

Recent Progress in Lithium Ion Battery Technology

Author's Details:

Ramalan, A. M^{*1}., Yusuf A. S²., Umar M., Buba, A. D. A

¹Department of Physics, University of Abuja ²Department of Physics, Federal university of technology minna

Abstract

this paper is aimed at giving a detailed review on the recent advancements in lithium ion battery technology focusing on the underlying principle; design and configuration; materials; fabrication techniques; application; and challenges of lithium ion batteries (LIBs). The first rechargeable Li-ion batteries with cathode of layered TiS₂ and anode of metallic Li was reported by Whittingham while working at Exxon in 1976 but this invention was not successful due to the problems of Li dendrite formation and short circuit upon extensive cycling and safety concern. However, there was a turnaround when Goodenough offered a theoretical framework for possible materials for effective intercalation/deintercalation and Yohsino carried out the first safety test on Li-ion batteries to demonstrate their enhanced safety features. LIBs consist of two electrodes, anode and cathode, immersed in an electrolyte and separated by a polymer membrane; and works by converting chemical energy into electrical energy and vice versa through charging and discharging processes. Most of the LIB models are derived from the porous electrode and concentrated solution theories which mathematically describe charge/discharge and species transport in the solid and electrolyte phases across a simplified 1D spatial cell structure. The cathode materials can be categorized based on voltage, typically 2-Volt, 3-Volt, 4-Volt and 5-Volt and currently LiCoO₂ and LiFePO₄ are most widely used in commercial Li-ion batteries because of their good cycle life (>500 cycles). Carbon is a dominant anode material although there are other materials available such as Nixelion; the choice of anode materials significantly influences the electrochemical performances, including cyclability, charging rate, and energy density of Li-ion batteries. A typical liquid electrolyte is a solution of lithium salts in organic solvents which must be carefully chosen to withstand the redox environment at both cathode and anode sides and the voltage range involved without decomposition or degradation. Separators are essential components of Li-ion batteries and plays a critical role to avoid direct physical contact between the cathode and anode, and prevents short circuit to occur. A number of benefits are offered by this technology such as lightweight, high energy density power sources for a variety of devices. However, cost is one of the major challenges in the development of LIBs, another issue that is yet to be resolved is that the battery capacity tends to fade upon electrochemical cycling. Hence, if the opportunities embedded in the LIB technology is properly harnessed, there will create an economically viable environment.

1.1 Introduction

The rapidly growing energy demands has given rise to a large increase in demand for more efficient, sustainable and renewable energy resources. Recent statistics shows that our society relies on fossil fuels for most of its energy needs and the combustion of these fossil fuels leads to the emission of greenhouse gases into the atmosphere. Global warming is a direct consequence of the accumulation of greenhouse gases. Internal combustion engines are a major source of CO₂ emission and hence alternative energy sources for automotive propulsion applications is one of the prime focuses of research throughout the world (Deshpande, 2011).

The renewable sources such as solar energy and wind energy are “green” sources of energy but these are intermittent sources. Energy may be available in amounts and at times and places that are different from those when and where one is in need of it; but for a continuous use, storage of energy is necessary. Thus, methods to store and transport energy from place to place can be of great importance, storage in chemical form is often a useful intermediate stage; this may involve the use of electrochemical systems and devices that act as transducers to convert between electrical and chemical quantities – energies, potentials, and fluxes (Huggins, 2009). Such electrochemical transduction systems are often called galvanic cells or

batteries with which one can store energy in the form of chemical potential difference and use it whenever and wherever it is needed (Huggins, 2009; Deshpande, 2011).

A major advantage of electrochemical transduction methods is that they can operate isothermally and thus avoid the so-called Carnot limitation (Huggins, 2009). This makes it possible to achieve much greater efficiencies than are available by the use of thermal conversion processes. In many cases, electrochemical cells can also be operated in the reverse direction. Thus, it is possible to devise reversible electrochemical systems in which electrical energy is converted to chemical energy (the chemical system is charged), and the process can later be reversed to give electrical energy again (the chemical system is discharged) (Huggins, 2009).

The application of batteries in different market segments has been growing at a very high rate and their requirements have been putting ever-increasing incentives on the development of better, and lower cost, energy storage devices and systems. This has led to a lot of research and development activity, and there have been a number of important technological changes in recent years. A number of these have not been just incremental improvements in already-known areas, but involve the use of new concepts, new materials, and new approaches. An important reason for this progress has been the fact that such things as the discovery of fast ionic conduction in solids and the possibility of solid electrolytes, the concept of the use of materials with insertion reactions as high-capacity electrodes, and the discovery of materials that can produce lithium-based batteries with unusually high voltages have caused a number of people with backgrounds in other areas of science and technology to be drawn into this area. The result has been the infusion of new materials, concepts, and techniques into battery research and development (Huggins, 2009).

Furthermore, among the various presently available battery technologies such as lead-acetate battery, metal-hydride battery, nickel-cadmium battery, lithium ion battery, among others, lithium based batteries are known to have the highest gravimetric and volumetric energy storage capacity (Deshpande, 2011; Obrovac *et al.*, 2007).

1.2 Li-Ion Batteries (LIBs)

Li-ion batteries are currently the dominant mobile power sources for portable electronic devices, exclusively used in cell phones and laptop computers (Deng *et al.*, 2009). Li-ion batteries are considered the powerhouse for the personal digital electronic revolution starting from about two decades ago, roughly at the same time when Li-ion batteries were commercialized (Deng, 2015). As one may have already noticed from his/her daily life, the increasing functionality of mobile electronics always demand for better Li-ion batteries. For example, to charge the cell phone with increasing functionalities less frequently as the current phone will improve quality of one's life. Another important expanding market for Li-ion batteries is electric and hybrid vehicles, which require next-generation Li-ion batteries with not only high power, high capacity, high charging rate, long life, but also dramatically improved safety performance and low cost (Deng, 2015).

The demand for Li-ion batteries increases rapidly, especially with the demand from electric-powered vehicles. It is expected that nearly 100 GW hours of Li-ion batteries are required to meet the needs from consumer use and electric-powered vehicles with the later takes about 50% of Li-ion battery sale by 2018 (Yoshino, 2012). Furthermore, Li-ion batteries will also be employed to buffer the intermittent and fluctuating green energy supply from renewable resources, such as solar and wind, to smooth the difference between energy supply and demand. For example, extra solar energy generated during the daytime can be stored in Li-ion batteries that will supply energy at night when sun light is not available. Large-scale Li-ion batteries for grid application will require next-generation batteries to be produced at low cost.

2.0 LITERATURE REVIEW

This chapter briefly reviews the history on the development of Li-ion batteries. It presents a basic concept, design and configuration, principle of operation. Recent experimental advances in Li-ion batteries are equally discussed.

2.1 Historical Overview: Invention and development of Li-ion batteries

Batteries are so ubiquitous today that they are almost invisible to us, yet they are a remarkable invention with a long and storied history, and an equally exciting future. Batteries have been with us for a long time. American scientist and inventor Benjamin Franklin first used the term “battery” in 1749 when he was doing experiments with electricity using a set of linked capacitors (Alarco and Talbot, 2015). The first true battery was invented by the Italian physicist Alessandro Volta in 1800. The chronological development of the battery technology is summarised in Table 2.1.

The first rechargeable Li-ion batteries with cathode of layered TiS_2 and anode of metallic Li was reported by Whittingham while working at Exxon in 1976 (Whittingham, 1976). Exxon subsequently tried to commercialize the Li-ion batteries, but was not successful due to the problems of Li dendrite formation and short circuit upon extensive cycling and safety concern (Levine, 2010). Also in 1976, Besenhard proposed to reversibly intercalate Li^+ ions into graphite and oxides as anodes and cathodes, respectively. In 1981, Goodenough first proposed to use layered LiCoO_2 as high energy and high voltage cathode materials. Interestingly, layered LiCoO_2 did not attract much attention initially (Mizushima *et al.*, 1981; Deng, 2015).

Table 2.1 Chronological development of battery technology (Dunning, 2016; LaVine, 2017; Richard, 2017)

Year	Inventor/National	Type of Invention
1791	Galvani (Italy)	Animal Electricity
1800	Alessandro Volta (Italy)	Invention of Voltaic Cell (Cu/brine/Zn)
1833	Michael Faraday (UK)	Faraday's Law of Electrolysis
1836	John Daniel (UK)	Daniel Cell (Cu/CuSO ₄ //ZnSO ₄ /Zn)
1868	Georges Leclanche (France)	$\text{Zn(s)} + 2 \text{MnO}_2\text{(s)} + 2 \text{NH}_4\text{Cl(aq)} \rightarrow \text{ZnCl}_2 + \text{Mn}_2\text{O}_3\text{(s)} + 2 \text{NH}_3\text{(aq)} + \text{H}_2\text{O}$
1899	Waldemar Jungner (Sweden)	$\text{Cd} + 2\text{NiO(OH)} + 2\text{H}_2\text{O} = \text{Cd(OH)}_2 + 2\text{Ni(OH)}_2$
1901	Thomas Edison (USA)	$\text{Fe} + 2\text{NiO(OH)} + 2\text{H}_2\text{O} = \text{Fe(OH)}_2 + 2\text{Ni(OH)}_2$
Mid 1960s	Union Carbide (USA)	$\text{Zn (s)} + 2\text{MnO}_2\text{(s)} \rightarrow \text{ZnO (s)} + \text{Mn}_2\text{O}_3\text{(s)}$
1970s	Various	Valve Regulated Lead Acid Cells
1981		
1990	Various	$\text{MH} + \text{NiO(OH)} = \text{M} + \text{Ni(OH)}_2$
1980s/90s	John Goodenough (USA)/Yoshino Akira (Japan)	Lithium Ion Batteries
2017	Helena Braga (Portuga)/John Goodenough (USA)	Glass Lithium Ion Batteries (Controversial)

In 1983, Goodenough also identified manganese spinel as a low-cost cathode material. However, the lack of safe anode materials limited the application of layered oxide cathode of LiMO_2 ($\text{M} = \text{Ni, Co}$) in Li-ion batteries. It was discovered that graphite, also with layered structure, could be a good candidate to reversibly store Li by intercalation/deintercalation in late 1970s and early 1980s (Deng, 2015). In 1987, Yoshino *et al.* filed a patent and built a prototype cell using carbonaceous anode and discharged LiCoO_2 as cathode (Deng, 2015). Both carbon anode and LiCoO_2 cathode are stable in air which is highly beneficial from the engineering and manufacturing perspectives. This battery design enabled the large-scale manufacturing of Li-ion batteries in the early 1990s (Deng, 2015).

Yoshino carried out the first safety test on Li-ion batteries to demonstrate their enhanced safety features without ignition by dropping iron lump on the battery cells, in contrast to that of metallic lithium batteries which caused fire (Yoshino, 2012). Yoshino's success is widely considered the beginning of modern commercial Li-ion batteries. Eventually Sony, dominant maker of personal electronic devices such as Walkman at that time, commercialised Li-ion batteries in 1991. It was a tremendous success and supported the revolution of personal mobile electronics. To acknowledge their pioneering contribution to the development of Li-ion battery, Goodenough, Yazami, and Yoshino were awarded the 2012 IEEE Medal for Environmental and Safety Technologies (Deng, 2015). Japan is still leading the share of global Li-ion battery market dominating 57% global market in 2010 (Deng, 2015). In the past two decades, there is some notable progress in development of Li-ion batteries, particularly the introduction of low-cost cathode of LiFePO_4 by Goodenough in 1996 and high capacity anode of C-Sn-Co by Sony in 2005 (Deng, 2015). The

recent development of high capacity anode based on nanostructured silicon (theoretical-specific capacity of 4200 mAh/g) is also worthy to be highlighted (Deng, 2015). In 1990s, Dahn and colleagues pioneered the exploration of composites of C/Si obtained from pyrolysis of silicon-containing polymers as promising candidate as anode materials for Li-ion batteries (Deng, 2015).

In 2017, a team of researcher at The University of Texas at Austin led by Goodenough announced the development of a glass Lithium ion battery which could achieve up to a 10-fold improvement in energy density—the amount of energy stored—in one case, and a three-fold improvement in another (LaVine, 2017). In one experiment, Goodenough estimates a 30-fold improvement on the best density in a lithium-ion battery today—8,500 watt-hours per kilogram. Moreover, this was accomplished not using exotic materials, but cheap sodium and sulfur. That means, unlike many other reported battery breakthroughs, this one could actually be used in mainstream-priced cars (LaVine, 2017). This discovery has since generated a lot of controversies among scientists on the law guiding the operation of the newly discovered invention. (LaVine, 2017).

2.2 Mechanism of Operation: Design and Configuration of the Li-Ion Batteries

2.3 Theoretical Framework

Most of the current rigorous Li-ion battery models are derived from the porous electrode and concentrated solution theories proposed by Newman and Tiedemann (1975) and Doyle *et al.* (1993) which mathematically describe charge/discharge and species transport in the solid and electrolyte phases across a simplified 1D spatial cell structure. This 1D model of a Li-ion battery considers dynamics along only one axis (the horizontal x-axis) and neglects the dynamics along the remaining two axes (y-axis and z-axis) (Dao, Vyasarayani, & McPhee, 2012). This approximation is applicable to most cell structures as the length scale of a typical Li-ion cell along the x-axis is on the order of 100 μm , whereas the length scale for the remaining two axes is on the order of 100,000 μm or more (Chaturvedi, Klein, Christensen, Ahmed, & Kojic, 2012).

Mathematical models could play a crucial role in guiding the development of new intercalation materials, electrode microstructures, and battery architectures, in order to meet the competing demands in power density and energy density for different envisioned applications, such as electric vehicles or renewable (e.g. solar, wind) energy storage. Porous electrode theory (PET), pioneered by J. Newman and collaborators, provides the standard modelling framework for battery simulations today (Ferguson, 2014).

In porous electrode theory for Li-ion batteries, transport is modelled via volume averaged conservation equations (DeVidts & White, 1997). The solid active particles are modelled as spheres, where intercalated lithium undergoes isotropic linear diffusion. For phase separating materials, such as Li_xFePO_4 (LFP), each particle is assumed to have aspherical phase boundary that moves as a ‘shrinking core’, as one phase displaces the other (Ferguson, 2014). In these models, the local Nernst equilibrium potential is fitted to the global open circuit voltage of the cell, but this neglects non-uniform composition, which makes the voltage plateau an emergent property of the porous electrode (Ferguson, 2014). For thermodynamic consistency, all of these phenomena should derive from common thermodynamic principles and cannot be independently fitted to experimental data. The open circuit voltage reflects the activity of intercalated ions, which in turn affects ion transport in the solid phase and Faradaic reactions involving ions in the electrolyte phase (Bazant, 2013).

2.4 Experimental Framework

Current rechargeable batteries based on ion insertion/extraction in electrodes, including Li-, Na-, Mg-, and Al-ion batteries, have been increasingly studied in both the academia and industry (Liu *et al.*, 2016). However, sodium, magnesium, and aluminum have a lesser reducing effect than lithium (- 2.71, - 2.37, and - 1.66 V vs. S.H.E. (Standard hydrogen electrode), respectively, compared with - 3.04 V for Li) as well as low gravimetric capacities (1165, 2046, and 2978 mAh/g, respectively; compared with lithium, 3850 mAh g^{-1}) (Liu *et al.*, 2016). Thus, devices based on metallic sodium, magnesium, or aluminum anodes have lower

energy densities and operating voltages than those with lithium metal anodes (Huie, Bock, Takeuchi, Marschilok, & Takeuchi, 2015; Liu, Neale, & Cao, 2016).

To date, only Li-ion rechargeable batteries have been successfully commercialized and become an irreplaceable power source. In Li-ion rechargeable batteries, the cathodes that store lithium ions via electrochemical intercalation must contain suitable lattice sites or spaces to store and release working ions reversibly. Robust crystal structures with sufficient storing sites are required to produce a material with stable cyclability and high specific capacity (Liu *et al.*, 2016). In addition, a cathode with high electrochemical intercalation potential can be used to develop a high energy density battery with a given anode. This is because the energy density of the device equals the product of the specific capacity of the electrode materials and the working voltage that is determined by the differential electrochemical potentials between the cathode and anode (Liu *et al.*, 2016).

The energy density and power density of a battery are two parameters essential to evaluating its practical performance, and they are commonly presented in Ragone plots (Dubal, Ayyad, V. Ruiz, & Gómez-Romero, 2015). Although batteries offer a much higher energy density than electric double-layer capacitors (EDLCs), also often referred to as supercapacitors or ultracapacitors, and electrochemical pseudocapacitors, they possess relatively lower power density and shorter cyclic life (Liu, Neale, & Cao, 2016). A significant number of studies have been conducted on the synthesis and characterization of various nanostructured cathode and anode materials with large specific surface area and short solid-state transport distance, offering an enhanced power density as well as a better cyclic stability (Liu, Neale, & Cao, 2016). The energy storage performance has been enhanced by conformably applying a thin (typically a couple of nanometres) and porous carbon film (with a pore size of a few nanometers or less) on nanostructured cathode or anode materials (Liu, Neale, & Cao, 2016). Other carbon materials including carbon nanotubes, graphene, and graphene oxide have been introduced into electrodes as electrically conductive additives, structural stabilizers, reactive precursors, or catalysts/promoters, leading to a significant enhancement in the electrical energy storage performance of electrodes and batteries (Liu, Neale, & Cao, 2016). A high power density can also be obtained by fabricating hybrid supercapacitor batteries. However, enhancement of the energy density in a battery is limited by the lithium-ion storage capacity and the cell potential. The storage capacity is determined by the amount of lithium ions that can be reversibly inserted and extracted through a reversible first-order phase transition in intercalation reactions under the operating conditions of the battery (Liu, Neale, & Cao, 2016).

The electrochemical potential varies with the materials in question, showing a direct correlation with their electronic configuration. Considerable research efforts have been devoted to achieving large specific capacity, good cyclic stability, and high rate capability in electrode materials (Liu, Neale, & Cao, 2016). However, experimental studies on controlling and tuning the electrochemical potentials of electrode materials are limited, although some notable theoretical studies have calculated and analysed electrochemical potentials based on the electronic structure and atomistic potentials (Islam & Fisher, 2013). The cell voltage and electrochemical potentials of electrode materials can provide insight for designing and developing suitable materials for batteries with high energy density in the future.

The choice of electrodes depends upon their electrochemical potential values (μ_A for anode and μ_C for cathode) as well as their positions to the highest occupied molecular orbital – lowest unoccupied molecular orbital (HOMO-LUMO) energy gap (E_g) of electrolyte (Roy & Srivastava, 2015). For a stable cell, μ_A must be lower in energy than the LUMO of electrolyte, otherwise the electrolyte will be reduced and on the other hand μ_C position should be in higher energy than HOMO of electrolyte to inhibit the oxidation of electrolyte as shown in Figure 2.2 (Goodenough, 2013). The high-energy storage density can be achieved in a cell with maximum electrochemical potential difference of anode and cathode as well as their high lithium intercalation ability though at the same time the stability of electrolyte should not be overlooked (Roy & Srivastava, 2015).

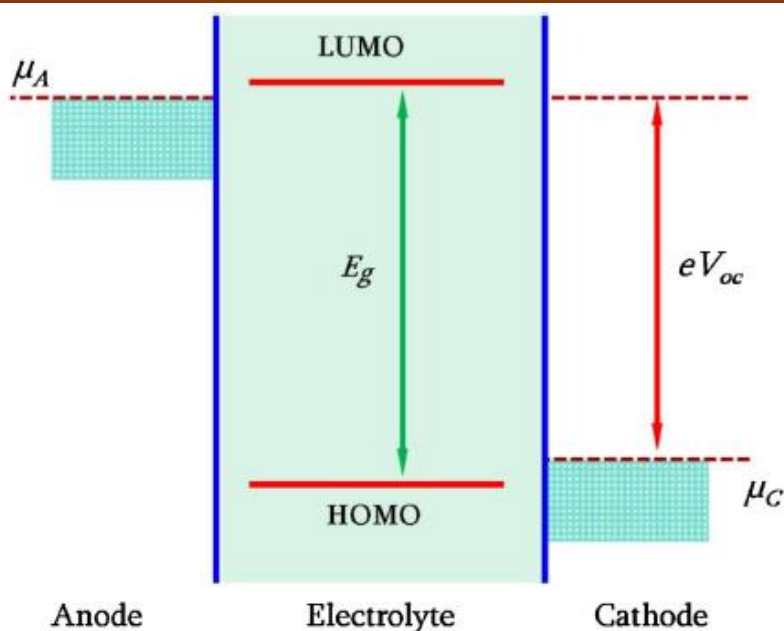


Figure 2.1 Relative energies of the electrolyte window, E_g , and the relationship between electrochemical potentials of electrodes and the HOMO or LUMO of the electrolyte (Liu, Neale, & Cao, 2016)

2.4.1 Voltage of a Battery

Cell voltage is determined by the compatibility of the whole system, including the anode, cathode, and electrolyte. In particular, the difference in chemical potential between the anode (m_A) and the cathode (m_C) is termed as the working voltage, also known as the open circuit voltage, V_{oc} (Obrovac and Chevrier, 2014):

$$V_{oc} = \frac{(\mu)_A - \mu_C}{e} \quad (2.)$$

where e is the magnitude of the electronic charge. This working voltage is also limited by the electrochemical window of the electrolyte, which, as illustrated in Figure 2, is determined by the energy gap from the highest occupied molecular orbital (HOMO) to the lowest unoccupied molecular orbital (LUMO). The anode and cathode must be selected such that the m_A of the anode lies below the LUMO and the m_C of the cathode is located above the HOMO; otherwise, the electrolyte will be reduced on the anode or oxidised on the cathode to form a passivating solid electrolyte interphase (SEI) film (Pistoia & Nazri, 2003). It is worth noting that this SEI film permits the diffusion of Li ions through the film under a uniform electric field and reduces the over potential and concentration polarization (Park, 2012). The SEI can also prevent the aggregation of electrochemically active particles and maintain a uniform chemical composition at the electrodes.

2.4.2 Potential Hysteresis

Hysteresis is always observed between the charge and discharge curves in all charge/discharge measurements of electrode materials, which can be explained in two ways. First, Goodenough (2013) consider the charge potential to be greater than the discharge potential (Figure 4a) due to the polarization arising from the internal resistance of the electrode materials (Goodenough and Park, 2013).

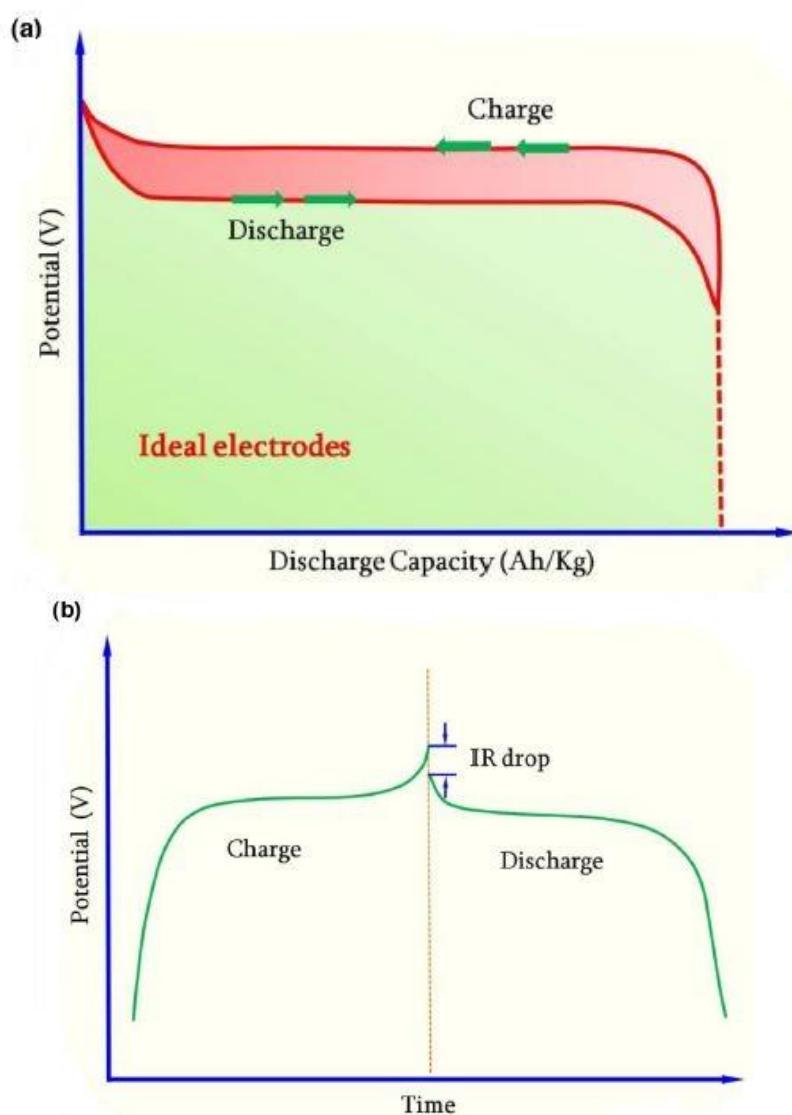


Figure 2.2 (a) Potential hysteresis in the charge/discharge procedure of an ideal insertion electrode material. (b) The potential drop in the interval between charge and discharge.

This polarization decreases the discharge potential below the open circuit voltage, and it increases the charge potential to reverse the chemical reaction on the electrode. In addition, the internal resistance drop (IR drop) also leads to a drop in potential (drop in IR) between the end of charge and the beginning of discharge (Figure 4b). Second, over potential is the driving force behind electrochemical phase transitions in insertion electrodes (Tang, Carter, & Chiang, 2010).

The plateau on the potential–capacity curve indicates the two-phase coexistence region of the phase transition, and the span of the plateau represents the width of the miscibility gap. In general, phase transitions during the charge step are accompanied by the extraction of Li ions from the host lattice and the dragging of electrons from the d orbitals of transition metal ions. Likewise, Li ions and electrons are inserted into the relative lattice positions and electronic orbitals during discharge. It is worth noting that the corresponding energy changes are different in this reversible phase transition. During the discharge step, Li ions enter the interstitial space of the host lattice and electrons are accepted into the transition metal d orbital, followed by an energy decrease and phase stabilization. However, in reverse, more energy is consumed as ions and electrons must be promoted from the lower energy states. In particular, the energy spent during charge is slightly higher than that delivered during discharge. This energy difference is the source of the potential gap between the charge and discharge curves. Thus, a higher over potential results in a phase transition at the electrode during the charge procedure. The IR drop originates from the change of internal resistance, including the resistance of the electrolyte, electrode materials, and other connectors or

auxiliaries. The drawback of the IR drop includes energy consumption, leading to a decrease in the efficiency of the battery and the safety issues from the released heat. These resistances can be decreased or eliminated to overcome the side effects efficiently. Effective approaches used in laboratories or factories include a conductive coating on the surface of active materials (Su, Jing, & Zhou, 2011), which enhances the performance of the connecting components and makes use of the highly conductive auxiliaries.

3.0 MATERIALS AND FABRICATION TECHNIQUES

A basic Li-ion cell consists of a cathode (positive electrode) and an anode (negative electrode) which are contacted by an electrolyte containing lithium ions. The electrodes are isolated from each other by a separator, typically microporous polymer membrane, which allows the exchange of lithium ions between the two electrodes but not electrons. This chapter highlights the materials for the fabrication of Li-ion batteries (LIBs). An overview of the recent advances in fabrication techniques of Li-ion batteries (LIBs) is given.

Various sections including electrode (anode and cathode), electrolytes, separators and electrode-electrolyte interface and also different types of these materials are discussed. The selection criteria of electrode materials for lithium-ion batteries are discussed, including societal, economical, and technical considerations. These include their natural abundance; lack of competition with other industrial applications; eco-friendly nature for processing, usage and recycle; and low cost.

3.1 Electrode Materials

The electrode (cathode and anode) and electrolyte are the most important active materials that determine the performance of a Li-ion battery. As anode materials offer a higher Li-ion storage capacity than cathodes do, the cathode material is the limiting factor in the performance of Li-ion batteries (Liu, Neale, & Cao, 2016). The energy density of a Li-ion battery is often determined collectively by the Li-ion storage capacity and the discharge potential of the cell. The factors determining the Li-ion storage capacity through intercalation are as follows: (1) the capability of the host, or the electrode, to change the valence states; (2) the available space to accommodate the Li ions; and (3) the reversibility of the intercalation reactions. The discharge potential of a cathode is directly proportional to the reduction of Gibbs free energy when Li ions are inserted into the electrode (Liu, Neale, & Cao, 2016).

3.1.1 Cathode Materials

There are a number of candidates that have been explored as cathode materials for Li-ion batteries. The cathode materials can be categorized based on voltage versus lithium. Typically: 2-Volt cathode materials are TiS_2 and MoS_2 with 2-D layered structure; 3-Volt cathode materials are MnO_2 and V_2O_5 ; 4-Volt cathode materials are LiCoO_2 , LiNiO_2 with 2-D layered structure and 3-D spinel LiMn_2O_4 and olivine LiFePO_4 ; 5-Volt cathode materials are olivine LiMnPO_4 , LiCoPO_4 , and $\text{Li}_2\text{M}_x\text{Mn}_{4-x}\text{O}_8$ ($\text{M} = \text{Fe}, \text{Co}$) spinel 3-D structure. Generally, high cathode voltage is desirable as energy stored is proportional to the cell operating voltage. However, electrolyte stability has to be taken into consideration in selecting high voltage cathode materials (Deng, 2015).

Currently LiCoO_2 and LiFePO_4 are most widely used in commercial Li-ion batteries because of their good cycle life (>500 cycles). LiCoO_2 can be easily manufactured in large scale and is stable in air. Its practical capacity is ~140 mAh/g and the theoretical capacity is 274 mAh/g upon full charge (Deng, 2015). In addition to its low practical capacity, other noticeable disadvantages of the LiCoO_2 are their high material cost and the toxicity of cobalt. On the other hand, LiFePO_4 -based cathode materials are attracting much attention in the past decade due to its low cost and low environmental impact. Compared to LiCoO_2 , LiFePO_4 also offers a number of advantages, such as stability, excellent cycle life, and temperature tolerance (-20 to 70°C). However, LiFePO_4 has a problem of poor electronic and ionic conductivity at 10⁻¹⁰ S/cm and 10⁻⁸ cm²/sec, respectively, as well as relatively low capacity (Chung & Chiang, 2002). The other issue is one-dimensional channels for lithium ion diffusion which can easily be blocked by defects and impurities.

3.1.2 Anode Materials

Anode materials are extensively investigated and there is a bigger pool of candidates and materials. The electrochemical performances, including cyclability, charging rate, and energy density of Li-ion batteries are significantly affected by anode materials selected. Since the first commercialization of carbonaceous anodes, carbon is still dominant in commercial Li-ion batteries today (Deng, 2015). Graphitic carbon with layered structure can facilitate the movement of lithium ions in and out of its lattice space with minimum irreversibly, resulting in an excellent cyclability (Megahed & Scrosati, 1994). However, the carbon anodes are soon approaching their theoretical maximum capacity of 372 mAh/g over the past two decades of development. Carbon alternatives with high-energy density and enhanced safety are required to meet the demands for increases in energy and power densities, especially to meet the demands from electric vehicles (Deng and Lee, 2013). Fuji Film introduced tin composite oxide (TCO) as a carbon alternative in 1997 but was not very successful due to the poor cycling performance (Idota *et al.*, 1997). Sony Cooperation announced new-generation Li-ion batteries with the trade name of Nexelion in 2005. The anode of Nexelion is based on a carbon–tin–transition-metal composite (e.g., Sn–Co–C), and the compound is mainly amorphous or microcrystalline aggregates. Those efforts have rekindled another wave of interest in anode materials for Li-ion batteries (Deng, 2015).

Besides Sn, many other elements that are known to alloy with lithium, including silicon, are good candidates to replace carbon for lithium storage. These elements could alloy and de-alloy with lithium electrochemically at room temperature. However, the alloying/dealloying process during charging/discharging is accompanied by substantial variations in the specific volume of the material. The induced huge mechanical stress could lead to the destruction of the crystal structures and disintegrate the active materials and current collectors within a few cycles, or the so-called “pulverization” issue (Deng, 2015). The resulting poor cyclability has significantly limited their usability in practical situations. The engineering approach to solve the poor cyclability problem is to introduce composites. In such a composite material, one component (usually carbon) functions as a stress absorber whereas the other (such as silicon or tin) provides the boost in capacity. Through this approach a composite with capacity higher than carbon and cyclability better than Sn or Si can be achieved. A number of combinations involving carbon have been explored, among them Si/C (Dimov, Xia, & Yoshio, 2007) and SnO₂/C (Winter & Besenhard, 1999) have attracted much interest.

Other carbon-based materials that have been extensively studied are buckminsterfullerene, carbon nanotubes, and graphene. Carbon nanotubes, in particular, can be a good lithium host on grounds of their excellent electronic conductivity and other properties associated with their linear dimensionality (Baughman, Zakhidov, & deHeer, 2002; Che, Lakshmi, Fisher, & Martin, 1998). However, current interest is focused on CNT-and graphene-based composites instead of pristine CNTs or graphene to achieve much higher capacity than that of pristine carbon (Wang, Zeng, & Lee, 2006; Kumar, Ramesh, Lin, & Fey, 2004). Another family of anode materials with high capacity is metal oxides, although metal oxides are generally poor in conductivity, properly tailored metal oxides at nanoscale have demonstrated promising characteristics (Deng, 2015).

3.2 Electrolytes

Electrolyte must be carefully chosen to withstand the redox environment at both cathode and anode sides and the voltage range involved without decomposition or degradation. Additionally, electrolyte should be inert and stable in an acceptable temperature range. In commercial Li-ion batteries, typically a liquid electrolyte is a solution of lithium salts in organic solvents. However, the existing organic liquid electrolyte can potentially catch fires under conditions of thermal runaway or short circuit due to volatile and flammable nature of the solvents which are highly toxic. Ideally, the electrolyte should also be environmentally benign and can be produced at low cost in the future (Deng, 2015). Polar aprotic organic solvents, such as carbonate solvents with high dielectric constant, are selected to solvate lithium salts at a high concentration (1 M typically). On the other hand, solvents with low viscosity and low melting point are required to meet the requirement for high ionic mobility in the operating temperature range. Various organic solvents have been explored, including dimethyl carbonate, diethyl carbonate, ethyl methyl carbonate,

propylene carbonate, ethylene carbonate, diethoxyethane, dioxolane, γ -butyrolactone, and tetrahydrofuran. Heteroatom-containing organic solvents have also been explored. Various lithium salts have been explored, including LiPF_6 , LiBF_4 , LiAsF_6 , LiClO_4 , and LiCF_3SO_3 (Deng, 2015). It should be noticed that anions are selected to avoid being oxidized on the charged surface of cathodes, which rules out those simple anions of Cl^- , Br^- , and I^- . LiPF_6 is a particular outstanding lithium salt from the perspective of safety, conductivity and the balance between ionic mobility and dissociation constant. However, LiPF_6 can react with water to form highly corrosive HF. Therefore, moisture must be minimized in handling of LiPF_6 electrolyte. In fact, the success of first commercial Li-ion batteries could be ascribed to the industrial scale availability of high-purity LiPF_6 with minimal amount of water (Deng, 2015).

The solvents are typically formulated and mixed to address the requirements on viscosity, conductivity and stability and to match with the lithium salts selected. For example, high dielectric solvents with high viscosity are typically mixed and balanced with solvents with low viscosity to achieve a liquid state electrolyte within a required temperature window (Deng, 2015). The commonly used electrolyte is 1M LiPF_6 in a 50:50 w/w mixture of ethylene carbonate (EC, melting point of 34°C and boiling point of 260.7°C) and diethyl carbonate (DEC, melting point of $2-4^\circ\text{C}$ and boiling point of 90°C) or dimethyl carbonate (DMC, melting point of 2°C and boiling point of 90°C). Generally, the EC can bind Li^+ ions more strongly than DEC or DMC (Zhu, Ng, & Deng, 2014). The formulated electrolyte offers reasonably good stability over a wide potential range. Additives to further enhance the electrolyte stability and improve the formation of good solid-electrolyte interphase (SEI) are also added in many cases. The various formulated additives in terms of chemical compositions and percentages used by different companies in making Li-ion batteries could be considered business secrets (Deng, 2015).

Other types of electrolyte have also been developed and proposed for Li-ion batteries, such as polymer, gel and ceramic electrolyte. Polymer electrolytes are solvent-free using high molecular weight-based polymers with dissolved lithium salts (Croce, Appetecchi, Persi, & Scrosati, 1998). One should be aware that polymer electrolyte is not considered polyelectrolyte. The obvious advantages of polymer electrolyte over liquid electrolyte are (1) improved safety properties due to low volatility, (2) design flexibility, and (3) potential to eliminate separators. Arguably, polymer electrolyte could be more conveniently processed as compared to that of liquid electrolyte. Simplified processes could reduce the cost significantly. Similar to other electrolyte, polymer electrolyte must be stable under the operating conditions of Li-ion batteries from electrochemical, thermal and mechanical perspectives (Deng, 2015). One of the widely studied polymer is poly(ethylene oxide) which has been coupled with various lithium salts, such as LiCF_3SO_3 and LiClO_4 . The ion conduction in poly(ethylene oxide) mainly occurs at amorphous phases. The ions can be transported by the semi random motion of short polymer segments. In order to maintain a good mechanical stability, ionic conductivity will be sacrificed. The conductivity is typically about 10^{-8} S/cm, which is significantly less than that of liquid electrolyte. Li-ion batteries based on polymer electrolyte are design flexible and can be fabricated as cylindrical, coin, prismatic, flat cells and other configurations (Deng, 2015).

Another type of electrolyte is based gels in which both lithium salts and polar solvents are dissolved and added into inactive networks of high-molecular-weight polymers. LiPF_6 and carbonate solvents are typically used similar to those in liquid electrolyte discussed above. The liquid phases are fully absorbed within the polymers which can avoid the leakage issue in contrast to that of pristine liquid electrolyte (Deng, 2015). Meanwhile, the ionic conductivity of gel electrolyte could be dramatically increased as compared to that of polymer electrolyte. There are a number of polymers explored as the hosts, including polyacrylonitrile, polyvinyl chloride, polyvinylidene fluoride and Poly(methylmethacrylate). In the preparation of gel electrolyte, one can simply increase the viscosity of liquid electrolyte by adding soluble polymers. Alternatively, one can soak the microporous polymer matrix into the electrolyte (Deng, 2015).

Recently, ceramic electrolyte is also re-attracting much attention. Ceramic electrolyte has long been explored for fuel cells, and their application in Li-ion batteries is attracting increasing interest. The obvious advantage to use ceramic electrolyte is safety, for example, no more flammable organic solvents needed. Those batteries with ceramic electrolyte can find applications in high-temperature environment, including handheld orthopaedic tools and other batteries powered medical devices that need to be sterilized in

autoclaves under high temperature and high pressure conditions. The batteries autoclaved should be able to withstand for at least 130°C and are impermeable up to 30 psi in heated water, and importantly, deterioration in performance should be minimum after sterilization. Another interesting advantage to use ceramic electrolyte for high-temperature applications is that the ionic conductivity of ceramic electrolyte increases with increasing temperature. This is because the creation and movement of ionic point defects, which determines the ionic conductivity, requires energy. One area of intensive research is to achieve ceramic electrolyte with reasonably high conductivity at room temperature. Various sulfides, oxides and phosphates have been explored. The author would anticipate that ceramic electrolyte will eventually be used in next-generation Li-ion batteries in electric vehicles, mainly for its excellent safety performance which can enhance the customer confidence and acceptance (Deng, 2015).

3.3 Separators

Separators are essential components of Li-ion batteries. In fact, separators are commonly used in most electrochemical systems with liquid electrolyte, including fuel cells, capacitors and various kinds of batteries based on different chemistry. The separator in a Li-ion battery plays the critical roles to avoid direct physical contact between the cathode and anode, and prevents short circuit to occur. At the same time, the separator allows lithium ions in the electrolyte to pass through it. The separators must be chemically stable and inert in contact with both electrolyte and electrodes. At the same time, it is required to be mechanically robust to withstand the tension and puncture by electrode materials and the pore size should be less than 1 μm . Although various separators, including microporous polymer membranes, nonwoven fabric mats and inorganic membranes have been explored, the microporous polyolefin materials based polymer membranes are dominantly used in commercial Li-ion batteries with liquid electrolyte.

The microporous polymer membranes could be made very thin (typically about $\sim 25 \mu\text{m}$) and highly porous (typically 40%) to reduce the resistance and enhance ionic conductivity (Deng, 2015). At the same time, the polymer membranes could still be mechanically robust. Other parameters that have to be considered in the selection of microporous polymer membranes are low yield or shrinkage, permeability, wettability and cost. Another interesting advantage to use microporous polymer membrane as the separator is that, with properly designed multilayer composites, the separator can shut the battery in the case of short circuit or thermal runaway, functioning similar to a thermal fuse (Deng, 2015). It is required to have at least two functional parts in the separator: one part that will melt to close the pores and the other part provides mechanical strength to keep isolating the anode and cathode. One typical example is the Celgard® (North Carolina, USA) microporous separator made of both polyethylene (PE) and polypropylene (PP), in the form of trilayer of PP-PE-PP. The melting points of PE and PP are 135 and 165°C, respectively (Deng, 2015). In the case of over-temperature approaching that of melting point of PE, the porosity of the membrane could be closed by PE, preventing further reactions. So for commercial Li-ion batteries, the shutdown temperature is about 130°C (Deng, 2015).

For the development of future Li-ion batteries for high-temperature applications, inorganic membranes as separators are highly attractive. The all-solid Li-ion batteries should also be further investigated to meet those niche markets of high-temperature applications. Another parameter that determines the commercial success of a separator is cost. The cost of the existing polymer separator in a Li-ion battery could be as high as one-fifth of the total cost of the battery (Deng, 2015). Therefore, intensified research on the development of highly improved separators at reasonably low price for Li-ion batteries is required (Deng, 2015).

3.4 Electrode/Electrolyte Interface

The cell capacity is referred by the total charge transferred in the electrode-electrolyte interface, which depends on the current passed through the external circuit during charging discharging process. At high current, during rapid charging the rate of ion transfer across electrode-electrolyte interfaces occurs in a diffusion-controlled mechanism (Marcicki, Conlisk, & Rizzoni, 2014). It is predicted that Li may accumulate on the negative electrode and electrolyte interface when the Li-ion flux during the charge transfer reaction becomes higher than the Li-ion diffusion flux into the negative electrode (Li, Huang, Liaw, Metzler, & Zhang, 2014; Purushothaman & Landau, 2006). The massive dendritic growth of Li can be

observed when the lithium ion concentration exceeds a certain saturation level ($0.077 \text{ mol cm}^{-3}$). Such deposition leads to the deformation of underneath electrode surface, and causes internal short and thermal runaway of battery (Li, Huang, Liaw, Metzler, & Zhang, 2014). Moreover, the dead Li deposited on the electrode surface creates internal resistance in cell and the changes at the electrode surfaces alters the rate due to slow diffusion of Li^+ -ion at the interface resulting irreversible capacity fading. The electrochemical decomposition of electrolyte at the electrode-electrolyte interface is also responsible for capacity fading forming the solid-electrolyte interphase (SEI) layer on the active material. Though the SEI layer leads to irreversible capacity fading in a cell, it also acts as a protective layer against further decomposition of electrolyte at the electrode-electrolyte interface (Roy and Srivastava, 2015). The characteristic Columbic efficiency associated with capacity fading can be calculated as the fraction of the electrical charge stored during charging that is recoverable during discharge after each cycles, $100 \times \frac{Q_{\text{disch}}}{Q_{\text{ch}}}$ (Roy and Srivastava, 2015).

The most common and fundamental source of capacity fade in successful Li-ion batteries (which manage to resist degradation over hundreds of cycles) is the loss of lithium to the solid-electrolyte interphase (SEI), which typically forms at the negative electrode during recharging. Initially, SEI formation protects the electrode against solvent decomposition at large negative voltage, but over time it leads to a gradual capacity fade as the SEI layer thickens. A solid theoretical understanding of this phenomenon will assist the design of batteries, for example by enabling the quantitative interpretation of accelerated aging tests, where a battery is cycled at a high temperature to hasten the progress of capacity fade (Thomas, Bloom, Christophersen, & Battaglia, 2008).

The selection of materials intimately depends on their crystal structure, physical properties (specific capacity, electrical conductivity, mechanical stability etc.), chemical properties (intercalation, reversibility) and many other factors. Other than the structure and properties of materials, size and shape of materials matter effectively on the performance of LIB. The first generation anode materials were basically micrometre sized particles where the Li intercalation/de-intercalation reactions occur. The rate of intercalation-deintercalation of lithium ion strongly depends upon the diffusivity of lithium ion (Bruce, Scrosati, & Tarascon, 2008). The Li ion diffusion in a host material is associated with Li-ion diffusion coefficient and diffusion length in the material. In an indirect way diffusivity or diffusion length is represented as:

$$\tau = \frac{L_{\text{ion}}^2}{D_{\text{Li}}} \quad (3.1)$$

where L_{ion} is diffusion length and D_{Li} is the diffusion coefficient. While D_{Li} depends upon the nature of material, L_{ion} depends upon the size of material. Thereby the strategy to achieve high energy and high power or fast Li intercalation-deintercalation up to certain extends depends on controlling the size of materials (Roy and Srivastava, 2015). For example, rutile TiO_2 having low diffusion coefficient of $10\text{-}15 \text{ cm}^2/\text{s}$ are believed to accommodate a negligible amount of Li ions at room temperature. However, significant changes can be observed for $5\text{-}15\text{nm}$ sized rutile TiO_2 nanoparticles showing a full loading of lithium ($x > 1$ in Li_xTiO_2) and about 0.7 Li per rutile TiO_2 insertion-removal in subsequent cycles (Roy & Srivastava, 2015). Miniaturization of electrode materials also allows a large surface area in contact with the electrolyte resulting higher charge/discharge rates (Goriparti, et al., 2014). However, reduction of material size has not found to be always beneficial for the purpose. The very fast Li^+ intercalation-deintercalation often leads to undesirable side reactions and damage the battery life (Roy and Srivastava, 2015). Consequently, in last few years, nanomaterials in different morphology have been investigated for application as anodes in LIB.

4.0 BENEFITS AND CHALLENGES OF LI-ION BATTERIES

4.1 Benefits/Applications

Li-ion batteries are highly advanced as compared to other commercial rechargeable batteries, in terms of gravimetric and volumetric energy. Figure 4.1 compares the energy densities of different commercial rechargeable batteries, which clearly shows the superiority of the Li-ion batteries as compared to other batteries (Tarascon & Armand, 2001). Although lithium metal batteries have even higher theoretical energy densities than that of Li-ion batteries, their poor recharge ability and susceptibility to misuses leading to fire even explosion are known disadvantages (Deng, 2015).

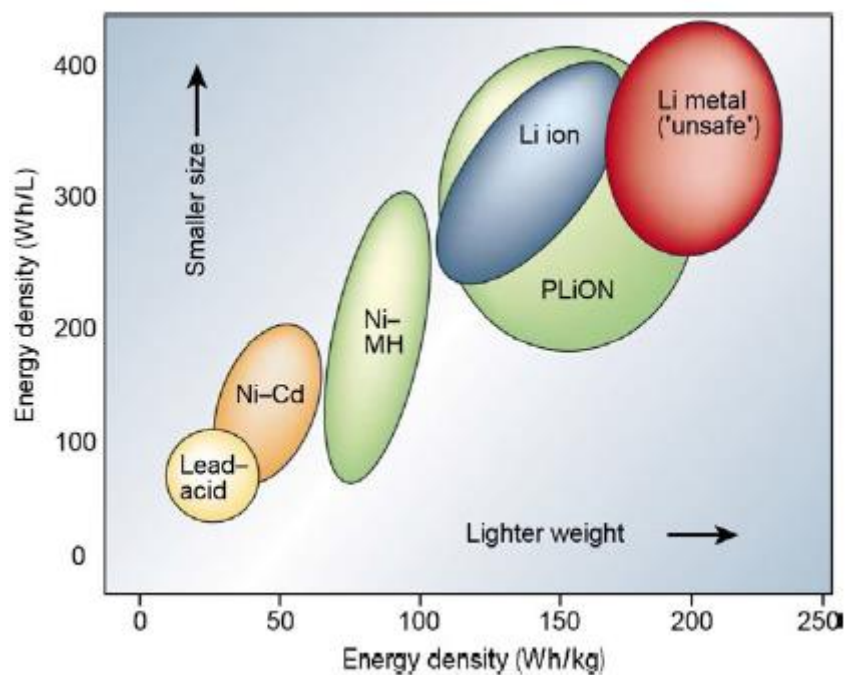


Figure 4.1 Comparison of energy densities and specific energy of different rechargeable batteries (Deng, 2015).

Li-ion batteries provide lightweight, high energy density power sources for a variety of devices. To power larger devices, such as electric cars, connecting many small batteries in a parallel circuit is more effective and more efficient than connecting a single large battery (Andrea, 2010). Such devices include portable devices: mobile phones and smartphones, laptops and tablets, digital cameras and camcorders, electronic cigarettes, handheld game consoles and torches (flashlights); power tools: Li-ion batteries are used in tools such as cordless drills, sanders, saws and a variety of garden equipment including whipper-snippers and hedge trimmers; and electric vehicles: including electric cars, hybrid vehicles, electric bicycles, personal transporters and advanced electric wheelchairs. Also radio-controlled models, model aircraft, aircraft, and the Mars Curiosity rover (Miller, 2015).

Li-ion batteries are used in telecommunications applications. Secondary non-aqueous lithium batteries provide reliable backup power to load equipment located in a network environment of a typical telecommunications service provider. Li-ion batteries compliant with specific technical criteria are recommended for deployment in the Outside Plant (OSP) at locations such as Controlled Environmental Vaults (CEVs), Electronic Equipment Enclosures (EEEs), and huts, and in uncontrolled structures such as cabinets. In such applications, li-ion battery users require detailed, battery-specific hazardous material information, plus appropriate fire-fighting procedures, to meet regulatory requirements and to protect employees and surrounding equipment (Wikipedia, 2017b).

4.2 Challenges

The increasing demand for energy storage requires further improvements in the existing Li-ion batteries and the development of next-generation Li-ion batteries, in particular, to reduce the cost of Li-ion batteries. It is still colossally challenging to develop new battery chemistry to replace the existing Li-ion battery technology. One of the critical challenges in advancing lithium ion battery technologies is that the battery capacity tends to fade upon electrochemical cycling. Fracture and decrepitation of the electrodes is observed as a result of lithium diffusion during the charging and discharging operations. During the battery operation, when lithium is inserted into (or extracted from) the active materials of both positive and negative electrodes, volume expansion (and contraction) occurs (Deshpande, 2011).

In order to increase energy density Li-ion batteries, it is desirable to find electrode couples with both high-specific capacities and high operating cell voltage. As discussed previous, there are a large number of anode candidates that could dramatically increase the specific capacities, in particular, with highly attractive Si- and Sn-based anodes. It is still challenging to prepare Si nanomaterials on a large scale with low cost. Sn-based anodes suffer from the issue of poor cycling performance due to pulverization. Therefore, one of the possible future anodes could be Si-Sn-based composites (Wang, Wen, Liu, & Wu, 2009). In contrast to that of anode candidates, the cell capacity is mainly limited by the low capacity of cathode candidates. The existing cathode material of LiCoO_2 is expensive and highly toxic. The increasingly popular LiFePO_4 has a low capacity. The facilely prepared Ni-Co-Mn-based cathodes developed by Argonne National Laboratory are highly attractive, especially from industrial prospective (Deng, 2015). However, the specific capacity is still considered moderate, and both Co and Ni are expensive and toxic. Future cathode materials should try to avoid the use of either Co or Ni, or other toxic elements, from environmental perspectives. Additionally, the ideal cathode should be able to reversibly insert/extract multiple electrons per 3d metal. The future low-cost cathode materials could be Mn-and/or Fe-based. The issue of intrinsically low conductivity should be creatively addressed, most likely by nanotechnology and nanocomposites. There is relatively no much room to increase the operating cell voltages with the current known cathode candidates under exploration. Composite cathodes with two or three 3d metals and polyanions are highly promising (Deng, 2015).

The safety concern is another challenge that needs to be properly addressed. The recent news on fires of Li-ion batteries, involving the Boeing 787 passenger aircrafts, Tesla Model S cars, highlights the importance of battery safety. To ensure the wide acceptance of electric vehicles and expanded the market of Li-ion battery powered vehicles, automakers should invest significantly on the battery management systems to enhance safety of the huge battery packs in vehicles (Deng, 2015). Alternatively, nonflammable Li-ion batteries should be developed, including those Li-ion batteries based on aqueous electrolyte or ceramic electrolyte, and all-solid-state batteries. Next-generation Li-ion batteries, most likely, will be using high voltage (5 V) cathodes and high capacity anodes (such as Si-or Sn-based). Therefore, intensive research is required to gain better understanding about those electrode materials in terms of stability and interaction with electrolyte. Instead of intensively pursuing of high-energy density, there should be increasing emphasis on battery safety as well. Standardized battery safety testing procedures should be widely employed (Deng, 2015).

It is still challenging to develop electrode materials with low carbon footprint, or the so-called “green batteries”. Ideally, future Li-ion batteries should use biologically derived organic or inorganic electrodes, using aqueous electrolyte. Carbon and silicon can be derived from biomasses. The recent attempts to explore virus-assisted synthesis of electrode materials for Li-ion batteries attracted much enthusiasm (Lee, et al., 2009). It will be interesting to explore large-scale synthesis at room temperature using biological templates, including genetically modified virus. Organic electrodes that will not be easily dissolved by electrolyte can be further developed for sustainable Li-ion batteries (Chen, et al., 2008). Therefore, one area of future research could be focusing on “sustainable” and “green” Li-ion batteries.

5.1 Conclusion

A review on the recent progress in lithium ion battery technology with the systematic appraisal of the historical background; theoretical and experimental concepts; applications and challenges of the energy storage device was carried out in this study. The history and theory of LIB, the experimental concept and

recent advances in the energy storage technology were discussed. The basic working principle and processes were also discussed. An overview of the materials involved in the fabrication of the LIB including cathode, anode, electrolytes and separators is given as well as their benefits and their limitation.

The solid-electrolyte interphase (SEI) which defines the cell capacity during charging discharging process was discussed. A range of practical benefits and applications in different areas were highlighted and the current challenges faced by the technology with the probable solutions were discussed.

5.2 Recommendations

The appraisal of the recent progress in lithium ion battery technology has revealed the enormous advantages of this technology. Based on these benefits, this study recommends that:

- i. research effort should focus on the replacement of LiCoO_2 commonly used cathode material which is expensive and highly toxic.
- ii. finding electrode couples with both high-specific capacities and high operating cell voltage should be of research interest.
- iii. government at all levels should invest in the development of this technology economically viable.

REFERENCES

- i Alarco, J., & Talbot, P. (2015, April 30). *Charged up: the history and development of batteries*. Retrieved from The Conversation: <http://theconversation.com/charged-up-the-history-and-development-of-batteries-40372>
- ii Andrea, D. (2010). *Battery Management Systems for Large Lithium-Ion Battery Packs*. Artech House.
- iii Baughman, R. H., Zakhidov, A. A., & deHeer, W. A. (2002). *Carbon nanotubes-the route toward applications*. *Science*, 297, 787–792.
- iv Bazant, M. Z. (2013). *Theory of chemical kinetics and charge transfer based on non-equilibrium thermodynamics*. *Accounts of Chemical Research*, 46, 1144-1160.
- v Bruce, P. G., Scrosati, B., & Tarascon, J.-M. (2008). *Nanomaterials for Rechargeable Lithium Batteries*. *Angewandte Chemie International Edition*, 47(16), 2930–2946. doi:10.1002/anie.200702505
- vi Chaturvedi, N. A., Klein, R., Christensen, J., Ahmed, J., & Kojic, A. (2012). *Estimation of Lithium Transport Rate in Lithium-ion Batteries -A Particle Filtering Approach*. *Workshop on Engine and Powertrain Control, Simulation and Modeling* (pp. 116 - 121). Rueil-Malmaison, France: The International Federation of Automatic Control.
- vii Che, G. L., Lakshmi, B. B., Fisher, E. R., & Martin, C. R. (1998). *Carbon nanotubule membranes forelectrochemical energy storage and production*. *Nature*, 393, 346–349.
- viii Chen, H., Armand, M., Demailly, G., Dolhem, F., Poizot, P., & Tarascon, J.-M. (2008). *From Biomass to aRenewable LiXC6O6 Organic Electrode for SustainableLi-Ion Batteries*. *Chemsuschem*, 1, 348–355.
- ix Chung, S. Y., & Chiang, Y. M. (2002). *Electronically conductive phospho-olivines as lithium storage electrodes*. *Nature Materials*, 1, 123–128.
- x Croce, F., Appetecchi, G. B., Persi, L., & Scrosati, B. (1998). *Nanocomposite polymer electrolytes for lithium batteries*. *Nature*, 394, 456–458.
- xi Dao, T. -S., Vyasrayani, C. P., & McPhee, J. (2012). *Simplification and order reduction of lithium-ion battery model based onporous-electrode theory*. *Journal of Power Sources*, 198, 329– 337.

- xii Deng, D. (2015). *Li-ion batteries: basics, progress, and challenges*. *Energy Science and Engineering*, 3(5), 385–418. doi:10.1002/ese3.95
- xiii Deng, D., & Lee, J. Y. (2013). *Meso-oblate Spheroids of Thermal-Stable Linker-Free Aggregates with Size-Tunable Subunits for Reversible Lithium Storage*. *ACS Applied Materials and Interfaces*, 6, 1173–1179.
- xiv Deng, D., Kim, M. G., Lee, J. Y., & Cho, J. (2009). *Green energy storage materials: Nanostructured TiO₂ and Sn-based anodes for lithium-ion batteries*. *Energy and Environmental Science*, 2, 818–837.
- xv Deshpande, R. D. (2011). *Understanding and Improving Lithium Ion Batteries through Mathematical Modeling and Experiments*. Kentucky: University of Kentucky, USA.
- xvi DeVidts, P., & White, R. E. (1997). *Governing equations for transport in porous electrodes*. *Journal of the Electrochemical Society*, 144(4), 1343–1353.
- xvii Dimov, N., Xia, Y., & Yoshio, M. (2007). *Practical silicon-based composite anodes for lithium-ion batteries: Fundamental and technological features*. *Journal of Power Sources*, 171, 886–893.
- xviii Doyle, M., Fuller, T., & Newman, J. (1993). *Modeling of Galvanostatic Charge and Discharge of the Lithium/Polymer/Insertion Cell*. *Journal of The Electrochemical Society*, 140(6), 1526–1533.
- xix Dubal, D. P., Ayyad, O., V. Ruiz, V., & Gómez-Romero, P. (2015). *Hybrid energy storage: the merging of battery and supercapacitor chemistries*. *Chemical Society Reviews*, 44(7), 1777–1790. doi: 10.1039/C4CS00266K
- xx Dunning, J. (2016). *The Inside Story of the Lithium Ion Battery*.
- xxi Ferguson, T. R. (2014). *Lithium-ion Battery Modeling Using Non-equilibrium Thermodynamics*. Massachusetts, USA: Massachusetts Institute of Technology.
- xxii Goodenough, J. B. (2013). *Evolution of Strategies for Modern Rechargeable Batteries*. *Accounts of Chemical Research*, 46(5), 1053 - 1061. doi:10.1021/ar2002705
- xxiii Goodenough, J. B., & Park, K. -S. (2013). *The Li-Ion Rechargeable Battery: A Perspective*. *Journal of the American Chemical Society*, 135(4), 1167–1176.
- xxiv Goriparti, S., Miele, E., De Angelis, F., Fabrizio, E. D., Zaccaria, R. P., & Capiglia, C. (2014). *Review on recent progress of nanostructured anode materials for Li-ion batteries*. *Journal of Power Sources*, 257, 421–443.
- xxv Huggins, R. A. (2009). *Advanced Batteries: Materials Science Aspects*. New York, NY 10013, USA: Springer.
- xxvi Huie, M. M., Bock, D., Takeuchi, E. S., Marschilok, A. C., & Takeuchi, K. J. (2015). *Cathode materials for magnesium and magnesium-ion based batteries*. *Coordination Chemistry Reviews*, 287, 15–27.
- xxvii Idota, Y. K., Matsufuji, A., Maekawa, Y., & Miyasaka, T. (1997). *Tin-based amorphous oxide: A high-capacity lithium-ion-storage material*. *Science*, 276, 1395–1397.
- xxviii Islam, M. S., & Fisher, C. A. (2013). *Lithium and sodium battery cathode materials: computational insights into voltage, diffusion and nanostructural properties*. *Chemical Society Reviews*, 43(1), 185–204.
- xxix Kumar, T. P., Ramesh, R., Lin, Y. Y., & Fey, G. T. (2004). *Tin-filled carbon nanotubes as insertion anode materials for lithium-ion batteries*. *Electrochemical Communication*, 6, 520–525.

- xxx LaVine, S. (2017, March 20). *Has lithium-battery genius John Goodenough done it again? Colleagues are skeptical*. Retrieved from Quartz: <https://qz.com/929794/has-lithium-battery-genius-john-goodenough-done-it-again-colleagues-are-skeptical/>
- xxxii Lee, Y. J., Yi, H., Kim, W. -J., Kang, K., Yun, D. S., & Strano, M. S. (2009). *Fabricating Genetically Engineered High-Power Lithium-Ion Batteries Using Multiple Virus Genes*. *Science*, 324, 1051–1055.
- xxxiii Levine, S. (2010). *The Great Battery Race*. *Foreign Policy*, 182, 88–95.
- xxxiiii Li, Z., Huang, J., Liaw, B. Y., Metzler, V., & Zhang, J. B. (2014). *A review of lithium deposition in lithium-ion and lithium metal secondary batteries*. *Journal of Power Sources*, 254, 168-182.
- xxxv Liu, C., Neale, Z. G., & Cao, G. (2016). *Understanding electrochemical potentials of cathode materials in rechargeable batteries*. *Materials Today*, 19(2), 109 - 123.
- xxxvi Marcicki, J., Conlisk, A. T., & Rizzoni, G. (2014). *A lithium-ion battery model including electrical double layer effects*. *Journal of Power Sources*, 251, 157-169.
- xxxvii Megahed, S., & Scrosati, B. (1994). *Lithium-ion rechargeable batteries*. *Journal of Power Sources*, 51, 79–104.
- xxxviii Miller, P. (2015). *Automotive Lithium-Ion Batteries*. *Johnson Matthey Technology Review*, 59(1), 4–13. doi:10.1595/205651315x685445
- xxxix Mizushima, K. J., Wiseman, P. J., & Goodenough, J. B. (1981). *Li_xCoO₂ (0 < x ≤ 1): A new cathode material for batteries of high energy density*. *Solid State Ionics*, 3 - 4, 171–174.
- xl Newman, J., & Tiedemann, W. (1975). *Porous-Electrode Theory with Battery Applications*. *AIChE Journal*, 21(1), 25–41.
- xli News. (2016, September 2). *Samsung recall for Galaxy Note 7*. Retrieved from *The news in colour*: <http://www.news.com.au/finance/business/breaking-news/samsung-to-recall-phones-after-explosions/news-story/3ef0b353b48e94477a75e2f08cbb2312>
- xlii Obrovac, M. N., & Chevrier, V. L. (2014). *Alloy Negative Electrodes for Li-Ion Batteries*. *Chemical Reviews*, 114(23), 11444 –11502. doi:10.1021/cr500207g
- xliii Obrovac, M. N., Christensen, L., Le, D. B., & Dahn, J. R. (2007). *Alloy Design for Lithium-Ion Battery Anodes*. *Journal of The Electrochemical Society*, 154, A849.
- xliv Oswal, M., Paul, J., & Zhao, J. (2010). *A comparative study of Lithium Ion Batteries*. *AME 578 Project*.
- xlvi Park, J.-K. (2012). *Principles and Applications of Lithium Secondary Batteries*. Germany: Wiley-VCH.
- xlvi Pistoia, G., & Nazri, G. -A. (2003). *Lithium Batteries: Science and Technology*. Kluwer : Academic Publishers.
- xlvi Purushothaman, B. K., & Landau, U. (2006). *Rapid Charging of Lithium Ion Batteries Using Pulsed Currents – A Theoretical Analysis*. *Journal of The Electrochemical Society*, 153, A533-A542.
- xlvi Richard. (2017, March 1). *Goodenough's All-Solid-State-Battery Cells*. Retrieved from *UPS Battery Center*: <http://www.upsbatterycenter.com/blog/goodenoughs-all-solid-state-battery-cells/>
- xlvi Roy, P., & Srivastava, S. K. (2015). *Nanostructured anode materials for lithium ion batteries*. *Journal of Material Chemistry A*, 3, 2454-2484. doi: 10.1039/C4TA04980B
- xlvi Su, L., Jing, Y., & Zhou, Z. (2011). *Li ion battery materials with core-shell nanostructures*. *Nanoscale*, 3, 3967-3983. doi:10.1039/C1NR10550G

- l Tang, M., Carter, W. C., & Chiang, Y. -M. (2010). *Electrochemically Driven Phase Transitions in Insertion Electrodes for Lithium-Ion Batteries: Examples in Lithium Metal Phosphate Olivines*. *Annual Review of Materials Research*, 40, 501-529. doi:10.1146/annurev-matsci-070909-104435
- li Tarascon, J. M., & Armand, M. (2001). *Issues and challenges facing rechargeable lithium batteries*. *Nature*, 414, 359–367.
- lii Thomas, E. V., Bloom, I., Christophersen, J. P., & Battaglia, V. S. (2008). *Statistical methodology for predicting the life of lithium-ion cells via accelerated degradation testing*. *Journal of Power Sources*, 184, 312 - 317.
- liii UTNews. (2017, February 28). *Lithium-Ion Battery Inventor Introduces New Technology for Fast-Charging, Noncombustible Batteries*. Retrieved from UTNews: <https://news.utexas.edu/2017/02/28/goodenough-introduces-new-battery-technology>
- liv Wang, X., Wen, Z., Liu, Y., & Wu, X. (2009). *A novel composite containing nanosized silicon and tin as anode material for lithium ion batteries*. *Electrochimica Acta*, 54, 4662–4667.
- lv Wang, Y., Zeng, H. C., & Lee, J. Y. (2006). *Highly reversible lithium storage in porous SnO₂ nanotubes with coaxially grown carbon nanotube overlayers*. *Advanced Materials*, 18, 645–649.
- lvi Whittingham, M. S. (1976). *Electrical Energy Storage and Intercalation Chemistry*. *Science*, 192, 1126–1127.
- lvii Wikipedia. (2017, July 31). *Lithium-ion battery*. Retrieved from Wikipedia: https://en.wikipedia.org/wiki/Lithium-ion_battery
- lviii Wikipedia. (2017b, August 7). *Lithium-ion battery*. Retrieved from Wikipedia: https://en.wikipedia.org/wiki/Lithium-ion_battery#cite_note-FOOTNOTEAndrea2010229-130
- lix Winter, M., & Besenhard, J. O. (1999). *Electrochemical lithiation of tin and tin-based intermetallics and composites*. *Electrochim Acta*, 45, 31–50.
- lx Xu, K. (2004). *Nonaqueous liquid electrolytes for lithium-based rechargeable batteries*. *Chemical Reviews*, 104, 4303-4417.
- lxi Yoshino, A. (2012). *The Birth of the Lithium-Ion Battery*. *Angewandte Chemie International Edition*, 51, 5798–5800.
- lxii Zhi, M., Xiang, C., Li, J., Ming Li, M., & Wu, N. (2013). *Nanostructured carbon–metal oxide composite electrodes for supercapacitors: a review*. *Nanoscale*, 5(1), 72-88. doi:10.1039/C2NR32040A
- lxiii Zhu, J., Ng, K. Y., & Deng, D. (2014). *Porous olive-like carbon decorated Fe₃O₄ based additive-free electrodes for highly reversible lithium storage*. *Journal of Material Chemistry A*, 2, 16008–16014.