리튬 이온 배터리용 양극 및 음극 재료의 최근 동향

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Recent Advances in Cathode and Anode Materials for Lithium Ion Batteries

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초 록

리튬 이온 배터리는 휴대용 전자 제품, 전기 자동차 및 그리드 규모의 에너지 저장 장치 등과 같이 일상 생활에서 다양한 용도로 널리 사용되고 있다. 최근 높은 에너지 밀도, 경량 및 저비용과 같은 상업적 요구를 만족하는 리튬 이온 배터리 전극 소재 개발을 위하여 상당한 노력이 진행되어 오고 있다. 이 총설에서는 리튬 이온 배터리 양극 및 음극 재료의 원리와 최근 연구 동향을 요약하였으며, 특히 전극 소재의 설계 및 고급 특성화 기술을 강조하였다.

Abstract

Lithium ion batteries have been broadly used in various applications to our daily life such as portable electronics, electric vehicles and grid-scale energy storage devices. Significant efforts have recently been made on developing electrode materials for lithium ion batteries that meet commercial needs of the high energy density, light weight and low cost. In this review, we summarize the principles and recent research advances in cathode and anode materials for lithium ion batteries, and particularly emphasize electrode material designs and advanced characterization techniques.

Keywords: Lithium ion battery, cathode material, anode material

1. Introduction

With the population increasing and industrial progress, the limited resources of the earth has not satisfied the demands of social development, therefore, forcing people to improve resource utilization. Also, the technological revolution such as mobile phones, laptop computers, electric vehicles (EVs) and hybrid electric vehicles (HEVs) led to growing demands for new energy source. Nickel metal hydride (Ni-MH), nickel cadmium (Ni-Cd), lead acid battery was commonly used in various application. However, above of them, lithium ion batteries (LIBs) has received much attention due to its high power efficiency and density (twice than Ni-MH battery). LIBs have made significant progress in terms of safety, electrochemical properties such as capacity, power, and cycling stability[1]. Developing high capacity or high voltage cathode and anode materials was released to increase the energy density of lithium batteries. The common concept of present

LIBs relies, at the cathode side, on transition metals oxides or phosphates active material ($LiCoO_2$, $LiMn_2O_4$, $LiCo_{1/3}Mn_{1/3}Ni_{1/3}O_2$, $LiFePO_4$, etc.), while alloying anodes (Si, Ge, Sn, etc.), chalcogenides (S, Se, and Te), and metal halides (F, Cl, Br, and I) was used as anode active material (Figure 1). This article aims to provide a useful survey of the most recent progress on the development of electrode materials for lithium ion batteries.
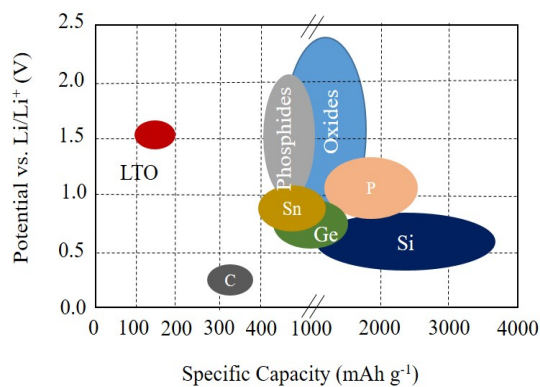
2. Cathode Materials

Cathode materials are generally comprised of the lithium compound, so that it is able to be paired with lithium de-intercalated anodes. It is expected that the cathode material must be reasonably stable in air at ambient temperature. Furthermore, anodes are generally having low voltage of approximately 0.1 V in compared to Li metal. In order to compensate it and maximize energy density, cathodes intended for use in lithium ion batteries have to have higher average potentials versus Li/Li^+. More than that, the requirement for high specific capacity generally restricts choices to compounds containing first-row transition metals (usually Mn, Fe, Co, and Ni). Environmental and toxicity concerns have precluded the development of most V or Cr-containing materials, although electroactive compounds containing these metals ex-
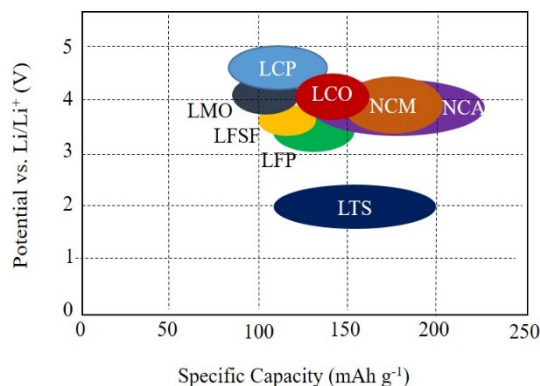
(a)

(b)

Figure 1. Discharge potentials and specific capacity of some of the most common (a) cathodes and (b) anodes (reproduced from[4]).

ist[2]. Cathode materials can be categorized into three common materials by their structure: layered structure material, spinel structure material, and olivine structure material.

2.1. Layered lithium transition metal oxide

Whittingham et al.[3], TiS_2 was identified as the first lithium intercalation material and this material showed reversible lithium intercalation involved only one phase of Li_xTiS_2 over the composition range $0 \leq x \leq 1$ with an average voltage of ~2 V[4]. However, the uneven lithium deposition on the anode and lithium dendrites at the surface of anode lead to an internal short circuit and cell failure. Furthermore, lithium has to be used in large excess to compensate for the poor columbic efficiency[5]. Those problems were somewhat alleviated by using lithium alloys instead of metallic lithium. However, the higher potential makes combination with TiS_2 unappealing since the cell voltage would yield ~1.6 V.

The research shifted to layered lithium transition metal oxide with higher potentials of > 3.5 V. Lithium cobalt oxide ($LiCoO_2$) was the most promising candidate with a capacity of ~135 mAh g^{-1} in the range of 3.0-4.2 V vs Li^+/Li. $LiCoO_2$ was studied and commercialized as the first of the layered structure material, and has been used until today in lithium ion batteries. Its structure was shown in Figure 2, where the cations order in the alternating planes of (111) planes with
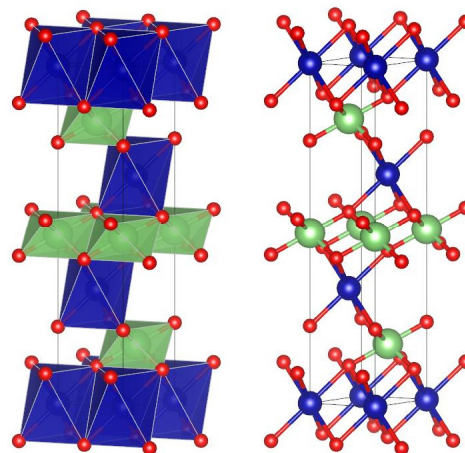

Figure 2. Layered lithium transition metal oxide structure of $LiCoO_2$ (red: oxygen, blue: cobalt, green: lithium).

cubic close-packed (ccp) oxygen array, forming a trigonal structure (space group R3m). This type of stacking arrangement is called O_3, and mean that there are three transition metal layers in one-unit cell and the Li ions are octahedrally coordinated. $LiCoO_2$ is fairly easy to synthesize without defects due to the large size difference between lithium and cobalt (r_{Li}^+: 0.76 Å; r_{Co}^{3+}: 0.545 Å). Lithium intercalation process proceeds over the range with $0.5 \leq x \leq 1.0$ in Li_xCoO_2, having a practical specific capacity of 140 mAh g^{-1} in 3.0-4.2 V vs. Li/Li^+[6,7]. If the lithium values of x < 0.5, the practical specific capacities will be higher, but cycling losses also increase[6]. This is owing to a change in the particle surface during charging/discharging process, which increase battery impedance and structural instability associated with phase changes at very low values of x in Li_xCoO_2[6,7]. These side reactions can be limited by coating $LiCoO_2$ particles, or rigorous heat treatment[8], resulting in improved cycling below 4.5 V vs. Li/Li^+, but cycling losses make the full lithium de-intercalation process is still not possible.

The major problems with $LiCoO_2$ are high cost, low thermal stability, and fast capacity fade at high current rates or during deep cycling. Some approaches have been achieved to enhance the ionic conductivity and cycling performance such as i) coating with carbon, and oxide compounds such as Al_2O_3, ZnO[9]; ii) doping with cationic on aluminum[10], chromium[11] and sliver[12]. Having achieved a mixed record of success, some coatings remarkably increased the initial discharge capacity of $LiCoO_2$ as high as 190 mAhg^{-1} while others significantly enhanced the cycling behavior. For instance, X. Dai et al.[9] reported an initial discharge capacity of 196 mAhg^{-1} for Al_2O_3-doped ZnO-coated $LiCoO_2$ (2.0 wt% Al_2O_3 doping) fabricated via radio frequency magnetron sputtering method with a good capacity retention upon cycling (90% after 150 cycles) and high reversible capacity of 112 mAh g^{-1} at 12C. Moreover, Al doping has received the greatest deal of attention as it has been proven to produce significant improvement on the capacity retention of upon cycling, which was attributed to an increase of the diffusion coefficient of lithium ions in Al-doped cathodes[10].

Another layered material is $LiNiO_2$ that has extensively study for lithium ion battery. $LiNiO_2$ first synthesized by Dyer et al. in 1954, was later extensively studied as an alternative to $LiCoO_2$ by Dahn et al. in the 1990s[13]. Nickel is more abundant than cobalt and would make for a cheaper alternative. In comparing with $LiCoO_2$, it has lower cost and higher energy density, which were driving forces for its development. Despite the similar structure with $LiCoO_2$, $LiNiO_2$ readily exhibits non-stoichiometry. During synthesis process, there is a tendency toward loss of lithium and reduction of some Ni to the +2 oxidation state. Because of the similar size between Ni and Li ions, Ni^{2+} is easy to migrate into Li^+ sites. The factors such as synthesis conditions, and the electrochemical performance are directly related to degree of disorder of structure, and are affected by the degree of non-stoichiometry. Therefore, $LiNiO_2$ is not a promising cathode material for commercial lithium ion battery, although its structure is nearly ideal. Doping with (e.g. Mg, Al, Co, Ga etc.)[14-16] has been studied for making $LiNiO_2$ easily. Cobalt doping was studied quite rigorously probably due to the fact that $LiCoO_2$ was already known to work well. The mixing of Ni with Co was later found to be effective at reducing the cationic disorder on 3a sites. The compositions such as $LiNi_{0.8}Co_{0.2}O_2$, exhibits high practical capacity of 180 mAh g^{-1} and excellent cyclability[14].

Pure $LiMnO_2$ (LMO) has considered as a material to alternative to $LiCoO_2$ and $LiNiO_2$ due to its cheaper and eco-friend. $LiMnO_2$ forms a monoclinic structure rather than rhombohedral structure, which can transform to a layered hexagonal structure during cycling[17]. In the cycling process, lithium ion has completely de-intercalated from the compounds in accompany with a result oxidation of Mn^{3+} to Mn^{4+}, leading to a structure change from monoclinic to more regular hexagonal crystal structure. The addition of nickel or nickel and cobalt mixture to $LiMnO_2$ can form the α-$NaFeO_2$ structure. Monoclinic $LiMnO_2$, with space group of C2/m, has cation ordering of α-$NaFeO_2$ structure type, where Li ions are located in the octahedral sites between MnO_2 sheets. It has high theoretical capacity of 285 mAh g^{-1} and thermally stable structure. However, the initial practical capacity of $LiMnO_2$ is only about 150 mAh g^{-1} and its capacity retention also decrease during cycling process. From cyclic voltammetry experiments a stark difference can be seen for the first cycle. This undesirable capacity loss is owing to the phase change from layered structure to spinel structure of material in charging/discharging process[18].

$Li(Ni,Mn,Co)O_2$ (NCM) such as $LiCo_{1/3}Mn_{1/3}Ni_{1/3}O_2$ are the most commonly used compositions, which contain equal amounts of the three transition metals and has high capacity, excellent rate capability and high voltages[19]. During charging process, a higher charging voltage lead to higher capacity and more sharp decrease of capacity. As with $LiNi_{1-x}Co_xO_2$, only with small amounts of cobalt of $0.2 \leq x \leq 0.25$ can reduce the amount of nickel and improve capacity. Furthermore, the loss in capacity during cycling process reduce with increasing cobalt amount[20]. This is owing to cobalt, which improves the structure stability and enhance the electronic conductivity. Although nickel can inhibit lithium transport in the lithium layer, but it also stabilizes the structure during lithium intercalation and thus im-
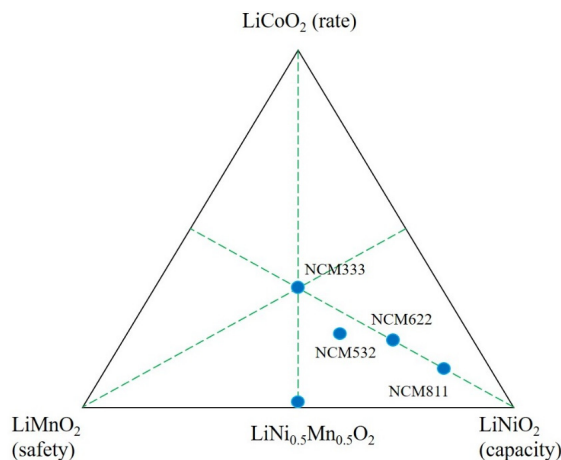

Figure 3. NCM product overview (reproduced from[21]).

prove cyclability. The lower cobalt content has, the better electrode performance is when NCM is overlithiated[20]. There can be an oxidative loss during the initial charge/discharge process, which is not recovered during normal cycling. However, deep discharging has been shown to recover this initial cycle loss.

In order to satisfy the need for high energy densities, the capacity of active materials has been increased. There is no significant difference in the raw material cost for different NCM composition. Hence, an increase in nickel content is a valid approach to higher capacities at the same cost. Figure 3 shows the recent trend in the NCM materials with higher content nickel nowadays. While NCM523 is a commercial reality higher nickel contents pose a number of problems which hinder their successes. Recently, NCM811 has been released and is ready to start producing battery cells. The new NCM 811 battery cells not only have better energy density, they are also cheaper to produce, especially since they require less cobalt[21].

$Li(Ni,Mn,Al)O_2$ (NCA) battery has also chosen to alternative $LiNiO_2$ due to its high specific energy, good specific power, and thermal stability. However, its drawback, the capacity fading and thermal runaway during charge-discharge process, limits applications. Cl, Mg, F, and Na doping at the catonic sites has been considered to improve its electrochemical performance. D. Y. Wan et al[22] reported Mn,Ti doping on NCA cathode material. In the results, Ti-doped NCA electrode exhibited superior performance with a high discharge capacity of 179.6 mAh g^{-1} and remains 93% after 30 cycles.

2.2. Spinel structure materials

Another promising cathode material is $LiMn_2O_4$ that was considered as a potential material to replace $LiCoO_2$. Its structure was shown in Figure 4, in which $LiMn_2O_4$ forms a spinel structure and has space group of Fd-3m, where manganese and lithium occupies the octahedral and tetrahedral sites, respectively[23]. Lithium intercalation/de-intercalation are through a 3-dimensional network rather than planes, as in the α-$NaFeO_2$ structure. In comparison with other cathode materials mentioned above, $LiMn_2O_4$ has lower cost, safer with high natural abundance of manganese, but has a lower theoretical capacity of 148
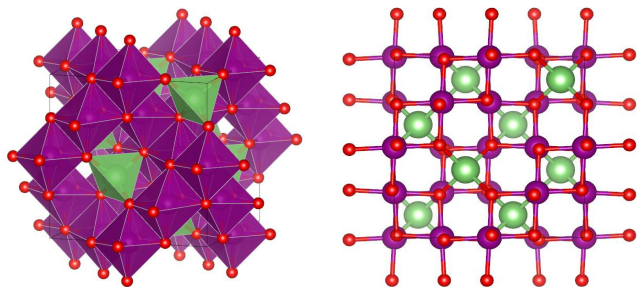
Figure 4. Spinel structure of LiMn$_2$O$_4$ (red: oxygen, purple: manganese, green: lithium).

Figure 5. Olivine structure of LiFePO$_4$ (red: oxygen, light purple: phosphorus, brown yellow: iron, green: lithium).

mAh g^{-1}[23]. However, the challenge in the use of LiMn$_2$O$_4$ is phase changes during cycling. During the operating test and storage, in the first few cycles, a rapidly loss of capacity occurred, but the rate of capacity loss subsequently decreased. The initial loss was owing to loss of oxygen during charge process. This loss is owing to the dissolution of manganese in the electrolyte, or the changes in particle sizes, shape or crystalline[23]. In order to improve this weakness, other transition metals have been used and added to LiMn$_2$O$_4$, such as iron and cobalt[24]. At high voltages, the iron addition increases the discharge plateau, while cobalt stabilizes the spinel crystal structure, resulting in the improved capacity retention during cycling. However, nickel is the most common addition material to LiMn$_2$O$_4$, which decreases the lattice parameter and the electrical conductivity of LiMn$_2$O$_4$. An increase in the capacity of LiMn$_2$O$_4$ while manganese content changes, especially the Mn : Ni ratio of 3 : 1. The Mg, Ni cations can arrange on the octahedral sub-lattice, but a disordered spinel structure has a higher capacity than the others. Besides, during cycling the cell performance can degrade by partially substituting a cobalt for nickel, which result to reduce the formation of Li$_x$Ni$_{1-x}$O. Furthermore, the nickel coating to the surface of LiMn$_2$O$_4$ can also improve capacity retention and improving safety during cycling process, which is rather than the other ones as bulk dopant[24].

2.3. Olivine structure materials

Another promising cathode materials are olivine type LiMPO$_4$ (M = Co, Fe, Mn, Ni or V) structures, in which phosphorous and transition metal occupies tetrahedral sites and octahedral sites, respectively. Furthermore, lithium forms one-dimensional chains along the [010] direction[25]. Among the phosphates, LiFePO$_4$ is the most commonly used material, in which Fe^{2+} oxidizes to Fe^{3+} and LiFePO$_4$ changes to FePO$_4$ form[25] (Figure 5). At the same time, the lithium sites can be occupied by iron ions, resulting in the neutral formation of Li$^+$ vacancies during charging process. Owing to the miscibility gap between FePO$_4$ and LiFePO$_4$, the lithium intercalation/de-intercalation process occurs by growth of a two-phase front rather than a continuous change in lithium content. The formation of a two-phase mixture establishes a fixed activity, which results in a relative flat discharge profile and the voltage remains relatively constant during discharge[26]. The electronic conductivity of LiFePO$_4$ occurs by small polaron hopping and is relatively low (10^{-9} S cm^{-1} for pure LiFePO$_4$[26]). In order to im-

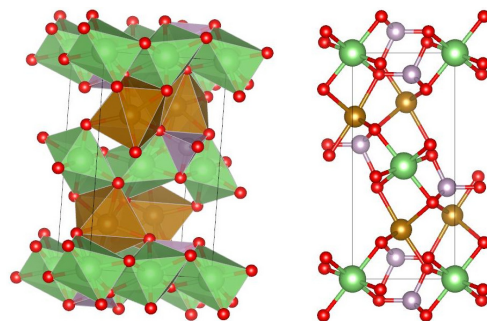prove the electronic conductivity, the heat treatment method, which increase the whole conductivity, is applied. Also, the addition of a conductive phase is generally needed for satisfactory performance[27]. The additive of Fe$_2$P, which can form during preparation, can improve cell performance. However, the weight of Fe$_2$P is harshly limited due small amounts can increase cell performance, but larger amounts will block lithium ion paths[27].

Other promising phosphate cathode materials in lithium ion batteries are LiMnPO$_4$, LiCoPO$_4$. 4.1 V of LiMnPO$_4$ and 4.8 V of LiCoPO$_4$ have higher open circuit voltages and lower capacities than 3.5 V of LiFePO$_4$[25]. For example, in comparing with the capacities of LiFePO$_4$ prepared by microwave hydrothermal method, the capacities of LiMnPO$_4$ and LiCoPO$_4$ prepared by same process were reported to be ~1/6 and ~1/3, respectively[27].

Additionally, during cycling process, Mn$_2$P$_4$O$_7$ and Co$_2$P$_4$O$_7$, which are formed in LiMnPO$_4$ and LiCoPO$_4$ electrodes, respectively, will degrades the lifetime and can be a safety concern as oxygen is evolved during the decomposition reaction. Further, the mixture phosphate cathodes of LiFePO$_4$ with LiMnPO$_4$ or LiCoPO$_4$[28] have been reported. In these mixture cathodes, the capacity increases with increasing iron content, while operating voltage increases with increasing manganese content.

Another cathode material such as LiNiPO$_4$ is not generally used regardless of forming the olivine structure. However, nickel has been added to other lithium transition metal phosphates such as LiFePO$_4$ and LiMnPO$_4$, or complex compounds, such as Li(Mn,Fe)PO$_4$ and Li(Mn,Fe,Co)PO$_4$[25,26].

Another promising phosphate cathode material is Li$_3$V$_2$(PO$_4$)$_3$. Li$_3$V$_2$(PO$_4$)$_3$ forms a monoclinic structure (P2$_{1/n}$) and has a high operating voltage of greater than 4 V and good performance at high rate currents[29]. Moreover, the addition of vanadium to LiFePO$_4$ have been shown to improve the capacity of LiFePO$_4$, especially at high discharge currents[30]. For example, at 140.2 mAh g^{-1} at 5 C, and 105.8 mAh g^{-1} at 20 C of V-doped has been reached[30]. This is owing to the addition of vanadium reduces the lattice distortion and weakness of the Li-O bonds, leading to the enhancement in lithium diffusion and reduce the energy required for nucleation of LiFePO$_4$ in the LiFePO$_4$-FePO$_4$ two-phase region.

Another group of poly-anionic compounds, silicates, have been ex-

Table 1. Properties of Cathode Materials Used in Commercial Lithium Ion Batteries

Cathode materials	Theoretical capacity (mAh g^{-1})	Advantages	Disadvantages	Reference
$LiCoO_2$	274	Good cycle life Good energy	Thermal runaway Low practical capacity	[6]
$LiMn_2O_4$	148	Good thermal stability Inexpensive Good Power capability	Moderate cycle life Lower energy	[23]
$Li(Ni,Co,Al)O_2$	274	Good energy Good power capability Good cycle life	Thermal runaway Sensitive with moisture Moderate cycle life	[22]
$Li(Ni,Co,Mn)O_2$	274	Good thermal stability Good energy, power, and cycle life	Patent issues	[19]
$LiFePO_4$	170	Good thermal stability Good cycle life Good power capability	Low energy Elevated self-discharge	[25]
$LiFeSO_4F$ $LiVPO_4F$	150 156	High potential Low activation energy	Toxicity & environmental impact Low capacity Low cycle life	[34] [31]

amined for their interesting electrochemical potential as cathode materials including $LiVPO_4F$[31], Li_2MnSiO_4[32], Li_2CoSiO_4[33], and $LiFeSO_4F$[34]. However, several limitations have to be overcome before a wide use of such materials becomes feasible. For example, J.C. Zheng et. at.[31] reported a preparation for nano-carbon coated $LiVPO_4$ cathode material. $LiVPO_4F$ particles are about 100 nm in diameter and wrapped by nano-carbon webs. The $LiVPO_4F$/C cathode delivers a discharge capacity of 143 mAh g^{-1} at 0.5 C in the range of 3.0-4.4 V at the first cycle, and high capacity remaining at both of 1C and 3C. However, in comparing with another cathode material, it has smaller capacity and potential, so need to be investigated more before a wide use.

2.4. Conversion cathode

Recently, owing to low cost and more abundant element in the nature, conversion cathode has been emerging as an alternative for intercalation cathode. Conversion cathode can store from 2-3 lithium ions per 1 atom of chalcogenide (e.g. O, S, etc,.) or transition metal (e.g. Fe or Cu), which is in contrast with intercalation cathode. Due to the different in the breaking and recombining chemcical bond during lithiation/ de-lithiation process, conversion cathode can be classified into 2 type A corresponding to reactions (4) and (5) as follow:

$$\text{Type A: } MX_z + y\ Li \leftrightarrow M + z\ Li_{y/z}X \qquad (4)$$

$$\text{Type B: } y\ Li + X \leftrightarrow Li_yX \qquad (5)$$
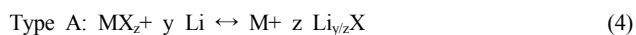
Type A cathode, true conversion has been made. In the contrary, in type B cathode, only phase of materials transforms to another single phase (chemical transformation). In type A, M are typically transition metal ions (Co^{2+}, Mn^{3+}, Fe^{3+}, Ni^{2+}, etc.), while X are typically halogen ions (such as F^-, Cl^-, Br^- and I^-) or chalcogenide ions (such as Se^{2-}, Te^{2-}, O^{2-} etc.). In type B, S, Se, Te, Br and I was lithiated to transform structure phase to Li_2S, Li_2Se, Li_2Te, $LiBr$ and LiI and exhibit high theoretical capacity.

Conversion cathode materials face substantial challenges that need to be resolved before achieving the desired performance characteristics. Low conductivity, voltage hysteresis, volume change during lithiation/de-lithiation are the main issues of conversion cathode, which leads to decrease the interactions between electrodes and electrolyte, resulting in poor cycling performance and high capacity fading. A lot of efforts has been made to overcome these issues such as i) design active particle (reducing particle size, changing morphology, coating, and doping)[35]; (ii) optimization electrolyte (developing salt composition, concentration, or using solid-state electrolyte)[36]; (iii) design battery (defining voltage range, C-rate, binder, separator, etc.)[37].

A summary of various cathode materials commonly used in LIBs with their theoretical capacity, advantages and disadvantages are shown in Table 1.

3. Anode Materials

Anode is the negative electrode in which lithium ion will exchange with anode material such as lithium metal, graphite, resulting in electrons flow out towards the external part of the circuit. Anode is generally required some characteristic such as low cost, stable in high thermal, ease of availability, and high conductivity. These requirements are very important in the choosing anode material because lithium ions from cathode and anode are easy to react with electrolyte at high temperature.

Currently, anode materials are most commonly made from carbonaceous such as graphite (naturally occurring or synthetic), hard carbon, soft carbon (made from organic precursors), or lithium titanium oxide, lithium metal. Anode materials also can be manufactured from silicon, and nanomaterials. Many materials are being tested such as Sn, Sb, and Al compounds silicides nitrides phosphides compounds, silicide, nitrides, phosphides, transition metal oxides, alloys and intermetallic.

3.1. Carbonaceous materials

Carbonaceous materials have higher practical capacity, higher voltage than other anode material such as lithium metal, metal oxide, polymers. So carbonaceous materials have been commercially used and is the most successful anode material in lithium ion batteries[38]. They could be recognized in various forms such as graphite, carbon, soft carbon (graphitizable carbons, same direction crystallite) and hard carbon (non-graphitizable carbons, disordered orientation). Each form has different structure and electrochemical properties.

Graphite has a layered structure containing a carbon hexagon network in an orderly arrangement. The polycrystalline carbon material, called highly ordered pyrolytic graphite (HOPG), is commonly used as an articular graphitic structure due to the limiting in manufacturing of defect-free ideal graphitic structure. Crystalline, morphology of graphite is the main factors effect to lithium intercalation of the materials as well as the lithium intercalation/de-intercalation potential.

Good graphitic material, which has highly crystalline, can take one Li atom for six C-atoms, resulting in a theoretical capacity of 372 mAh g^{-1} with a completely reversible process.

Carbon is abundance and amorphous in nature. Carbon consists of two morphology corresponding to two types of carbon depended on amount of electrons reacted with lithium ion. One is low specific charge nongraphitic carbon, which have $0.5 \leq x \leq 0.8$ in Li_xC_6. Other one is high specific charge carbonaceous material, which have $1.2 \leq x \leq 5$ in Li_xC_6 with a high practical capacity of 200-600 mAh g^{-1} and high current density capability[39]. However, it has defects that is poor electrical conductivity and large irreversible capacity, which limits their applications as an anode material[40].

Recently, the carbon based anode materials such as carbon nanotubes (CNTs), nanofibers and graphene has been strongly investigated. CNTs are characterized by highly ordered carbon nanostructures, realized through a self-assembly unidirectional growth process. Both single wall CNTs and multi-wall CNTs were extensively investigated as anode materials and in composites. In particular, due to superior electronic conductivity, good thermal stability and high lithium ion transport properties, CNT was used together with other active anode materials[41]. CNTs conjugated with a variety of nanostructured materials (Si, Ge, Sn, and Sn-Sb) or metal oxides (M_xO_y; M = Fe, Mn, Ni, Mo, Cu, or Cr) to improve the battery cycling life and capacity[42-45]. These hybrid systems result in CNTs with enhanced electrical conductivity and reduced volume changes during the charging and discharging processes.

Graphene is a crystalline allotrope of carbon with 2-dimensional sheets. Its carbon atoms are packed densely in a regular atomic-scale chicken wire (hexagonal) pattern. Graphene consists in a honeycomb with thickness of nanometer. Graphene has good electrical conductivity, relevant mechanical strength, high values of charge mobility and high surface area. Despite lithium ion amount adsorbed by a single layer of graphene is low compared to graphite (372 mAh g^{-1})[46], the graphene performance is significantly higher when a number of graphene sheets is considered together, which leads to higher capacity of 780 mAh g^{-1} or 1,116 mAh g^{-1}.

3.2. Metal alloys

Huggin and Besenhard was first proposed about metal alloys as an effective anode material for lithium ion battery[47,48]. Later on, extensive investigations on metal and metal oxide alloys with their electrochemical performance were carried out. The primary choices of metal alloys were Li-based alloys, Li_xM. Inhere, M plays a role as an electrochemically active metal, which support the strain generated during the lithium intercalation/deintercalation process, as well as to improve the electrical conductivity[49]. However, due to volume expansion during the charge-discharge process caused by incorporation of electrochemically inactive material in alloys, cracks appears on the surface of alloys, leading to a decrease in the cycling performance of battery, especially in reversible capacity. The use of electrochemically active metal alloys in the nano-dimensional structure have drawn much attention to improve reversible capacity with good cycling performance. In this case, electroactive metals, such as Si, Sn, Al, Ga, Ge, Pb, and Sb[50-53] are extensively studied as matrix metals with the reversible formation of Li-M different phases including phase transitions in several steps during the lithium intercalation/deintercalation process. For example, in the case of pure aluminum, alloying with lithium occurs with several successive phase formations: the formation of the α-phase (~7% Li in LiAl), β-phase (a non-stoichiometric phase with ~47 to ~56% Li), and several lithium-rich phases. During discharge some Li remains in the Al (the α-phase is kept, only the β-phase is cycled), so that the Li_xAl is cycled within the stoichiometric range of $0.1 \leq x \leq 1$ (~50% Li)[54]. The choice of metal matrices is depending on their specific reversible capacity values, their structure as well as thermal stability properties[55]. Among them, Si is the most commonly researched anode material due to Si is the 2nd most abundant element on earth (inexpensive and eco-friend), involving alloy formation with lithium as Li_7Si_3, and $Li_{13}Si_4$ in several steps. However, the high volumetric change during cycling leads to an irreversible cracking and disconnection of the active mass from the current collector, resulting in decreasing cycle life and capacity of battery. A lot of efforts were focused on nanostructured Si, especially on their morphology aspect. Owing to the ability to provide the necessary free volume for Si expansion during alloying/de-alloying process, nanowires, nanotubes and nanospheres with high reversible capacity of 2,000 mAh g^{-1} were received a lot of attention. Carbon coating has been focused to make a higher cycle life with superior cycling performance. M.G. Jeong et al.[56] nitrogen doped carbon coating layer on porous silicon was synthesized to minimize the large volume expansion effect. The prepared anode was showed good capacity retention after 100 cycles at 0.8 A g^{-1} and high capacity of 1,904 mAh g^{-1} at current density of 20 A g^{-1}.

3.3. Transition metal oxides

Transition metal oxides (TMO) is promising alternative anodes for graphite because of its very high capacity. Moreover, TMO has good reversibility and maintained in the nanoscale system. TMO can be combine with some materials or change nanostructure to improve its limitation such as low electronic conductivity and thick solid electro-

lyte interface (SEI) layer. Among different TMOs materials, tin oxide (SnO_2) was the preliminary choice for use as an anode material, because of its high theoretical capacity[57]. The reaction between tin oxide and lithium is pointed out below.

$$SnO_2 + 4Li^+ + 4e \rightarrow Sn + 2Li_2O \qquad (1)$$

$$Sn + xLi^+ + xe^- \rightarrow 4Li_xSn \ (0 \leq x \leq 4.4) \qquad (2)$$
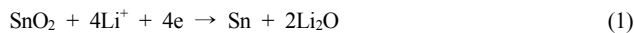
From equations (1), (2), because of having 8.4Li for one SnO_2 formula unit, the corresponding theoretical capacity is 1491 mAh g^{-1}. However, due to the irreversible nature of the reaction with the lithium ion leads to large capacity loss initially. The capacity of SnO_2 reduces to 783 mAh g^{-1} after 2 cycles. Therefore, 783 mAh g^{-1} is commonly considered as the actual theoretical capacity. Furthermore, severe electrode degradation is observed because of the consistent volume change (> 200%) upon cycling. In order to reduce the volume, change and improve the cycling stability of SnO_2, a lot of attention was made such as changing morphological structures of SnO_2 to nanowires, nanotubes, nanorod, nanoboxes and nanosheets[57-60]. For example, L. Yu et al. reported the synthesis of SnO_2 and $SnO_2@C$ nanorods by a hydrothermal method[60]. Owing to the nanostructure, SnO_2 nanorods do not exhibit fast capacity fading and the carbon coating helps stabilizing the electrode structure and results in a more stable cycling performance. The material has an 1st and 2nd discharge capacity of 1,963 and 939 mAh g^{-1} which is much higher than the theoretical capacity.

Another promising anode material used in lithium ion batteries is titanium dioxide (TiO_2). Due to its non-toxic, eco-friendly environment, it is extensively studied and used in much of applications, such as catalysis, dye-sensitized solar cell, electrical ceramics, and chemical intermediates. Numerous efforts have been made to get a higher theoretical specific capacity. The lithiation/delithiation process in TiO_2 anode can be presented as the following reaction below:

$$xLi^+ + TiO_2 + xe^- \leftrightarrow Li_xTiO_2 \ (0 \leq x \leq 1) \qquad (3)$$
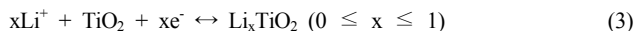
Owing to a lithiation process, a phase transition from tetragonal to orthorhombic TiO_2 is observed. Among TiO_2 existence such as anatase, rutile, and imenite, the anatase TiO_2 is known to be most electroactive material because in the anatase structure lithium ion can be anisotropically diffuse along the c-axis. On the contrary, the lithium diffusion is inhibited in rutile TiO_2 due to its crystal orientation. Moreover, the anatase TiO_2 with higher percentages of (001) exposed facets is more reactive than (101) facets and undergoes fast reversible lithium intercalation/de-intercalation[61]. However, its limitation, poor electrical conductivity limits applications of pristine TiO_2 in lithium ion batteries. Therefore, the doping of TiO_2 is also a solution to improve the electronic conductivity doping of TiO_2. The doping of N with TiO_2 is attracted many attentions because of its potential for environmental catalysis[62].

Beside of materials mentioned above, spinel $Li_4Ti_5O_{12}$ (LTO) is considered the most appropriate titanium based oxide material for lithium
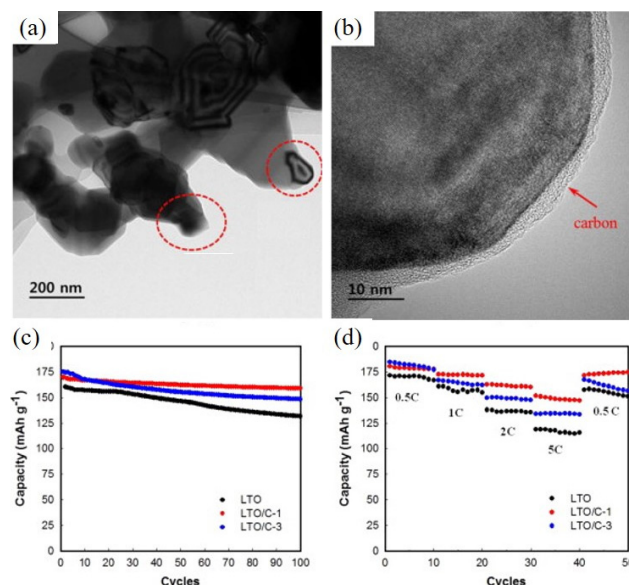

Figure 6. (a) TEM images of LTO/C, (b) high-resolution images of the areas marked in red dashed circles, (c) cycling performance of LTO anode at a 0.5 C rate, and (d) rate capabilities of LTO anode (reproduced from[64]).

storage purposes because it exhibits excellent Li-ion reversibility at the high operating potential of 1.55 V vs. Li/Li$^+$. Lithium insertion/extraction in LTO occurs by the lithiation of spinel $Li_4Ti_5O_{12}$ yielding rock salt type $Li_7Ti_5O_{12}$. Its low electrical conductivity (~10^{-9} S cm^{-1}), however, is an impediment to achieving the high rate capability needed for high-power applications. A lot of efforts are made to overcome these issues such as surface treatments[63], or coating with carbon sources[64]. LTO/C composites were synthesized by an emulsion reaction using soybean oil as the carbon source. LTO/C composite particle size is in the range of 100 to 200 nm. LTO/C anode exhibits a high capacity of 150.44 mA h g^{-1} at a high rate of 5 C with superior capacity remaining after 100 cycles (Figure 6).

3.4. Conversion anode materials

Conversion anode materials (M_xN_y; M = Fe, Co, Cu, Mn, Ni and N = O, P, S and N) and its compound with lithium compounds exhibit high reversible capacities (500-1,000 mAh g^{-1}) owing to the participation of a high number of electrons in the conversion reactions. The electrochemical conversions reactions can be described as follows:

$$M_xN_y + zLi^+ + ze^- \leftrightarrow Li_zN_y + xM \qquad (4)$$
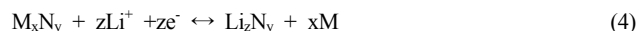
Among conversion anode materials, iron oxides have been extensively studied for LIB owing to their low cost and eco-friendly environment. However, iron oxides tend to exhibit poor cycling performance due to low electrical conductivity, low diffusion of Li-ions, high volume expansion and iron aggregation during charging and discharging. Many efforts have been made to overcome these disadvantages such as modifying size, shape or porosity. For example, Y. Zhu et al.[65] reported cross-linked porous α-Fe$_2$O$_3$ nanorods as an

Table 2. Properties of Anode Materials Used in Commercial Lithium Ion Batteries

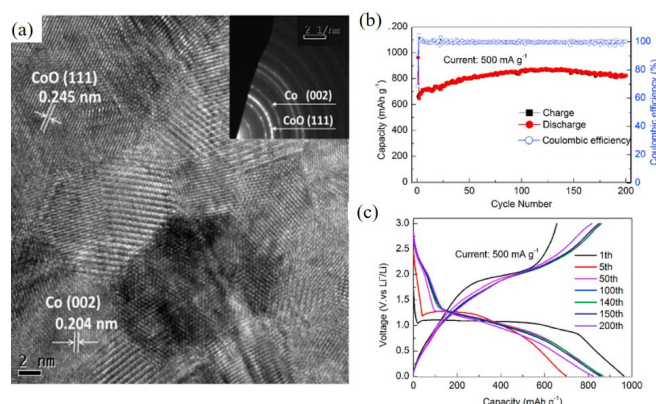| Anode Materials	Theoretical capacity (mAh g^{-1})	Advantages	Disadvantages	Reference
Graphite	372	Good working potential	Low coulombic efficiency	[43]
Hard carbons	1,116	Low cost	High voltage	[36]
CNT	780/1,116	Good safety	High irreversible capacity	[39]
LiTi$_4$O$_5$	175	Extreme safety Good cycle life	Very low capacity	[58]
TiO$_2$	330	Low cost High power capability	Low energy density	[57]
Silicon	4,200	Good thermal stability	Large irreversible capacity	[47]
Tin	960	High energy density	Huge capacity fading	[48]
Germanium	1,384	Good safety	Poor cycling	[49]
Fe$_2$O$_3$				[65]
Fe$_3$O$_4$	500-1,200	High capacity	Unstable SEI formation	[65]
CoO		Low cost	Poor and short cycle life	[66]
RuO$_2$				[67]

Figure 7. (a) TEM image with inset showing SAED patterns of CoO-Co nanocomposite, (b) Cycling performance of CoO-Co nanocomposite, and (c) Discharge-charge profile of CoO-Co anode at current density of 500 mA g^{-1} (reproduced from[66]).

anode material. The cross-linked porous α-Fe$_2$O$_3$ nanorods are synthesized via a facile hydrothermal-calcination method. The α-Fe$_2$O$_3$ nanorods display high initial discharge capacity of 740.2 mAh g^{-1} and excellent cycle stability at high rate density (600 mAh g^{-1} at 0.5C and 520 mAh g^{-1} at 1C) after 300 cycles. The improved electrochemical properties may be attributed to the regular 1D nanostructure, the cross-linked nanostructure and the abundant pores in the nanorods.

Another promising conversion anode material is cobalt oxide. Co$_3$O$_4$ and CoO (theoretical capacity of 890 and 715 mAh g^{-1}, respectively) are the most used for cobalt oxide anode material. For example, Y. Qin et al.[66] reported CoO-Co nanocomposite films as anode material. CoO-Co nanocomposite films were successfully deposited at room temperature by pulsed laser deposition. CoO and Co particles with average size of 5-10 nm (Figure 7) exhibited good cycling stability (830 mA h g^{-1} at a specific current of 500 mA g^{-1} after 200 cycles) and superior rate capability (578 mAh g^{-1} at current density of 10,000 mA g^{-1}).

A summary of various anode materials commonly used in LIBs with their theoretical capacity, advantages and disadvantages are shown in Table 2.

4. Conclusion

LIBs are considered of crucial role nowadays and become mandatory for most important electronics devices. This paper summarized the characteristics of different types of cathode and anode materials for LIBs and compare between their advantages and disadvantages performance such as specific capacity, thermal stability, volume changes and hysteresis phenomena encountered with alloying and conversion materials. By overcoming the inherent disadvantages of the above-mentioned cathode and anode materials, it is expected that lithium ion batteries having high energy and power density with long-term stability can be used inexpensively in the near future.

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