

# Reality and Future of Rechargeable Lithium Batteries

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**Abstract:** Compared to other types of rechargeable batteries, the rechargeable lithium battery has many advantages, such as: higher energy density, lower self-discharge rate, higher voltages and longer cycle life. This article provides an overview of the cathode, anode, electrolyte and separator materials used in rechargeable lithium batteries. The advantages and challenges of various materials used in rechargeable lithium batteries will be discussed, followed by a highlight of developing trends in lithium battery research.

**Keywords:** Rechargeable lithium battery, cathode, anode, electrolyte, separator, review.

## 1. INTRODUCTION

Energy and environment are the two most challenging issues faced by our society. With the production of oil predicted to decline and the number of vehicles and their pollution impact to increase globally, a safe, low-cost, high-efficiency and environmentally friendly alternative power sources have become a most urgent need. Solar energy, H<sub>2</sub> energy, fuel cells and batteries are attracting considerable interest as alternative power sources. Specifically, batteries are portable and easily replaced, commonly used in household and industrial applications such as energy storage and management [1]. Among various existing batteries (Fig. 1), lithium batteries have raised the most interest and have a high priority on the development of energy projects in many countries because of their high energy density, long cycle life, cost-effective, long lasting, and abuse-tolerant properties [2].

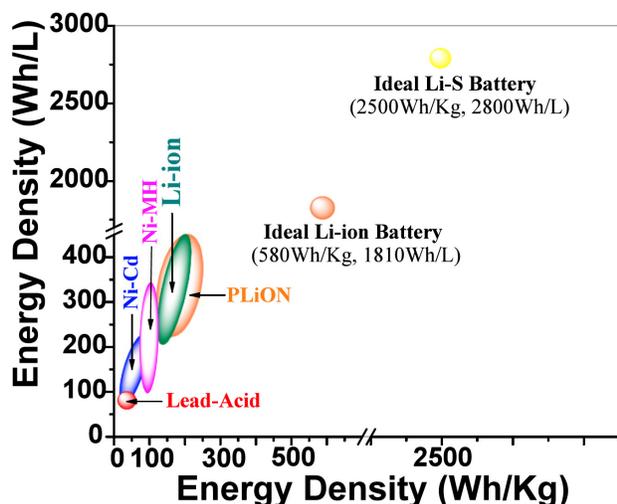


Fig. (1). The energy density of different batteries.

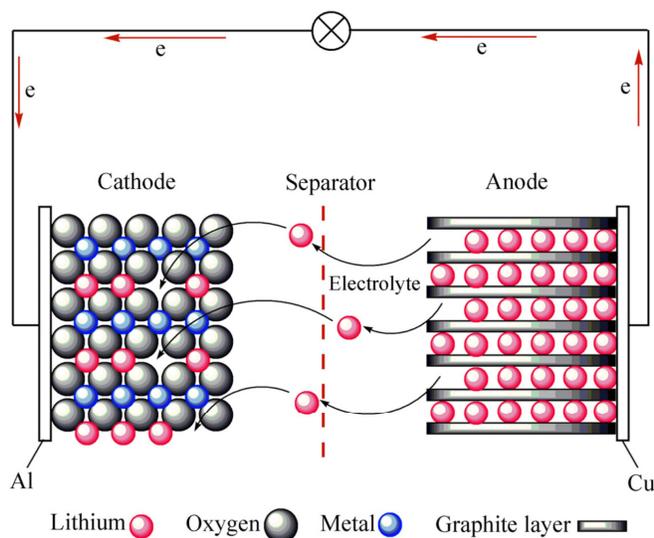
Rechargeable lithium battery is of present interest. There are many kinds of rechargeable lithium batteries. They have different classifications according to the forms of lithium (e.g. lithium metal as anode directly, we call it lithium battery. For lithium trans-metal salt as anode, we call it lithium ion battery. Usually, we simply call them lithium battery). Based on the types of electrolytes (such as lithium-aqueous battery, lithium-organic battery), and the kinds of cathodes (such as lithium cobalt oxide battery, lithium nickel oxide battery, lithium manganese oxide battery, lithium iron phosphate battery, sulfur battery), we have several other classifications as well.

However, each battery composes of one or several cells, and each cell has its own characteristic cell potential (V), capacity (Ah kg<sup>-1</sup> or Ah L<sup>-1</sup>), and energy density (Wh kg<sup>-1</sup> or Wh L<sup>-1</sup>). These characteristics are determined by the chemical properties of each component of the cell. To provide the required voltage and capacity, the cells can be connected in series or parallel configuration. Three primary functional components of an individual cell are the anode (negative electrode), the cathode (positive electrode), and the electrolyte. The transfer of Li ions between the two electrodes is facilitated by the dissociated lithium salts in the electrolyte. To fabricate a complete cell, however, requires additional components, such as a separator, current collector, tab and cell can.

In the case of discharge, the transfer of energy and current of a rechargeable lithium battery occurs when the electrodes are connected externally to a load (Fig. 2). Li ions are liberated from the anode, pass through the separator, and are "inserted" into the cathode. At the same time, the anode releases electrons, which pass through the external circuit and then arrive at the cathode. In the case of charge, the process is reversed. The cycling of a battery depends not only on the property of individual components: cathode, anode, electrolyte and separator, but also on the compatibility among different components. During the development of rechargeable lithium batteries, the first breakthrough was the discovery of Li ion intercalation compounds that enable reversible Li ion intercalation/deintercalation, which opened the concept of

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rechargeability. A second breakthrough was the application of nanostructured materials, which continuously improve the performance of rechargeable lithium batteries [3]. Nanostructured materials can increase the specific surface area as well as reduce diffusion length for electronic and Li ion transport, leading to a high charge/discharge rate.



**Fig. (2).** Schematic illustration of a lithium battery (in the case of discharge).

As one of the great successes of modern electrochemistry, the lithium battery has played a key role in the consumer electronic market. Thanks to the improvement of the electrodes and electrolytes, the lithium battery is moving to dominate not only portable battery industry (MP3 player, laptop, cell phone and camera etc.), but also electronic automotive transportation (electric vehicles, full hybrid electric and plug-in electric vehicles). But the reality is complex: although scientists have produced numerous potential battery chemistries, problems of various natures still prevent the large scale application of lithium batteries for the electronic automotive transportation. None of them perform well on all the crucial factors of cost, safety, durability, power and capacity [4]. To further advance in the science and technology of lithium batteries, new strategies must be implemented. This includes modifications of the electrode and electrolyte components and further improvements in their safety, environmental sustainability and energy content.

The following sections provide a review of rechargeable lithium batteries in terms of cathode, anode, electrolyte and separator. Significant changes to the properties and performance of these battery components brought by the development of intercalation and nanostructured materials are demonstrated. The challenges and potentials of rechargeable lithium batteries are also discussed.

## 2. CATHODES

The material for an ideal cathode of a rechargeable lithium battery should have following properties: First, the material may be capable of reversibly intercalating/deintercalating Li ions at a large capacity and high potential. Second, the material should undergo minimal structural change during Li ion intercalation/ deintercalation,

as required for good cycle performance. Third, the material should suffer minimal redox potential change during Li ion intercalation/deintercalation, as required for smooth charge/discharge curves. Fourth, the material should have high electronic conductivity, high Li ion diffusion rate and conductivity, as required for high charge/discharge rate. Lastly, the material should be chemically stable with the electrolyte under operating potentials.

The intensively studied cathode materials mainly include lithium cobalt oxide, lithium nickel oxide, lithium manganese oxide, and olivine phases, in particular, lithium iron phosphate ( $\text{LiFeO}_4$ ). Additionally, sulfur based cathode materials have attracted significant attention recently, because of their high specific capacity ( $1670 \text{ Ah Kg}^{-1}$ ). For lithium cobalt oxide and lithium nickel oxide, both of them contained layered structure which could offer highly accessible ion diffusion pathways. The benefit in using lithium iron phosphate is that, in addition to being naturally abundant and inexpensive, they are less toxic than cobalt, manganese, and nickel compounds. There are many merits making sulfur as a very suitable cathode material, such as the low equivalent weight, low cost, high capacity, and environmental friendliness. The advantages and disadvantages of different cathode materials are discussed below.

### 2.1. Lithium Cobalt Oxide and Lithium Nickel Oxide

Lithium cobalt oxide ( $\text{LiCoO}_2$ ) is an intercalation material allowing reversible intercalation/deintercalation of Li ion.  $\text{LiCoO}_2$  has a large tap density ( $2.8 \sim 3.0 \text{ g cm}^{-3}$ ), large gravimetric capacity ( $\sim 140 \text{ Ah Kg}^{-1}$ ), excellent cyclability (500–800 cycles), and high operating voltage (3.6 V). These desirable qualities make  $\text{LiCoO}_2$  a widely used cathode material in commercial batteries. However, when the cell is over-charged or over-discharged, the instability of  $\text{LiCoO}_2$  structure could lead to severe material degradation and even explosion of the cells. This raises serious operation concerns for commercial operation, but even more so for personal batteries. Additionally, cobalt is a relatively rare and expensive metal, which limits the widespread implementation of  $\text{LiCoO}_2$  in power batteries for electric vehicles.

Besides  $\text{LiCoO}_2$ , there are several other well-known Li ion intercalation compounds. Lithium nickel oxide ( $\text{LiNiO}_2$ ) is considered a preferred cathode material for its larger gravimetric capacity ( $275 \text{ Ah Kg}^{-1}$ ), higher natural abundance and lower toxicity as compared with  $\text{LiCoO}_2$ . But, the structure of  $\text{LiNiO}_2$  is not as stable as that of  $\text{LiCoO}_2$  [5–8]. To mitigate the structural instability, partial substitution of Ni with Al, Ga, Mg or Ti is considered. For example,  $\text{LiNi}_{0.75}\text{Al}_{0.25}\text{O}_2$  has shown higher thermal stability and safer operation during over-charge. Moreover, a novel layered material of  $\text{LiNi}_{0.32}\text{Mn}_{0.33}\text{Co}_{0.33}\text{Al}_{0.01}\text{O}_2$  with  $\alpha\text{-NaFeO}_2$  structure synthesized by sol-gel method has been used as a cathode in lithium batteries. The capacity retention of  $\text{LiNi}_{0.32}\text{Mn}_{0.33}\text{Co}_{0.33}\text{Al}_{0.01}\text{O}_2$  has been improved to 97% [9]. Another problem with  $\text{LiNiO}_2$  is the capacity fading [10], which may be solved by partially substituting Ni with Ti and Mg. A typical example is  $\text{LiNi}_{1-x}\text{Ti}_{x/2}\text{Mg}_{x/2}\text{O}_2$ , which has been used as a cathode material at a high capacity of  $180 \text{ Ah Kg}^{-1}$  and good thermal stability [11].

The high capacity of Ni-rich  $\text{Li}[\text{Ni}_{1-x}\text{M}_x]\text{O}_2$  ( $\text{M}=\text{Co}, \text{Mn}$ ) is very attractive, if the structural instability and thermal properties are improved. Yang-Kook Sun *et al.* synthesized a spherical core-shell structure with a high capacity (from the  $\text{Li}[\text{Ni}_{0.8}\text{Co}_{0.1}\text{Mn}_{0.1}]\text{O}_2$  core) and a good thermal stability (from the  $\text{Li}[\text{Ni}_{0.5}\text{Mn}_{0.5}]\text{O}_2$  shell) [12]. This core-shell structured  $\text{Li}[(\text{Ni}_{0.8}\text{Co}_{0.1}\text{Mn}_{0.1})_{0.8}(\text{Ni}_{0.5}\text{Mn}_{0.5})_{0.2}]\text{O}_2/\text{carbon}$  cell has a superior cyclability and thermal stability relative to the  $\text{Li}[\text{Ni}_{0.8}\text{Co}_{0.1}\text{Mn}_{0.1}]\text{O}_2$  at the 1 C rate for 500 cycles. Expanding on this idea, a concentration-gradient cathode material for rechargeable lithium batteries based on a layered lithium nickel cobalt manganese oxide was developed [13]. This novel high-capacity and safe cathode material with an average composition of  $\text{Li}[\text{Ni}_{0.68}\text{Co}_{0.18}\text{Mn}_{0.18}]\text{O}_2$ , in which each particle consists of bulk material  $\text{Li}[\text{Ni}_{0.8}\text{Co}_{0.1}\text{Mn}_{0.1}]\text{O}_2$  coated by a concentration-gradient outer layer which the reactive nickel ions are gradually substituted by manganese ions. As expected, this concentration-gradient cathode material achieved a high capacity of  $209 \text{ Ah Kg}^{-1}$  and also showed superior thermal stability.

## 2.2. Lithium Manganese Oxides

Lithium manganese oxides yield a high operating voltage (3.7 V) and are favored over  $\text{LiCoO}_2$  and  $\text{LiNiO}_2$  in electric vehicles because they are safe, cheap and non-toxic. There are two well known "lithium-rich" manganese oxides, the spinel  $\text{LiMn}_2\text{O}_4$  [14-17] and orthorhombic  $\text{LiMnO}_2$  [18]. Unfortunately, the capacity of these materials decreases rapidly during cycling at normal operating temperatures due to structural instability, but this problem can be solved through cationic substitution with Cr, Al, Mg, and Fe [15, 19-23]. It was reported that Al-doped  $\text{LiAl}_{0.1}\text{Mn}_{1.9}\text{O}_4$  materials using a room-temperature solid-state grinding reaction followed by calcination showed the obviously improved cyclability compared with the pristine  $\text{LiMn}_2\text{O}_4$  [24]. Another problem is its limited cycling and storage performance at elevated temperatures ( $>40^\circ\text{C}$ ), which can be improved by changing the structure (such as using synthesizing bi-substituted  $\text{LiMn}_{2-x}\text{Al}_x\text{O}_{4-z}\text{F}_z$ ) [25, 26], or modifying the surface (such as acetylacetone, boron oxide and alkali-hydroxydes solution treatment) [27, 28].

## 2.3. Lithium Iron Phosphate

In 1996, lithium iron phosphate ( $\text{LiFePO}_4$ ) was discovered and used as a cathode material for rechargeable lithium batteries [29, 30]. It gained vehicle market acceptance because of its low cost, low toxicity, excellent thermal stability, and high gravimetric capacity ( $170 \text{ Ah Kg}^{-1}$ ). However, the main application barrier of  $\text{LiFePO}_4$  was its intrinsically low electrical conductivity [31]. This may be overcome by synthesizing  $\text{LiFePO}_4$  in nanoparticles. Alternatively, the same improvement in electrical conductivity can be achieved by carbon coating of  $\text{LiFePO}_4$  [32-34] or doping  $\text{LiFePO}_4$  with various metal elements [35-37]. It was reported that stoichiometric Cu-doped lithium ion phosphate  $\text{LiFe}_{1-x}\text{Cu}_x\text{PO}_4/\text{C}$  ( $x = 0, 0.01, 0.015, 0.02, 0.025$ ) cathode materials had been synthesized by a solid state high temperature reaction in an inert atmosphere using  $\text{Cu}(\text{Ac})_2$  as a dopant and  $\text{FePO}_4$  as a precursor. The charge/discharge test showed that the cathode materials possessed the excellent

charge/discharge capacities, about  $150 \text{ Ah Kg}^{-1}$  and  $297 \text{ Ah L}^{-1}$  at a rate of 0.1 C and more than  $127 \text{ Ah Kg}^{-1}$  and  $252 \text{ Ah L}^{-1}$  at a rate of 2 C [38]. These approaches do not increase the lattice electronic conductivity or chemical diffusion coefficient of lithium within the crystal.

The power density (i.e., the charge/discharge rate) of  $\text{LiFePO}_4$  is limited by the rate of Li ion and electron migration through the electrolyte into the electrode [39]. Strategies to increase the charge/discharge rate of  $\text{LiFePO}_4$  have focused on improving electron transport overall [35] or simply at the cathode surface [31, 40], along with reducing the diffusion distance by using nano-sized materials [41, 42]. Moreover,  $\text{LiFePO}_4$  nanoparticles coated with a lithium phosphate layer demonstrated an extremely high charge/discharge rate [43] due to the lithium phosphate outer layer providing an ultrafast charging and discharging Li ion tunnel. Another promising cathode material is  $\text{LiFeSO}_4\text{F}$  [44]. By introducing fluorine and by replacing phosphate group with more electron-withdrawing sulphate groups, this material does not need nanostructuring or carbon coating.

## 2.4. Sulfur-Based Materials

The specific capacity of sulfur (S) cathodes is high ( $1670 \text{ Ah Kg}^{-1}$ ) compared to that of most other materials, e.g.,  $\text{LiCoO}_2$ ,  $\text{LiNiO}_2$ ,  $\text{LiMn}_2\text{O}_4$ ,  $\text{LiMnO}_2$  and  $\text{LiFePO}_4$ . In addition, S has a low cost and readily available, having a wide operation temperature range and possibility of long cycling. However, it has not been widely commercialized because of the poor electrical conductivity of elemental S and polysulfide shuttling that occurs during charge/discharge cycles [45]. To solve these problems as well as large volume change of S, a nanostructured S-carbon [46] and a hierarchically structured S-carbon nanocomposite [47] were developed for cathodes.

Lithium sulfide ( $\text{Li}_2\text{S}$ ) is also a possible cathode material. Similar to S, the poor electronic conductivity of  $\text{Li}_2\text{S}$  restricts its practical application, despite a high theoretical capacity of  $1166 \text{ Ah Kg}^{-1}$  [48, 49]. Metal additives (such as Cu, Co, and Fe) have been employed to enhance the conductivity of  $\text{Li}_2\text{S}$ -based cathodes [48-50]. But the metal additives result in a lower output voltage [49, 50]. A nanostructured  $\text{Li}_2\text{S}$ -carbon [47] has been employed as a cathode material to solve the insulation and solubility of polysulphide anions during charge/discharge [51].

Both S-carbon and  $\text{Li}_2\text{S}$ -carbon nanostructured materials use electrical conductive micro/mesoporous carbon for loading S or  $\text{Li}_2\text{S}$ . These materials have a high specific surface area in contact with electrolytes as well as a reduced diffusion length for electronic and Li ion transport. These properties lead to a high charge/discharge rate. Furthermore, the spatial confinement of micro/mesoporous carbon represses the solubility of polysulphide anions.

There are a number of commercial cathode materials available. However few of them can meet all the necessary requirements. Considering of these, ternary materials [Such as  $\text{LiCo}_x\text{Mn}_y\text{Ni}_{1-x-y}\text{O}_2$  ( $0 < x < 0.5, 0 < y < 0.5$ )] and sulfur are the possible cathodes to be commercialized. Table 1 summarizes the properties of commonly used materials in rechargeable lithium batteries.

**Table 1. Comparison of Typical Cathode Materials**

	LiCoO <sub>2</sub>	LiMn <sub>2</sub> O <sub>4</sub>	LiFePO <sub>4</sub>
Theoretical Capacity (Ah Kg <sup>-1</sup> )	145	148	170
Commercial Capacity (Ah Kg <sup>-1</sup> )	135~140	100~110	140~160
Tap Density (Kg L <sup>-1</sup> )	2.6~3.0	1.8~2.4	0.8~1.4
Discharge Plateau (V)	3.6	3.7	3.3
Cycle Life (Cycles)	500-800	1000-1500	> 3000
Working Temperature (°C)	-20~55	-20~50	-20~60
Advantages	1. Simple process 2. High volumetric capacity	1. Cheap 2. Simple process	1. Cheap 2. Eco-friendly 3. Safe
Disadvantages	1. Expensive 2. Toxic	1. Capacity fades at elevated temperature	1. Low conductivity 2. Complex process 3. Low volumetric Capacity
Applied Areas	Portable Devices	Electric Vehicles	Electric Vehicles

### 3. ANODES

The materials for the ideal anode of rechargeable lithium batteries should have following properties: First, the anode materials may have the ability to reversibly intercalate/deintercalate Li ion, at a large capacity and low potential. Similar to cathode materials, the anode materials should suffer minimal structural and redox potential change during the Li ion intercalation/deintercalation. These two requirements are important for good cycle performance and a smooth charge/discharge curve. Second, the anode materials should have high electronic conductivity, high Li ion diffusion rate and conductivity. Lastly, the anode materials should form a good solid-electrolyte interface with electrolytes at the first cycle, and remain chemically stable with the electrolyte in the subsequent cycles.

Carbon-based materials are generally used in commercial Li ion batteries as the anode. However, based on the limitation of the theoretical gravimetric capacities of these materials (372 Ah Kg<sup>-1</sup>, LiC<sub>6</sub>), many efforts have been carried out to develop higher capacity anode materials, such as Li-based materials, Tin-based materials, Transition-metal oxides and silicon. The advantages and disadvantages of different types of anode materials are discussed below.

#### 3.1. Li-Based Materials

Lithium is a most electropositive (-3.04 V versus standard hydrogen electrode) as well as the lightest metal in the elemental table [3]. As an anode material, it has a theoretical capacity of 3860 Ah Kg<sup>-1</sup>. However, lithium can react with organic electrolytes, resulting in an insulating layer or gas evolution, thus increasing the internal pressure in the cell. Meanwhile, lithium dendrites form on the lithium electrode surface during charge/discharge, bringing in two serious results: a gradual fading of capacity due to the fracture of dendrites, and internal short circuiting of cells due to the penetration of dendrites through the separator. Ionic conductors, lithium phosphorus oxynitride, lithium nitride, lithium superionic conductors (LISICON) and different

electrolytes have been used to restrain the formation of lithium dendrites [52-60].

In order to improve the safety of lithium batteries, Li<sub>3-x</sub>Co<sub>x</sub>N (x=0.1~0.6) was used as a new material to substitute the existing lithium anode. Despite the large and reversible capacity (760 Ah Kg<sup>-1</sup> or 1500 Ah L<sup>-1</sup>), moisture sensitivity can restrict the practical use of this material [61].

#### 3.2. Carbon-Based Materials

In commercial Li ion batteries, soft carbon (such as nature graphite) and hard carbon (such as pyrolytic carbon from polymer) are widely used as the anode, because of their low and smooth charge/discharge potential, and good cycle performance. It has some shortcomings, however, such as low capacity (372 Ah Kg<sup>-1</sup> or 830 Ah L<sup>-1</sup>), bad performance under high charge/discharge rates (lithium can deposit on the surface of graphite), and cointercalation of organic solvent into graphite [62, 63]. Many current research efforts are focused on searching for new materials to substitute graphite anodes.

Graphene is a two-dimensional aromatic monolayer of carbon atoms. It has been proposed that Li ion could be adsorbed on both sides of graphene sheets, which leads to two layers of lithium for each graphene sheet, with a theoretical capacity of 744 Ah Kg<sup>-1</sup> through the formation of Li<sub>2</sub>C<sub>6</sub> [64, 65]. It was reported that the electrochemical performances were supposed to be greatly enhanced if combined with Fe<sub>3</sub>O<sub>4</sub> nanoparticles and graphene [66]. The Fe<sub>3</sub>O<sub>4</sub> nanoparticles were dispersed on graphene sheets *via* microwave irradiation synthesis. As anode materials for Li ion batteries, they showed high reversible capacities, as well as significantly enhanced cycling performances (about 650 Ah Kg<sup>-1</sup> after 50 cycles) and high rate capabilities (350 Ah Kg<sup>-1</sup> at 5 C), which might be attributed to graphene sheets not only acted as electron conductors, but also buffers which accommodated the strains of Li ion insertion/extraction and relieved the strain associated with the volume variations during cycles.

### 3.3. Tin-Based Materials

Lithium will form alloys with some metals under certain conditions, in which Li ion can reversibly intercalate/deintercalate. Metals and alloys have been investigated for anode application since 1970, and have a much larger capacity than that of graphite. A commercial battery based on a low-melting alloy (an alloy of Bi, Pb, Sn and Cd) for anodes was introduced in the 1980s [67, 68].

$\text{Li}_{22}\text{Sn}_5$  has a high theoretical capacity of  $990 \text{ Ah Kg}^{-1}$  or  $7200 \text{ Ah L}^{-1}$ . However, the volume and composition of this kind of alloy change during the electrochemical reaction, leading to fragmentation of the alloy [69, 70].

Intermetallic compounds  $\text{MM}'$  (M is an “active” element, can form an alloy with lithium, and M’ is an “inactive” element, cannot form an alloy with lithium) have been used as anode materials, and the cycling performance of these compounds can be improved significantly if the active alloy element is finely dispersed completely in an inactive matrix [71]. Therefore, it is believed that the inactive species provides structural stability and combats the expansion of the alloy composite. The reversible reactivity of intermetallic compound SnFe with Li ion has been explored for an anode material [72-74]. The benefit arises from the alloy formation between Li ion and Sn atoms at the grain boundaries of  $\text{SnFe}_3$  particles [75]. However, the cycling performance was improved at the expense of the capacity. Another approach to improve the cycling performance was that Li ion could be intercalated into the intermetallic compound  $\text{Cu}_6\text{Sn}_5$  to yield the product  $\text{Li}_{13}\text{Cu}_6\text{Sn}_5$  with the volumetric capacity of  $2964 \text{ Ah L}^{-1}$ . In addition, Li ion does not alloy or react with the “inactive” component (i.e., Cu), which further increases the stability of the anode. Note that  $\text{Cu}_6\text{Sn}_5$  has relatively small irreversible capacities compared to tin oxides [76].

Tin-based amorphous oxides,  $\text{SnM}_x\text{O}_y$  (M is B, P or Al,  $x \geq 1$ ), have a high volumetric specific capacity of more than  $2200 \text{ Ah L}^{-1}$ . In these compounds, Sn forms the electrochemically active center for Li ion intercalation, and the other metal group provides an electrochemical inactive network of  $-(\text{M}-\text{O})-$  bonding, to confer high reversibility in Li ion storage and release [77, 78]. This type of the material has not been commercialized because of poor long-term cyclability and the fact that a large amount of the capacity is irreversibly lost during the first cycle (because many Li ions have reacted to form  $\text{Li}_2\text{O}$  and solid-electrolyte interface film).

Tin-transition metal-carbon (Sn-TM-C) alloys have been used to replace graphite as the anode for Li ion batteries [79]. The Sony Corporation launched in 2005 a Li ion battery that uses a “tin-based amorphous anode” comprising tin, cobalt and carbon as the anode [80]. The Sn-Co-C system has been proposed to be the best choice among Sn-TM-C (TM= transition metal) for anodes in Li ion batteries since a nanostructure consisting of amorphous CoSn grains in a carbon matrix is formed during sputtering or during mechanical milling [81-83]. It was reported that  $\text{Sn}_{30}\text{Co}_{30}\text{C}_{40}$  had good capacity retention for at least 100 cycles at around  $425 \text{ Ah Kg}^{-1}$ , and  $\text{Sn}_{30}\text{Co}_{15}\text{TM}_{15}\text{C}_{40}$  also showed good capacity retention for at least 100 cycles ranging from 270

$\text{Ah Kg}^{-1}$  for samples with TM=Ni to  $500 \text{ Ah Kg}^{-1}$  for samples with TM=Ti, which might be attributed to the desired nanostructured-type XRD pattern [84].

### 3.4. Transition-Metal Oxides

Transition-metal oxides (MO) were proposed as anode materials for their large capacity at low potentials [85, 86]. The reaction mechanism between MO (M is Co, Ni, Cu or Fe) and Li ion differs from the classical Li ion intercalation/deintercalation or Li-alloying processes [87]. It involves the composition and decomposition of  $\text{Li}_2\text{O}$ , accompanied with the reduction and oxidation of the transition metal, respectively. The capacities of these transition-metals are all greater than  $700 \text{ Ah Kg}^{-1}$ , with high capacity retention and high recharging rate. These systems hold much promise for future development.

Among MO materials, the capacities of Ti-based oxides are less than half that of graphite ( $175 \text{ Ah Kg}^{-1}$  for  $\text{Li}_4\text{Ti}_5\text{O}_{12}$ ). However, these materials have many advantages, such as outstanding stability, rapid charge rate, and wide operating temperature (range from  $-50 \text{ }^\circ\text{C}$  to  $75 \text{ }^\circ\text{C}$ ). The combination of these advantages results in ultra long durability (around 20 years) and cycle life (9000 cycles). In addition, these batteries do not explode or result in thermal runaway under harsh conditions [88, 89].

### 3.5. Silicon

Among all the compounds proposed to replace the graphite anode, silicon is very promising because it has a theoretical specific capacity of  $4200 \text{ Ah Kg}^{-1}$  (for  $\text{Li}_{22}\text{Si}_5$ ) [90, 91]. Moreover, silicon is the second most abundant element on earth and already has a mature industrial infrastructure in existence. It is an attractive material when considering commercial applications. But the biggest holdback preventing the commercial application of silicon is the large inherent change in specific volume (up to about 410%) during the intercalation/deintercalation of Li ion. This causes crumbling, and a loss of electrical contact between the active material and the current collector [69, 92-95]. Recently, Si nanowires were developed as the anode material to accommodate the large volume change and to avoid capacity loss during cycling [96-102]. In addition, nanowires form direct chemical bonds with the current collector for good adhesion and electron transport, which makes the binding polymer and conducting graphite unnecessary. The observed specific capacity was about  $2800 \text{ Ah Kg}^{-1}$  [84]. Yushin *et al.* conducted a large-scale hierarchical bottom-up assembly route for the formation of Si in the nanoscale-containing rigid and robust spheres with irregular channels for rapid access of Li ions into the particle bulk. Reversible capacities of the C-Si nanocomposite reached up to  $1,950 \text{ Ah Kg}^{-1}$ , which is over five times higher than that of the theoretical capacity of graphite [103, 104].

The capacity of different anode materials is shown in Fig. (3). Despite many candidates for anode materials, graphite is the only widely used commercial anode material. Other anode materials, such as  $\text{Li}_4\text{Ti}_5\text{O}_{12}$  and  $\text{Li}_{22}\text{Sn}_5$ , are currently on a small scale application. Looking into the future, the trend of anode materials may shift to high capacity lithium or silicon materials.

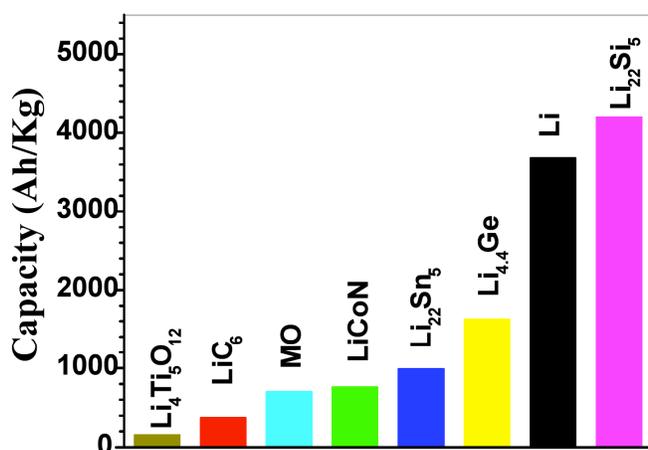


Fig. (3). The capacity of different anode materials.

#### 4. ELECTROLYTES

Electrolyte is one of the key components of a battery, which is commonly referred to as a solution comprising solvents and salts (such as LiPF<sub>6</sub>, which is well known for its rapid dissolution in carbonate solvents, lower cost and good conductivity [105, 106]). The choice of electrolytes is very crucial, and depends on the choice of the anode and the cathode. For instance, graphite anodes operate in a highly reducing voltage range (<1.2 V vs lithium), at which point most electrolytes are thermodynamically reduced. To ensure reversible behavior, the deposition of an efficient passivating layer at the graphite surface is necessary during the first cycle. The electrolyte was probably oxidized when the lithium oxide cathode materials were charged up to more than 4 V vs lithium [7, 107]. Electrolyte oxidation leads to irreversible loss of capacity, because of the generation of new chemical species, which deposit on the electrode surface as an insulating layer or evolve as a gas, thus increasing the internal pressure in the cell. Electrolyte oxidation is believed to be the main failure mechanism for rocking-chair technology [108]. Thus, minimizing electrolyte oxidation is a major requirement in enhancing the cycle life and improving the performance of lithium batteries at elevated temperatures. Fortunately, the electrolyte oxidation reaction is limited. Most of the electrolytes can be used beyond the voltage range of their thermodynamic stability [108].

##### 4.1. Traditional Organic Liquids

There are numerous liquid compounds available to be selected as electrolytes. Viscosity, dielectric constants and ionic conductivity of an organic liquid should be considered first to determine a suitable electrolyte. Most liquid electrolytes are composed of ethylene carbonate (EC) and dimethyl carbonate (DMC). EC is present in almost all commercial compositions, because of its low cost, good electrochemical stability, and high dielectric constant which permits better ionic dissociation of the salt and improves the ionic conductivity. Furthermore, it can provide a protective layer on the surface of graphite that prevents further reaction [109]. However, a pure EC-based electrolyte was not used because of its high freezing point (35-38 °C), which is not compatible with practical application. DMC, commonly known as a thinning solvent, is used with EC to reduce the viscosity. Note that a pure DMC-based electrolyte is not

compatible with graphite anodes, since no passivation layer can build up during cycling [108]. In general, the traditional liquid electrolytes have several disadvantages, such as flammability and a narrow range of operating temperatures [110]. These problems could be solved by novel electrolytes such as ionic liquids, organic solid electrolytes or inorganic solid electrolytes.

##### 4.2. Ionic Liquids

Ionic liquids as electrolytes for lithium batteries have been studied in recent years [111-113]. The ionic liquids are nonflammable as they contain no volatile compound. In addition, they show a broad electrochemical stability window (generally >4 V). Early attempts to cycle Li ion batteries using electrolytes on the basis of ionic liquids failed because of electrolyte reduction occurring at the low potential [114]. One type of good ionic liquid utilized as an electrolyte is an aluminum chloride (AlCl<sub>3</sub>) based solution. However, AlCl<sub>3</sub> is toxic and difficult to process [115-117]. N-methyl-N-propylpiperidinium-bis (trifluoromethylsulfonyl) imide [111] and n-hexyltrimethylammonium-bis (trifluoromethylsulfonyl) imide [118] (AlCl<sub>3</sub>-free ionic liquids) were successfully developed and have been used as electrolytes. Highly reversible and stable cycling have also been obtained using 1-ethyl-3-methylimidazolium-bis (trifluoromethylsulfonyl) imide as the electrolyte [119]. A solvent-free, ternary polymer electrolytes based on a novel poly (diallyldimethylammonium) bis (trifluoromethanesulfonyl) imide polymeric ionic liquid (PIL) as polymer host and incorporating PYR14TFSI ionic liquid and LiTFSI salt are reported (Ternary polymer electrolytes containing pyrrolidinium-based polymeric ionic liquids for lithium batteries) [120]. The PIL-based polymer electrolytes exhibited room temperature ionic conductivity above 10<sup>-4</sup> S cm<sup>-1</sup>, and the Li/PIL-LiTFSI-PYR14TFSI /LiFePO<sub>4</sub> solid-state batteries are capable to deliver above 140 Ah Kg<sup>-1</sup> at 40 °C. Over all, still only a few ionic liquid electrolytes have been found suitable for lithium batteries because of their high viscosity issues [121].

##### 4.3. Organic Solid Electrolytes

Many efforts have been dedicated to develop all-solid-state Li ion batteries [2]. Organic polymers (rubbery electrolytes) are the promising candidates. Polymer electrolytes are commonly composed of a lithium salt (LiX) and a high-molecular-weight polymer such as polyethylene oxide (PEO). However, PEO crystallization below 60 °C is a challenge for electrolyte application at lower temperature. As a result, PEO-LiX electrolytes work only at temperatures above 60 °C. The most common approach for lowering the operational temperature is adding liquid plasticizers (such as propylene carbonate or polyethylene glycol ethers) or gels (contain 60-95% liquid) [122]. But this method promotes the deterioration of the electrolyte's mechanical properties and increases its reactivity towards the lithium anode. A series of "polymer-in-salt" materials were developed as electrolytes, in which lithium salts were mixed with small quantities of the polymers, e.g., polypropylene oxide and polyethylene oxide. The glass transition temperature of these materials is low enough to remain rubbery at room temperature with good Li ion conductivity and high electrochemical stability

[123]. When using  $\text{TiO}_2$  or  $\text{Al}_2\text{O}_3$  nanoparticles as solid plasticizers in PEO, a solid-state polymer electrolyte has been developed [124]. The conductivity of these electrolytes increased and the crystallization was well prevented. Li ion doped plastic crystalline matrixes are stable over a potential of 5 V and very attractive for battery applications in combination of possible structural variations of plastic crystal matrixes and conductivities [125]. Huang *et al.* have prepared a novel solid-state composite polymer electrolyte based on poly (ethylene oxide) (PEO) by using  $\text{LiClO}_4$  as doping salts and inorganic-organic hybrid poly (cyclotriphosphazene-co-4, 40-sulfonyldiphenol) (PZS) microspheres as fillers [126]. Compared with traditional ceramic fillers such as  $\text{SiO}_2$ , PZSMS in PEO-based polymer electrolytes leads to higher enhancement in ionic conductivity.

#### 4.4. Inorganic Solid Electrolytes

Other promising candidates for solid electrolytes are inorganic materials (brittle superionic glass electrolytes). For inorganic solid electrolytes, lithium superionic conductors (LISICON) are very importance with respect to achieving an all solid-state lithium battery. This technology may solve the safety problems of the rechargeable Li ion batteries using nonaqueous liquid electrolytes. In 1978,  $\text{Li}_{14}\text{Zn}(\text{GeO}_4)_4$ , a type of LISICON was found [127], which attracted attention for its potential application as a solid electrolyte [128].

A new solid system based on lithium germanium sulfide and lithium silicon sulfide was found [129, 130], named "thio-LISICON". This is the first example of crystalline ionic conductor with a high ionic conductivity and high decomposition potential at room temperature. Sulfide-based electrolytes generally have a higher Li ion conductivity, by several orders of magnitude, compared with oxide-based electrolytes. For example, the Li ion conductivity of thio-LISICON is around  $10^{-3} \text{ S cm}^{-1}$  for  $\text{Li}_{3.25}\text{Ge}_{0.25}\text{P}_{0.75}\text{S}_4$ , four orders of magnitude higher than  $\text{Li}_{14}\text{Zn}(\text{GeO}_4)_4$ , a typical oxide LISICON.

The thio-LISICON has high electrochemical stability, which is important for all solid-state lithium batteries. Many studies focused on the binary  $\text{Li}_2\text{S-P}_2\text{S}_5$  system [131].  $70\text{Li}_2\text{S-30P}_2\text{S}_5$  (mol%) glass was prepared by a quenching melt techniques [132]. The obtained glass-ceramic showed high Li ion conductivity of  $2.1 \times 10^{-3} \text{ S cm}^{-1}$  at room temperature. Glass-ceramic  $\text{Li}_2\text{S-P}_2\text{S}_5$  electrolytes were prepared by a single step ball milling process at  $55^\circ\text{C}$  [133]. The produced crystalline glass-ceramic materials exhibit high Li ion conductivity over  $10^{-3} \text{ S/cm}$  at room temperature with a wide electrochemical stability window of 5 V.

Ideally, liquid electrolytes will be replaced by solid state electrolytes that can perform similarly without excessive safety issues [134]. The current barriers with solid state electrolytes include inferior charge/discharge rate, ionic conductivity, interfacial stability and mechanical strength [135, 136]. Efforts have been carried out to find a solid state electrolyte that can outperform liquid electrolytes.

#### 5. SEPARATORS

A separator is an important component of a battery cell, as it prevents short circuit by separating the anode from the cathode, as well as providing passages for Li ion [137]. In a

Li ion battery, the separator is required to be capable of battery shutdown at the temperature below that at which thermal runaway occurs, and the shutdown should not result in loss of mechanical integrity. Otherwise, the electrodes could come into direct contact and the resulting chemical reactions cause thermal runaway [111]. Shutdown is an important trait of a good separator for the safety of lithium batteries. The promising separators are those with high electrolyte permeability and mechanical strength, as well as good thermal, chemical, and electrochemical stability.

#### 5.1. Organic Separators

In commercially available lithium batteries, microporous membranes fabricated from polyethylene (PE) and polypropylene (PP) are used as separators [138-140]. These polyolefin separators are suitable for batteries, since they can be used for hundreds of cycles without any chemical or physical degradation. The collapse of the pores occurs when the temperature approaches the melting point of the material, which forms a nonporous insulated film and results in a sharp increase in impedance. Since the impedance of a PP separator increases less than that of a PE separator, the impedance of the PP separator may not be large enough for complete shutdown, and thermal runaway could still happen. Therefore, PE is the preferred separator material for most Li ion batteries [141, 142]. Robust mechanical properties of the separator are expected even above the shutdown temperature because the battery temperature may increase continuously after shutdown. When the separator undergoes a meltdown, the mechanical properties of the separator could deteriorate greatly and the cell may experience an internal short circuit, resulting in a hazard. The shutdown temperature of a separator should be lower than its meltdown temperature. A sandwiched separator containing one porous PE layer between two porous PP layers (PP-PE-PP trilayer) has been made to maintain the robust mechanical properties. The PE layer offers a lower shutdown temperature; whereas the PP provides mechanical stability above the shutdown temperature (such as Celgard® [143]). The shutdown temperature and meltdown temperature were increased to  $142^\circ\text{C}$  and  $155^\circ\text{C}$  respectively, when the separator was coated with diethylene glycol dimethacrylate [144]. When silica nanoparticles were added to the separator, the meltdown temperature increased to  $170^\circ\text{C}$  [145]. Polyolefin membrane separators, however, have several drawbacks, such as large thermal shrinkage near its melting/softening temperature, low porosity and low wettability in electrolyte solutions. Silica-composite nonwovens using polyolefin fiber and nanosize silica powder showed not only better wettability than the polyolefin-based membrane and nonwoven, but also thermal shrinkage of  $\sim 3\%$  at  $160^\circ\text{C}$  under air atmosphere and thermally stable at  $150^\circ\text{C}$  in the liquid electrolyte [146].

#### 5.2. Inorganic Separators

Separators can also be made of inorganic sub-micron sized particles and a small amount of polymer binder, which have dimensional stability at a high temperature as well as wettability [147]. This type of separator is highly desirable for the development of large-size lithium batteries, especially those installed in electric vehicles and power tools. Nonwoven support materials can improve the mechanical

strength of inorganic separators [146]. Recently, nonwoven supported inorganic separators prepared *via* a sol-gel coating method were commercialized for Li ion batteries [148, 149]. Kim *et al.* prepared an inorganic separator by coating inorganic submicrometer sized  $\text{Al}_2\text{O}_3$  particles on a nonwoven matrix Aramid fiber followed by an E-beam irradiation treatment [150]. The mechanical and thermal properties of the separator were greatly enhanced by the simple curing under E-beam irradiation. Remarkable improvements of the separators with respect to the battery safety have been demonstrated by a series of abuse tests. However, the practical application of the inorganic particle coated nonwoven separators using polymeric binders has not been realized, because of insufficient mechanical strength to withstand the roll-to-roll manufacturing process [150].

## CONCLUSIONS

The performance of rechargeable lithium batteries depends on the properties of cathodes, anodes, electrolytes and separators. The discovery of intercalation materials has played a significant role in increased performance. The intercalation materials, such as the graphite anode and the  $\text{LiCoO}_2$  cathode, impact the large scale commercialization of rechargeable lithium batteries. Besides intercalation materials, the application of nanostructured materials results in substantial improvements of rechargeable lithium batteries. Currently, lithium cobalt oxide, lithium manganese oxide and lithium iron phosphate are the most used cathode materials. Other promising cathode materials, such as sulfur and lithium sulfide, are under development. In the area of anode materials, graphite is the most widely used. However, the tin-based anode material technology is maturing, and the lithium or silicon-based materials are also becoming next generation anode materials. In the past, lithium was chosen as the anode material of lithium batteries due to its largest theoretical energy density. However, the market for lithium anodes has dropped due to safety concerns and battery stability. As shown in Fig. (1), the highest energy density of existing Li ion batteries is only about  $150 \text{ Wh Kg}^{-1}$  or  $300 \text{ Wh L}^{-1}$ , and the maximum energy density of the ideal Li ion batteries is about  $580 \text{ Wh kg}^{-1}$  or  $1810 \text{ Wh L}^{-1}$ . The ideal lithium-sulfur (Li-S) battery has a much higher energy density of  $2500 \text{ Wh kg}^{-1}$  or  $2800 \text{ Wh L}^{-1}$ . In this regard, the Li-S battery may be the rechargeable lithium battery of the future.

From portable electronics to electric vehicles or hybrid electric vehicles, power sources that have a high charge/discharge rate, high power density, long cycle life, and safe operation are in constant demand. The successful design of new assembly technology, discovery of new materials, and development of new theories will promote the development of next generation rechargeable lithium batteries.

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