic gap analysis of carbon nanotube-based lithium-ion batteries and electrochemical capacitors

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ABSTRACT

Since the discovery of electricity, the demand for effective energy storage methods has increased. Energy storage devices are efficient tools used to manage power supply and produce resilient and cost-effective energy frameworks. Advanced technologies in modern economy and society require the application and design of inexpensive, highly efficient, and various infrastructures for energy storage systems. For instance, fuel cells, batteries, electrochemical capacitors, and conventional capacitors are used as energy storage devices because they can enhance energy or power densities. They can also supply energy within short or long periods. Their performances have also been improved. This review emphasizes carbon nanotubes as electrode materials for lithium-ion batteries and electrochemical capacitors. Different types of substrates and thin films may yield various structural and electrochemical properties of carbon nanotubes. This review also discusses their electrochemical performance observed through cyclic voltammetry and charge-discharge.

1. Introduction

With rapid global industrialization, the demand for energy storage has increased [1]. Energy storage systems, such as batteries and electrochemical capacitors (ECs), have been widely used and often equipped with nanostructured components. The use of nanomaterials, such as carbon nanotubes (CNT), for energy storage applications enhances energy or power densities and increases the overall performance and cost effectiveness of devices. Devices should possess high energy density that can be released rapidly to achieve an optimum energy storage performance. Thus, energy storage devices with high energy and power densities should be developed.

High costs of lithium-ion batteries (LIBs) have been greatly reduced through various methods, such as developing Li-ion with low-cost materials and modifying LIB manufacturing techniques [2]. Batteries have been used as the main electricity source. The first practical power source of electricity was used for electrical telegraphs and telephone networks. With the rapid development of high-power and high-energy-density batteries, various electrical devices, such as portable electronics, power tools [3,4], mobile phones, and electric vehicles [5–7], have been manufactured. Furthermore, rechargeable batteries have been used in highly versatile lead-acid batteries to replace primary batteries since they were introduced in 1860 [8]. Commercially available rechargeable batteries include Li-ion, nickel-cadmium (Ni-Cd), and nickel-metal-hydride (Ni-MH). LIBs have been used for high-performance rechargeable batteries because they possess higher energy density, longer lifetime, and light weight [9] than Ni-Cd and Ni-MH do; They were first commercialized by Sony Corporation in the early 1990s [10,11].

ECs are promising energy storage devices because of their high rate performance, stability, and low environmental impact [12]. ECs or supercapacitors have been used for many applications since they were first patented. Well-known companies, such as Panasonic and Maxwell Technologies, invest in the production of ECs for energy storage devices [13].

Carbon-based materials, especially CNTs, have been extensively investigated since they were discovered by Sumio Iijima in 1991 [14–19] and have been widely known as 21st century materials [20,21]. Their potential in many important applications has been explored because of their unique structural and physical features and excellent electrical, mechanical, and chemical properties [15,22]. CNTs are carbon allotropes, which appear as cylindrical carbon molecules composed of graphene sheets rolled into a seamless cylinder. Ideal CNTs possess crystalline structures formed by benzene molecules. Their unique one-dimensional structure with a curved sidewall is a paradigm in low-dimensional systems of inter-disciplinary research.

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CNTs are a good choice for high-power electrode materials [23], implantable microchips [24], and flexible and stretchable electronic [25] applications because of their large mesoporosity and high electrolyte accessibility. They can also be used for electrochemical energy storage and conversion systems, such as electrodes for ECs, Li-ion secondary batteries, and fuel cells [26]. CNTs are commonly classified into single-walled CNTs (SWCNTs) and multi-walled CNTs (MWCNTs). SWCNTs consist of single graphene sheet rolled into a cylindrical tube with a diameter measuring within the nanometer scale. The typical length of a SWCNT is between 1 and 100 μm. MWCNTs contain multiple concentric nanotubes with an inherently higher degree of impurities and defects than SWCNTs.

The performances of ECs and LIBs are determined on the basis of various criteria, such as electrolyte, electrode materials, and electrolyte and electrode interfaces [27]. The performances of ECs and LIBs can be enhanced by using electrode materials with a high specific area, a high electrical conductivity [28], and a wide operating voltage range [29].

Differences or gaps between CNT-based ECs and CNT-based LIBs should be elucidated to establish new approaches for the development of high-performance energy storage devices. This study aims to review the electrochemical performances of energy storage devices, such as LIBs and ECs, in terms of electrical charge storage ability (capacitance or capacity), life cycle, and rate capability because of the high demand for their use as power supplies in current technologies. This study also (1) provides a brief history of these devices, (2) presents their characteristics, potential applications, and commercial examples, (3) describes the significance, properties, structures, types, and applications of CNT-based electrode materials, and (4) discusses the main factors, such as electrode material, electrolyte, electrolyte, and electrode interfaces that help enhance the performances of these devices. Section 2 describes the batteries, mechanisms, types, components, such as cathodes and electrolytes, and electrochemical performance of CNT-based LIBs. Section 3 discusses the types of ECs and their components, including electrode materials and electrolytes, and the electrochemical performance of CNT-based ECs. This study also compares the characteristics of LIBs and ECs to predict the commercialization potential of energy storage devices.

2. Lithium-ion batteries (LIBs)

2.1. An overview of LIBs

Batteries are devices that convert stored chemical energy into electrical energy through a redox reaction involving cation reduction at the cathode and anion oxidation at the anode. A typical battery contains one or more electrochemical cells. Each cell is composed of two electrodes electrically connected via a conductive electrolyte exhibiting polarity caused by transporting anions and cations. LIB cells are composed of an electrolyte, an anode, and a cathode. These batteries are measured on the basis of the amount of electric charge that they deliver at a rated voltage known as capacity in unit amp-hour [28].

The mechanisms of rechargeable LIBs are based on a chemical process, namely, intercalation or insertion. Li-ions are extracted from the anode. They then migrate across the electrolyte into the crystal lattice of the cathode without changing the crystal structure during discharging. Ions are subsequently extracted from the cathode. They then migrate across the electrolyte into the crystal lattice of the anode without altering the crystal structure during charging [30] (Fig. 1).

Batteries can be divided into two types: rechargeable and disposable. Rechargeable batteries, including Ni-Cd, Ni-MH, Ni-Zn, lead-acid, and Li-ion cells, can be restored to their original composition through charging. Among electrochemical cells, LIBs are the most efficient because of their high energy density and moderate weight; LIBs do not also elicit memory effects. By contrast, disposable batteries, such as zinc-carbon and alkaline batteries [31], irreversibly convert chemical energy into electrical energy. They also yield a higher energy density than rechargeable batteries do.

2.2. Main components of LIBs

An anode typically consists of graphitic carbon or pure or composite metals, which act as the negative terminal of batteries during charging; a cathode typically consists of lithium metal oxides or transition metal oxides, which act as the positive terminal of batteries during discharging [28]. A separator is used to physically isolate anode and cathode electrodes and ensure safe operation. It also permits the diffusion of Li ions from the anode to the cathode during discharging and from the cathode to the anode during charging [32]. Carbon-based materials and Li-based alloys are common anode materials used for LIB applications. Both materials reduce Li activity compared with Li metal, which decreases the reactivity with electrolyte, reduces the cell voltage, and improves safety [33]. Compared with graphite, nanostructured carbon materials, including CNTs, have been widely investigated for use as anode materials in LIBs because their unique structure allows a rapid insertion or de-insertion of Li ion [34]. Negative graphite electrodes, such as mesocarbon microbeads, are an example of materials used in LIBs [35].

Cathodes are normally formed by Li metal oxides (e.g., $LiCoO_2$, V_2O_5, and $LiMO_2$) and transition metal oxides [e.g., $LiFePO_4$ and $Li_3V_2(PO_4)_3$], which are widely used as cathode materials in LIBs [36]. Vanadium oxides possess useful properties as rechargeable lithium cathode materials. Nanostructured vanadium oxides have been synthesized in the form of nanoribbons and nanowires in room-temperature ionic liquid (RTIL) by using $[C_3mpyr][NTf_2]$ containing 1 M $LiNTf_2$ as an electrolyte [37]. Porous nanostructured $LiFePO_4$ powders with a narrow particle size distribution of 100–300 nm are widely used as high-rate LIB cathodes [38]. Nanostructured $LiFePO_4$ with carbon nanocomposites consisting of monodispersed nanofibers of a $LiFePO_4$ electrode material mixed with an electronically conductive carbon matrix have also been used as cathode materials [39]. Likewise, nanostructured electrodes composed of intrinsically conducting polymers, such as poly(aniline) or poly(methylthiophene) and CNTs are excellent cathode materials for LIBs. A polyaniline (PANI)/MWCNT composite has been synthesized through in situ chemical polymerization and used as an active cathode material in lithium metal-polymer cells with IL electrolyte [40].

Electrolytes are typically classified as aqueous, non-aqueous, solid, or gel-type polymers. They can form a solution containing a lithium salt mixed with organic solvents, such as $LiPF_6$ mixed with ethylene carbonate-dimethyl carbonate (EC-DMC) embedded in a separator felt [35]. They can also form a mixture of organic carbonates, such as ethylene carbonate or diethyl carbonate, containing Li-ion complexes [41]. Fenton et al. [42] investigated polymer electrolytes when they were launched in 1973. Armand et al. then introduced alkali metal salts and poly(ethylene oxide) in the form of crystalline complexes for their potential use as electrolytes in batteries because of their excellent ionic conductivity. Solid or gel-type polymers have been widely used as electrolytes in LIBs [43] because they allow electrolyte leakage, prevent internal shorting, and generate non-combustible reaction products at electrode surfaces existing in liquid electrolytes [44].

2.3. Electrochemical performance of CNT-based LIBs

CNTs are grown on a round stainless steel foil through plasma-enhanced chemical vapor deposition (PECVD) [45]. Scanning electron microscopy (SEM) reveals that the diameters of CNT-Ni-Si core shell nanowires are increased from 200 nm to 400 nm. During galvanostatic cycling, the initial de-lithiation capacity is 2527 mA h g^{-1}, and this value continuously increases in the second cycle after the capacity remains stable. Surface activation against electrochemical reactions may reduce the initial capacity. After 110 cycles, the capacity is