

# Reality and Future of Rechargeable Lithium Batteries

Haisheng Tao, Zhizhong Feng, Hao Liu, Xianwen Kan and P. Chen\*

*Department of Chemical Engineering, University of Waterloo, 200 University Avenue West, Waterloo, Ontario, N2L 3G1, Canada*

**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].

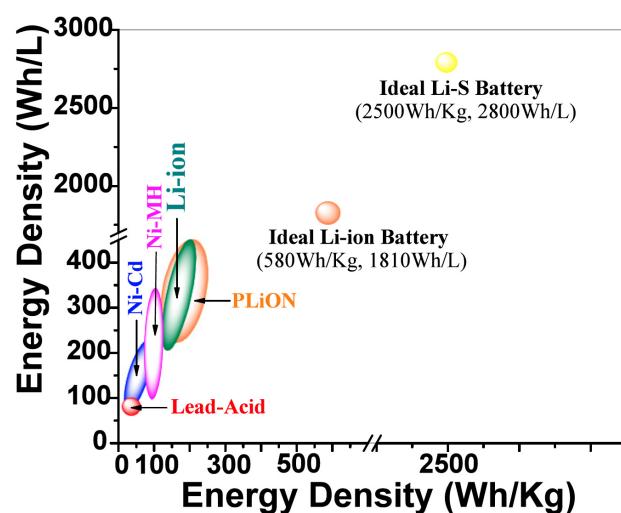


Fig. (1). The energy density of different batteries.

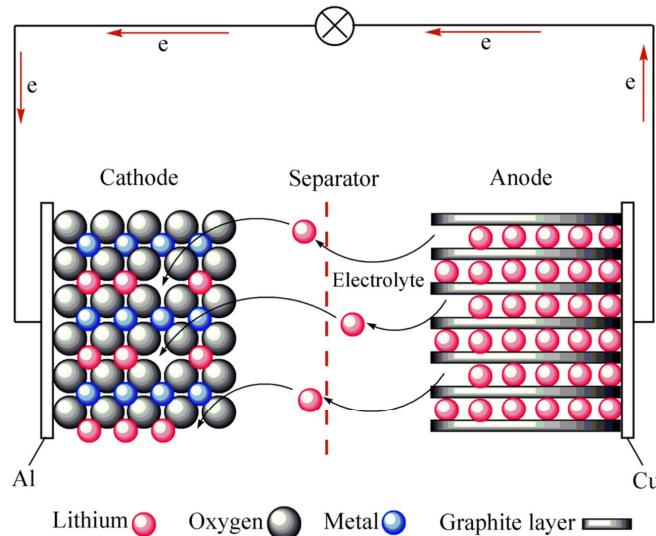
Rechargeable lithium battery is of present interest. There are many kinds of rechargeable lithium batteries. They have different classifications according to the forms of lithium (e.g. lithium metal as anode directly, we call it lithium battery. For lithium trans-metal salt as anode, we call it lithium 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

\*Address correspondence to this author at the Department of Chemical Engineering, University of Waterloo, 200 University Avenue West, Waterloo, Ontario, N2L 3G1, Canada; Tel: (519) 888-4567x35586; Fax: (519) 746-4979; E-mail: p4chen@uwaterloo.ca

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 Li[Ni<sub>1-x</sub>M<sub>x</sub>]O<sub>2</sub> (M=Co, 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 Li[Ni<sub>0.8</sub>Co<sub>0.1</sub>Mn<sub>0.1</sub>]O<sub>2</sub> core) and a good thermal stability (from the Li[Ni<sub>0.5</sub>Mn<sub>0.5</sub>]O<sub>2</sub> shell) [12]. This core-shell structured Li[(Ni<sub>0.8</sub>Co<sub>0.1</sub>Mn<sub>0.1</sub>)<sub>0.8</sub>(Ni<sub>0.5</sub>Mn<sub>0.5</sub>)<sub>0.2</sub>]O<sub>2</sub>/carbon cell has a superior cyclability and thermal stability relative to the Li[Ni<sub>0.8</sub>Co<sub>0.1</sub>Mn<sub>0.1</sub>]O<sub>2</sub> 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 Li[Ni<sub>0.68</sub>Co<sub>0.18</sub>Mn<sub>0.18</sub>]O<sub>2</sub>, in which each particle consists of bulk material Li[Ni<sub>0.8</sub>Co<sub>0.1</sub>Mn<sub>0.1</sub>]O<sub>2</sub> 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 Ah Kg<sup>-1</sup> 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 LiCoO<sub>2</sub> and LiNiO<sub>2</sub> in electric vehicles because they are safe, cheap and non-toxic. There are two well known "lithium-rich" manganese oxides, the spinel LiMn<sub>2</sub>O<sub>4</sub> [14-17] and orthorhombic LiMnO<sub>2</sub> [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 LiAl<sub>0.1</sub>Mn<sub>1.9</sub>O<sub>4</sub> materials using a room-temperature solid-state grinding reaction followed by calcination showed the obviously improved cyclability compared with the pristine LiMn<sub>2</sub>O<sub>4</sub> [24]. Another problem is its limited cycling and storage performance at elevated temperatures (>40 °C), which can be improved by changing the structure (such as using synthesizing bi-substituted LiMn<sub>2-x</sub>Al<sub>x</sub>O<sub>4-z</sub>F<sub>z</sub>) [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 (LiFePO<sub>4</sub>) 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 Ah Kg<sup>-1</sup>). However, the main application barrier of LiFePO<sub>4</sub> was its intrinsically low electrical conductivity [31]. This may be overcome by synthesizing LiFePO<sub>4</sub> in nanoparticles. Alternatively, the same improvement in electrical conductivity can be achieved by carbon coating of LiFePO<sub>4</sub> [32-34] or doping LiFePO<sub>4</sub> with various metal elements [35-37]. It was reported that stoichiometric Cu-doped lithium ion phosphate LiFe<sub>1-x</sub>Cu<sub>x</sub>PO<sub>4</sub>/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 Cu(Ac)<sub>2</sub> as a dopant and FePO<sub>4</sub> as a precursor. The charge/discharge test showed that the cathode materials possessed the excellent

charge/discharge capacities, about 150 Ah Kg<sup>-1</sup> and 297 Ah L<sup>-1</sup> at a rate of 0.1 C and more than 127 Ah Kg<sup>-1</sup> and 252 Ah L<sup>-1</sup> 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 LiFePO<sub>4</sub> 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 LiFePO<sub>4</sub> 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, LiFePO<sub>4</sub> nanoparticals 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 LiFeSO<sub>4</sub>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 Ah Kg<sup>-1</sup>) compared to that of most other materials, e.g., LiCoO<sub>2</sub>, LiNiO<sub>2</sub>, LiMn<sub>2</sub>O<sub>4</sub>, LiMnO<sub>2</sub> and LiFePO<sub>4</sub>. 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 (Li<sub>2</sub>S) is also a possible cathode material. Similar to S, the poor electronic conductivity of Li<sub>2</sub>S restricts its practical application, despite a high theoretical capacity of 1166 Ah Kg<sup>-1</sup> [48, 49]. Metal additives (such as Cu, Co, and Fe) have been employed to enhance the conductivity of Li<sub>2</sub>S-based cathodes [48-50]. But the metal additives result in a lower output voltage [49, 50]. A nanostructured Li<sub>2</sub>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 Li<sub>2</sub>S-carbon nanostructured materials use electrical conductive micro/mesoporous carbon for loading S or Li<sub>2</sub>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 LiCo<sub>x</sub>Mn<sub>y</sub>Ni<sub>1-x-y</sub>O<sub>2</sub> (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

	<b>LiCoO<sub>2</sub></b>	<b>LiMn<sub>2</sub>O<sub>4</sub></b>	<b>LiFePO<sub>4</sub></b>
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 circle, 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 theirs 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 Ah  $\text{Kg}^{-1}$  or 7200 Ah  $\text{L}^{-1}$ . 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 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  $\text{SnFe}$  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 Ah  $\text{L}^{-1}$ . 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 Ah  $\text{L}^{-1}$ . In these compounds, Sn forms the electrochemically active center for Li ion intercalation, and the other metal group provides an electrochemical inactive network of -(M-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 Ah  $\text{Kg}^{-1}$ , 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

Ah  $\text{Kg}^{-1}$  for samples with TM=Ni to 500 Ah  $\text{Kg}^{-1}$  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 Ah  $\text{Kg}^{-1}$ , 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 Ah  $\text{Kg}^{-1}$  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 °C to 75 °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 Ah  $\text{Kg}^{-1}$  (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 Ah  $\text{Kg}^{-1}$  [84]. Yushin *et al.* conducted a large-scale hierarchical bottom-up assembly route for the formation of Si on 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 Ah  $\text{Kg}^{-1}$ , 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.

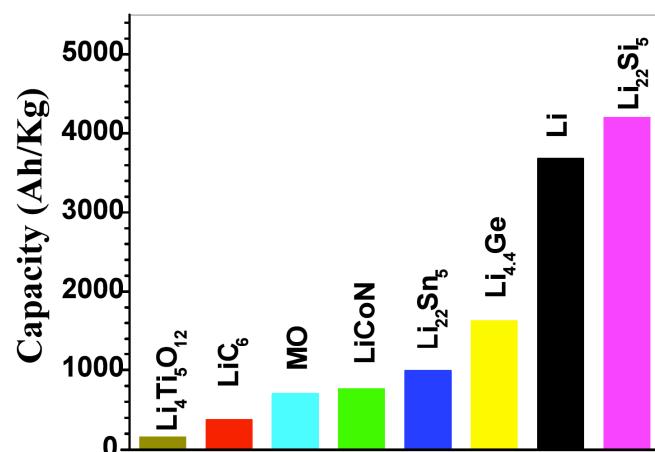


Fig. (3). The capacity of different anode materials.

#### 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  $\text{LiPF}_6$ , 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 ( $35\text{--}38$  °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 ( $\text{AlCl}_3$ ) based solution. However,  $\text{AlCl}_3$  is toxic and difficult to process [115-117]. N-methyl-N-propylpiperidinium-bis(trifluoromethylsulfonyl) imide [111] and n-hexyltrimethylammonium-bis(trifluoromethylsulfonyl) imide [118] ( $\text{AlCl}_3$ -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  $10^{-4}$  S cm $^{-1}$ , and the Li/PIL-LiTFSI-PYR14TFSI /LiFePO $_4$  solid-state batteries are capable to deliver above 140 Ah Kg $^{-1}$  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 important 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  $10^{-3}$  S cm<sup>-1</sup> 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  $\text{Li}_2\text{S}-\text{P}_2\text{S}_5$  system [131]. 70Li<sub>2</sub>S-30P<sub>2</sub>S<sub>5</sub> (mol%) glass was prepared by a quenching melt techniques [132]. The obtained glass-ceramic showed high Li ion conductivity of  $2.1 \times 10^{-3}$  S cm<sup>-1</sup> at room temperature. Glass-ceramic  $\text{Li}_2\text{S}-\text{P}_2\text{S}_5$  electrolytes were prepared by a single step ball milling process at 55 °C [133]. The produced crystalline glass-ceramic materials exhibit high Li ion conductivity over 10<sup>-3</sup> 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 °C and 155 °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 °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 ~3% at 160 °C under air atmosphere and thermally stable at 150 °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 Wh  $\text{Kg}^{-1}$  or 300 Wh  $\text{L}^{-1}$ , and the maximum energy density of the ideal Li ion batteries is about 580 Wh  $\text{kg}^{-1}$  or 1810 Wh  $\text{L}^{-1}$ . The ideal lithium-sulfur (Li-S) battery has a much higher energy density of 2500 Wh  $\text{kg}^{-1}$  or 2800 Wh  $\text{L}^{-1}$ . 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.

## REFERENCES

- [1] Howell D. Progress Report for Energy Storage Research and Development. U. S. Department of Energy 2009.
- [2] Tarascon J-M, Armand M. Issues and challenges facing rechargeable lithium batteries. *Nature* 2001; 414: 359-67.
- [3] Arico AS, Bruce P, Scrosati B, Tarascon JM, Van Schalkwijk W. Nanostructured materials for advanced energy conversion and storage devices. *Nat Mater* 2005; 4 (5): 366-77.
- [4] Tolleson J. Charging up the future. *Nature* 2008; 456: 436-40.
- [5] Thomas M, David WIF, Goodenough JB, Groves P. Synthesis and structural characterization of the normal spinel  $\text{LiNi}_2\text{O}_4$ . *Mater Res Bull* 1985; 20 (10): 1137-46.
- [6] Dahn JR, Vonsacken U, Michal CA. Structure and electrochemistry of  $\text{Li}_{1+y}\text{NiO}_2$  and a new  $\text{Li}_2\text{NiO}_2$  phase with the  $\text{Ni(OH)}_2$  structure. *Solid State Ionics* 1990; 44 (1-2): 87-9.
- [7] Dahn JR, Vonsacken U, Juzkow MW, Aljanaby H. Rechargeable  $\text{LiNiO}_2$  carbon cells. *J Electrochem Soc* 1991; 138 (8): 2207-11.
- [8] Plichta E, Salomon M, Slane S, *et al.* A rechargeable  $\text{Li/Li}_x\text{CoO}_2$  cell. *J Power Sources* 1987; 21: 25-31.
- [9] Wang F, Yang J, NuLi YN, Wang JL. Highly promoted electrochemical performance of 5 V  $\text{LiCoPO}_4$  cathode material by addition of vanadium. *J Power Sources* 2010; 195 (19): 6884-7.
- [10] Ohzuku T, Yanagawa T, Kouguchi M, Ueda A. Innovative insertion material of  $\text{LiAl}_{1/4}\text{Ni}_{3/4}\text{O}_2$  ( $R \sim 3$  m) for lithium-ion (shuttlecock) batteries. *J Power Sources* 1997; 68 (1): 131-4.
- [11] Gao Y, Yakovleva MV, Ebner WB. Novel  $\text{LiNi}_{1-x}\text{Ti}_{x/2}\text{Mg}_{x/2}\text{O}_2$  compounds as cathode materials for safer lithium-ion batteries. *Electrochim Solid State Lett* 1998; 1: 117-9.
- [12] Sun YK, Myung ST, Kim MH, Prakash J, Amine K, Synthesis and characterization of  $\text{Li}[(\text{Ni}_{0.8}\text{Co}_{0.1}\text{Mn}_{0.1})_{0.8}(\text{Ni}_{0.5}\text{Mn}_{0.5})_{0.2}] \text{O}_2$  with the microscale core-shell structure as the positive electrode material for lithium batteries. *J Am Chem Soc* 2005; 127 (38): 13411-8.
- [13] Sun YK, Myung ST, Park BC, Prakash J, Belharouak I, Amine K. High-energy cathode material for long-life and safe lithium batteries. *Nat Mater* 2009; 8: 320-4.
- [14] Guyomard D, Tarascon JM. Rechargeable  $\text{Li}_{1+x}\text{Mn}_2\text{O}_4/\text{carbon}$  cells with a new electrolyte- composition-potentiostatic studies and application to practical cells. *J Electrochim Soc* 1993; 140 (11): 3071-81.
- [15] Tarascon JM, Wang E, Shokoohi FK, McKinnon WR, Colson S. The spinel phase of  $\text{LiMn}_2\text{O}_4$  as a cathode in secondary lithium cells. *J Electrochim Soc* 1991; 138 (10): 2859-64.
- [16] Tarascon JM, Guyomard D. Li metal-free rechargeable batteries based on  $\text{Li}_{1-x}\text{Mn}_2\text{O}_4$  cathodes ( $0 \leq x \leq 1$ ) and carbon anodes. *J Electrochim Soc* 1991; 138 (10): 2864-8.
- [17] Gummow RJ, Liles DC, Thackeray MM. Lithium extraction from orthorhombic lithium manganese oxide and the phase transformation to spinel. *Mat Res Bull* 1993; 28: 1249-56.
- [18] Armstrong AR, Bruce PG. Synthesis of layered  $\text{LiMnO}_2$  as an electrode for rechargeable lithium batteries. *Nature* 1996; 381 (6582): 499-500.
- [19] Cho J, Park B.  $\text{Li}_{2+x}\text{Mn}_{0.91}\text{Cr}_{1.09}\text{O}_4$  cathode materials for Li-ion cells. *Electrochim Solid State Lett* 2000; 3 (8): 355-8.
- [20] Davidson IJ, McMillan RS, Slegir H, *et al.* Electrochemistry and structure of  $\text{Li}_{2-x}\text{Cr}_y\text{Mn}_{2-y}\text{O}_4$  phases. *J Power Sources* 1999; 81: 406-11.
- [21] Dahn JR, Zheng T, Thomas CL. Structure and electrochemistry of  $\text{Li}_2\text{Cr}_x\text{Mn}_{2-x}\text{O}_4$  for  $1.0 \leq x \leq 1.5$ . *J Electrochim Soc* 1998; 145 (3): 851-9.
- [22] Jang YI, Huang BY, Chiang YM, Sadowa DR. Stabilization of  $\text{LiMnO}_2$  in the  $\alpha\text{-NaFeO}_2$  structure type by  $\text{LiAlO}_2$  addition. *Electrochim Solid State Lett* 1998; 1:13-6.
- [23] Thackeray MM. Manganese oxides for lithium batteries. *Prog Solid State Chem* 1997; 25 (1-2): 1-71.
- [24] Yuan AB, Tian L, Xu WM, Wang YQ. Al-doped spinel  $\text{LiAl}_{0.1}\text{Mn}_{1.9}\text{O}_4$  with improved high-rate cyclability in aqueous electrolyte. *J Power Sources* 2010; 195 (15): 5032-8.
- [25] Amatucci G, Du Pasquier A, Blyr A, Zheng T, Tarascon JM. The elevated temperature performance of the  $\text{LiMn}_2\text{O}_4/\text{C}$  system: Failure and solutions. *Electrochim Acta* 1999; 45 (1-2): 255-71.
- [26] Amatucci GG, Pereira N, Zheng T, Tarascon JM. Failure mechanism and improvement of the elevated temperature cycling of  $\text{LiMn}_2\text{O}_4$  compounds through the use of the  $\text{LiAl}_x\text{Mn}_{2-x}\text{O}_{4-z}\text{F}_z$  solid solution. *J Electrochim Soc* 2001; 148 (2): A171-82.
- [27] Amatucci GG, Blyr A, Sigala C, Alfonse P, Tarascon JM. Surface treatments of  $\text{Li}_{1+x}\text{Mn}_{2-x}\text{O}_4$  spinels for improved elevated temperature performance. *Solid State Ionics* 1997; 104 (1-2): 13-25.
- [28] Wang EI, Mass M. Methode of Treating Lithium Manganese Oxide Spinel. US5783328, July 21, 1998.
- [29] Padhi AK, Nanjundaswamy KS, Goodenough JB. Phospho-olivines as positive-electrode materials for rechargeable lithium batteries. *J Electrochim Soc* 1997; 144 (4): 1188-94.

- [30] Goodenough JB, Padhi AK, Nanjundaswamy KS, Masquelier C. Cathode materials for secondary (rechargeable) lithium batteries. US5910382, June 8, 1999.
- [31] Herle PS, Ellis B, Coombs N, Nazar LF. Nano-network electronic conduction in iron and nickel olivine phosphates. *Nat Mater* 2004; 3 (3): 147-52.
- [32] Wang YG, Wang YR, Hosono E, Wang KX, Zhou HS. The design of a LiFePO<sub>4</sub>/Carbon nanocomposite with a core-shell structure and its synthesis by an in situ polymerization restriction method. *Angew Chem Int Ed* 2008; 47: 7461-5.
- [33] Ravet N, Abouimrane A, Armand M. From our readers. *Nat Mater* 2003; 2: 702.
- [34] Sun YK, Oh SM, Myung ST, Amine K, Scrosati B. 15th International Meeting on Lithium Batteries; July 2010; Montréal, Québec, Canada; 1010.
- [35] Chung SY, Bloking JT, Chiang YM. Electronically conductive phospho-olivines as lithium storage electrodes. *Nat Mater* 2002; 1 (2): 123-8.
- [36] Guo YG, Hu JS, Wan LJ. Nanostructured materials for electrochemical energy conversion and storage devices. *Adv Mater* 2008; 20 (15): 2878-87.
- [37] Wu SH, Chen MS. 15th International Meeting on Lithium Batteries; July 2010; Montréal, Québec, Canada; 1010.
- [38] Chang ZR, Lv HJ, Tang H, Yuan XZ, Wang HJ. Synthesis and performance of high tap density LiFePO<sub>4</sub>/C cathode materials doped with copper ions. *J Alloys Compd* 2010; 501 (1): 14-7.
- [39] Nishimura S, Kobayashi G, Ohoyama K, Kanno R, Yashima M, Yamada A. Experimental visualization of lithium diffusion in Li<sub>x</sub>FePO<sub>4</sub>. *Nat Mater* 2008; 7 (9): 707-11.
- [40] Ravet N, Chouinard Y, Magnan JF, Besner S, Gauthier M, Armand M. Electroactivity of natural and synthetic triphylite. *J Power Sources* 2001; 97-8: 503-7.
- [41] Delacourt C, Poizot P, Levasseur S, Masquelier C. Size effects on carbon-free LiFePO<sub>4</sub> powders. *Electrochim Solid State Lett* 2006; 9 (7): A352-5.
- [42] Kim DH, Kim J. Synthesis of LiFePO<sub>4</sub> nanoparticles in polyol medium and their electrochemical properties. *Electrochim Solid State Lett* 2006; 9 (9): A439-42.
- [43] Kang B, Ceder G. Battery materials for ultrafast charging and discharging. *Nature* 2009; 458: 190-3.
- [44] Recham N, Chotard JN, Dupont L, et al. A 3.6 V lithium-based fluorosulphate insertion positive electrode for lithium-ion batteries. *Nat Mater* 2010; 9 (1): 68-74.
- [45] Kolosnitsyn VS, Kuzmina EV, Karaseva EV. 15th International Meeting on Lithium Batteries; July 2010; Montréal, Québec, Canada; 1010.
- [46] Ji XL, Lee KT, Nazar LF. A highly ordered nanostructured carbon-sulphur cathode for lithium-sulphur batteries. *Nat Mater* 2009; 8: 500-6.
- [47] Liang CD, Dudney NJ, Howe JY. Hierarchically structured sulfur/Carbon nanocomposite material for high-energy lithium battery. *Chem Mater* 2009; 21: 4724-30.
- [48] Hayashi A, Ohtsubo R, Ohtomo T, Mizuno F, Tatsumisago M. All-solid-state rechargeable lithium batteries with Li<sub>2</sub>S as a positive electrode material. *J Power Sources* 2008; 183 (1): 422-6.
- [49] Zhou YN, Wu CL, Zhang H, Wu XJ, Fu ZW. Electrochemical reactivity of Co-Li<sub>2</sub>S nanocomposite for lithium-ion batteries. *Electrochim Acta* 2007; 52 (9): 3130-6.
- [50] Obrovac MN, Dahn JR. Electrochemically active lithia/metal and lithium sulfide/metal composites. *Electrochim Solid State Lett* 2002; 5 (4): A70-3.
- [51] Yang Y, McDowell MT, Jackson A, Cha JJ, Hong SS, Cui Y. New nanostructured Li<sub>2</sub>S/silicon rechargeable battery with high specific energy. *Nano Lett* 2010; 10: 1486-91.
- [52] Chu MY. Rechargeable Positive Electrodes. US5686201, November 11, 1997.
- [53] Visco SJ, Katz BD, Nimon YS, Jonghe LCD. Protected active metal electrode and battery cell structures with non-aqueous interplayer architecture. US2008/0038641A1, February 14, 2008.
- [54] Skotheim TA, Sheehan CJ, Mikhaylik YV, Affinito J. Lithium anodes for electrochemical cells. US7247408B2, June 24, 2007.
- [55] Visco SJ, Nimon YS, Katz BD. Ionically conductive composites for protection of active metal anode. US2008/0057387A1, March 6, 2008.
- [56] Bates JB, Protective lithium ion conducting ceramic coating for lithium metal anodes and associate method. US5314765, May 24, 1994.
- [57] Visco SJ, Katz BD, Nimon YS, Jonghe LCD. Protected active metal electrode and battery cell structures with non-aqueous interplayer architecture. US2008/0038641A1, February 14, 2008.
- [58] Visco SJ, Katz BD, Nimon YS, Jones PC. Protected active metal electrode and battery cell structures with non-aqueous interplayer architecture. US7282295B2, October 16, 2007.
- [59] Visco SJ, Nimon YS, Li/air non-aqueous batteries. US2007/0117007A1, May 24, 2007.
- [60] Yuryit VM, Chariclea SK, Igor K, Cathie B. Separation of electrolytes. US2010/0129699A1, May 27, 2010.
- [61] Shodai T, Okada S, Tobishima S, Yamabi I. Study of Li<sub>3-x</sub>M<sub>x</sub>N (M=Co, Ni or Cu) system for use as anode in lithium rechargeable cells. *Solid State Ionics* 1996; 86-88: 785-9.
- [62] Besenhard JO, Yang J, Winter M. Will advanced lithium-alloy anodes have a chance in lithium-ion batteries? *J Power Sources* 1997; 68 (1): 87-90.
- [63] Winter M, Besenhard JO, Spahr ME, Novak P. Insertion electrode materials for rechargeable lithium batteries. *Adv Mater* 1998; 10 (10): 725-63.
- [64] Dahn JR, Zheng T, Liu YH, Xue JS. Mechanisms for lithium insertion in carbonaceous materials. *Science* 1995; 270 (5236): 590-3.
- [65] Liu YH, Xue JS, Zheng T, Dahn JR. Mechanism of lithium insertion in hard carbons prepared by pyrolysis of epoxy resins. *Carbon* 1996; 34 (2): 193-200.
- [66] Zhang M, Lei DN, Yin XM, et al. Magnetite/graphene composites: Microwave irradiation synthesis and enhanced cycling and rate performances for lithium ion batteries. *J Mater Chem* 2010; 20 (26): 5538-43.
- [67] Winter M, Besenhard JO. Electrochemical lithiation of tin and tin-based intermetallics and composites. *Electrochim Acta* 1999; 45: 31-50.
- [68] Anani A, Crouch-Baker S, Huggins RA. Kinetic and thermodynamic parameters of several binary lithium alloy negative electrode materials at ambient temperature. *J Electrochim Soc* 1987; 134: 3098-102.
- [69] Boukamp BA, Lesh GC, Huggins RA. All-solid lithium electrodes with mixed-conductor matrix. *J Electrochim Soc* 1981; 128 (4): 725-9.
- [70] Wang JQ, Raistrick ID, Huggins RA. Behavior of some binary lithium alloys as negative electrodes in organic solvent-based electrolytes. *J Electrochim Soc* 1986; 133 (3): 457-60.
- [71] Zhang SC, Fang Y, Xing YL, Jiang T, Sun MM. 15th International Meeting on Lithium Batteries; July 2010; Montréal, Québec, Canada; 1010.
- [72] Mao O, Dunlap RA, Dahn JR. Mechanically alloyed Sn-Fe(-C) powders as anode materials for Li-ion batteries-I. The Sn<sub>2</sub>Fe-C system. *J Electrochim Soc* 1999, 146 (2), 405-13.
- [73] Mao O, Dahn JR. Mechanically alloyed Sn-Fe(-C) powders as anode materials for Li-ion batteries-II. The SnFe system. *J Electrochim Soc* 1999; 146 (2): 414-22.
- [74] Mao O, Dahn JR. Mechanically alloyed Sn-Fe(-C) powders as anode materials for Li-ion batteries-III. Sn<sub>2</sub>Fe: Sn<sub>2</sub>Fe<sub>3</sub>C active/inactive composites. *J Electrochim Soc* 1999; 146 (2): 423-7.
- [75] Beaulieu LY, Larcher D, Dunlap RA, Dahn JR. Reaction of Li with grain-boundary atoms in nanostructured compounds. *J Electrochim Soc* 2000; 147 (9): 3206-12.
- [76] Kepler KD, Vaughn JT, Thackeray MM. Li<sub>x</sub>Cu<sub>6</sub>Sn<sub>5</sub> (0<x<13): An intermetallic insertion electrode for rechargeable lithium batteries. *Electrochim Solid State Lett* 1999; 2 (7): 307-9.
- [77] Idota Y, Kubota T, Matsufuji A, Maekawa Y, Miyasaka T. Tin-based amorphous oxide: A high-capacity lithium-ion-storage material. *Science* 1997; 276 (5317): 1395-7.
- [78] Courtney IA, Dahn JR. Electrochemical and in situ x-ray diffraction studies of the reaction of lithium with tin oxide composites. *J Electrochim Soc* 1997; 144 (6): 2045-52.
- [79] Park MS, Kim JH, Kang YM. 15th International Meeting on Lithium Batteries; July 2010; Montréal, Québec, Canada; 1010. <http://www.sony.net/SonyInfo/News/Press/200502/05-006E/>.
- [80] Todd ADW, Mar RE, Dahn JR. Tin-transition metal-carbon systems for lithium-ion battery negative electrodes. *J Electrochim Soc* 2007; 154 (6): A597-604.

- [82] Ferguson PP, Todd ADW, Dahn JR. Comparison of mechanically alloyed and sputtered tin-cobalt- carbon as an anode material for lithium-ion batteries. *Electrochim Commun* 2008; 10 (1): 25-31.
- [83] Ferguson PP, Dahn JR. Effect of annealing on  $\text{Sn}_{30}\text{Co}_{50}\text{C}_{40}$  prepared by mechanical attriting. *Electrochim Solid State Lett* 2008; 11 (11): A187-9.
- [84] Ferguson PP, Martine ML, George AE, Dahn JR. Studies of tin-transition metal-carbon and tin- cobalt-transition metal-carbon negative electrode materials prepared by mechanical attrition. *J Power Sources* 2009; 194 (2): 794-800.
- [85] Lazzari M, Scrosati B. Rechargeable lithium batteries with non-metal electrodes. US4464447, August 7, 1984.
- [86] Idota Y. Nonaqueous Secondary battery. US5478671, December 26, 1995.
- [87] Poizot P, Laruelle S, Grugeon S, Dupont L, Tarascon JM. Nanosized transition-metaloxides as negative-electrode materials for lithium-ion batteries. *Nature* 2000; 407 (6803): 496-9.
- [88] Kavan L, Gratzel M. Facile synthesis of nanocrystalline  $\text{Li}_4\text{Ti}_5\text{O}_{12}$  (spinel) exhibiting fast Li insertion. *Electrochim Solid State Lett* 2002; 5 (2): A39-42.
- [89] Ohzuku T, Ueda A, Yamamoto N. Zero-strain insertion material of  $\text{Li}[\text{Li}_{1/3}\text{Ti}_{5/3}]O_4$  for rechargeable lithium cells. *J Electrochim Soc* 1995; 142 (5): 1431-5.
- [90] Wen CJ, Huggins RA. Chemical diffusion in intermediate phases in the lithium-silicon system. *J Solid State Chem* 1981; 37 (3): 271-8.
- [91] Loveridge M, Lain M, Liu FM, Coowar F, Macklin B, Green M. 15th International Meeting on Lithium Batteries; July 2010; Montréal, Québec, Canada; 1010.
- [92] Green M, Fielder E, Scrosati B, Wachtler M, Moreno JS. Structured silicon anodes for lithium battery applications. *Electrochim Solid State Lett* 2003; 6 (5): A75-9.
- [93] Li H, Huang XJ, Chen LQ, Wu ZG, Liang Y. A high capacity nano-Si composite anode material for lithium rechargeable batteries. *Electrochim Solid State Lett* 1999; 2 (11): 547-9.
- [94] Graetz J, Ahn CC, Yazami R, Fultz B. Highly reversible lithium storage in nanostructured silicon. *Electrochim Solid State Lett* 2003; 6 (9): A194-7.
- [95] Kasavajjula U, Wang CS, Appleby AJ. Nano- and bulk-silicon-based insertion anodes for lithium-ion secondary cells. *J Power Sources* 2007; 163 (2): 1003-39.
- [96] Park MH, Kim MG, Joo J, et al. Silicon nanotube battery anodes. *Nano Lett* 2009; 9 (11): 3844-7.
- [97] Cui LF, Yang Y, Hsu CM, Cui Y. Carbon-silicon core-shell nanowires as high capacity electrode for lithium ion batteries. *Nano Lett* 2009; 9 (9): 3370-4.
- [98] Chan CK, Ruffo R, Hong SS, Huggins RA, Cui Y. Structural and electrochemical study of the reaction of lithium with silicon nanowires. *J Power Sources* 2009; 189 (1): 34-9.
- [99] Chan CK, Ruffo R, Hong SS, Cui Y. Surface chemistry and morphology of the solid electrolyte interphase on silicon nanowire lithium-ion battery anodes. *J Power Sources* 2009; 189 (2): 1132-40.
- [100] Cui LF, Ruffo R, Chan CK, Peng HL, Cui Y. Crystalline-amorphous core-shell silicon nanowires for high capacity and high current battery electrodes. *Nano Lett* 2009; 9 (1): 491-5.
- [101] Chan CK, Peng HL, Liu G, et al. High-performance lithium battery anodes using silicon nanowires. *Nat Nanotechnol* 2008; 3 (1): 31-5.
- [102] Ruffo R, Hong SS, Chan CK, Huggins RA, Cui Y. Impedance analysis of silicon nanowire lithium ion battery anodes. *J Phys Chem C* 2009; 113 (26): 11390-8.
- [103] Magasinski A, Dixon P, Hertzberg B, Kvít A, Ayala J, Yushin G. High-performance lithium-ion anodes using a hierarchical bottom-up approach. *Nat Mater* 2010; 9 (4): 353-8.
- [104] Magasinski A, Hertzberg B, Dixon P, Yushin G. 15th International Meeting on Lithium Batteries; July 2010; Montréal, Québec, Canada; 1010.
- [105] Tarascon JM, Guyomard D. New electrolyte compositions stable over the 0-V to 5-V voltage range and compatible with the  $\text{Li}_{1+x}\text{Mn}_2\text{O}_4$  Carbon Li-ion cells. *Solid State Ionics* 1994; 69 (3-4): 293-305.
- [106] Ding MS, Xu K, Zhang SS, Amine K, Henriksen GL, Jow TR. Change of conductivity with salt content, solvent composition, and temperature for electrolytes of  $\text{LiPF}_6$  in ethylene carbonate-ethyl methyl carbonate. *J Electrochim Soc* 2001; 148 (10): A1196-204.
- [107] Guyomard D, Tarascon JM. Li matal-free rechargeable  $\text{LiMn}_2\text{O}_4/\text{Carbon}$  cells-Their understanding and optimization. *J Electrochim Soc* 1992; 139 (4): 937-48.
- [108] Guyomard D, Tarascon JM. High-voltage stable liquid electrolytes for  $\text{Li}_{1-x}\text{Mn}_2\text{O}_4/\text{Carbon}$  rocking- chair lithium batteries. *J Power Sources* 1995; 54 (1): 92-8.
- [109] Oh B, Rempel J, Ofer D, Sriramulu S, Barnett B. 15th International Meeting on Lithium Batteries; July 2010; Montréal, Québec, Canada; 1010.
- [110] Liu ZQ, Huang FQ, Yang JH, Wang BF, Sun JK. New lithium ion conductor, thio-LISICON lithium zirconium sulfide system. *Solid State Ionics* 2008; 179: 1714-6.
- [111] Sakaebi H, Matsumoto H. N-methyl-N-propylpiperidinium bis (trifluoromethanesulfonyl) imide (PP13-TFSI)-novel electrolyte base for Li battery. *Electrochim Commun* 2003; 5: 594-8.
- [112] Nakagawa H, Izuchi S, Kuwana K, Nukuda T, Aihara Y. Liquid and polymer gel electrolytes for lithium batteries composed of room-temperature molten salt doped by lithium salt. *J Electrochim Soc* 2003; 150: A695-700.
- [113] Ishikawa M, Yamagata M. 15th International Meeting on Lithium Batteries; July 2010; Montréal, Québec, Canada 1010.
- [114] Holzapfel M, Jost C, Nova'k P. Stable cycling of graphite in an ionic liquid based electrolyte. *Chem Comm* 2004; (18): 2098-9.
- [115] Carlin RT, Fuller J, Hedenskoog M. Reversible lithium-graphite anodes in room-temperature choroaluminate melts. *J Electrochim Soc* 1994; 141: L21-2.
- [116] Fuller J, Osteryoung RA, Carlin RT. Rechargeable lithium and sodium anodes in chloroaluminate molten-salts containing thionyl chloride. *J Electrochim Soc* 1995; 142: 3632-6.
- [117] Fuller J, Carlin RT, Osteryoung RA. The room temperature liquid 1-ethyl-3-methylimidazolium tetrafluoroborate: Electrochemical couples and physical properties. *J Electrochim Soc* 1997; 144: 3881-6.
- [118] Katayama Y, Yukumoto M, Miura T. Electrochemical intercalation of lithium into graphite in room- temperature molten salt containing ethylene carbonate. *Electrochim Solid-State Lett* 2003; 6: A96-7.
- [119] Holzapfel M, Jostb C, Novak P. Stable cycling of graphite in an ionic liquid based electrolyte. *Chem Commun* 2004; 2098-9.
- [120] Appetecchi GB, Kim GT, Montanina M, et al. Ternary polymer electrolytes containing pyrrolidinium-based polymeric ionic liquids for lithium batteries. *J Power Sources* 2010; 195 (11): 3668-75.
- [121] Lewandowski A, Swiderska-Moczek A. Ionic liquids as electrolytes for Li-ion batteries-An overview of electrochemical studies. *J Power Sources* 2009; 194 (2): 601-9.
- [122] Stallworth PE, Fontanella JJ, Wintersgill MC, et al. NMR, DSC and high pressure electrical conductivity studies of liquid and hybrid electrolytes. *J Power Sources* 1999; 81: 739-47.
- [123] Angell CA, Liu C, Sanchez E. Rubbery solid electrolytes with dominant cationic transport and high ambient conductivity. *Nature* 1993; 362 (6416): 137-9.
- [124] Croce F, Appetecchi GB, Persi L, Scrosati B. Nanocomposite polymer electrolytes for lithium batteries. *Nature* 1998; 394 (6692): 456-8.
- [125] MacFarlane DR, Huang JH, Forsyth M. Lithium-doped plastic crystal electrolytes exhibiting fast ion conduction for secondary batteries. *Nature* 1999; 402 (6763): 792-4.
- [126] Zhang JW, Huang XB, Wei H, Fu JW, Huang YW, Tang XZ. Novel PEO-based solid composite polymer electrolytes with inorganic-organic hybrid polyphosphazene microspheres as fillers. *J Appl Electroch* 2010; 40 (8): 1475-81.
- [127] Alpen UV, Bell MF, Wichelhaus W. Ionic conductivity of  $\text{Li}_{1-x}\text{Zn}(\text{GeO}_4)_4$  (LISICON). *Electrochim Acta* 1978; 23: 1395-7.
- [128] Hong HYP. Crystal structure and ionic conductivity of  $\text{Li}_{1-x}\text{Zn}(\text{GeO}_4)_4$  and other new  $\text{Li}^+$  superionic conductors. *Mat Res Bull* 1978; 13: 117-24.
- [129] Murayama M, Sonoyama N, Yamada A, Kanno R. Material design of new lithium ionic conductor, thio-LISICON, in the  $\text{Li}_2\text{S}-\text{P}_2\text{S}_5$  system. *Solid State Ionics* 2004; 170 (3-4): 173-80.
- [130] Kanno R, Hata T, Kawamoto Y, Irie M. Synthesis of a new lithium ionic conductor, thio-LISICON- lithium germanium sulfide system. *Solid State Ionics* 2000; 130 (1-2): 97-104.
- [131] Hayashi A, Kitaura H, Ohtomo T, Hama S, Tatsumisago M, 15th International Meeting on Lithium Batteries; July 2010; Montréal, Québec, Canada; 1010.

- [132] Minami K, Mizuno F, Hayashi A, Tatsumisago M. Lithium ion conductivity of the Li<sub>2</sub>S-P<sub>2</sub>S<sub>5</sub> glass-based electrolytes prepared by the melt quenching method. *Solid State Ionics* 2007; 178 (11-12): 837-41.
- [133] Trevey J, Jang JS, Jung YS, Stoldt CR, Lee SH. Glass-ceramic Li<sub>2</sub>S-P<sub>2</sub>S<sub>5</sub> electrolytes prepared by a single step ball milling process and their application for all-solid-state lithium-ion batteries. *Electrochim Commun* 2009; 11 (9): 1830-3.
- [134] Mizuno F, Hama S, Hayashi A, Tadanaga K, Minami T, Tatsumisago M. All solid-state lithium secondary batteries using high lithium ion conducting Li<sub>2</sub>S-P<sub>2</sub>S<sub>5</sub> glass-ceramics. *Chem Lett* 2002; (12): 1244-5.
- [135] Hashimoto Y, Machida N, Shigematsu T. Preparation of Li<sub>4.4</sub>Ge<sub>x</sub>Si<sub>1-x</sub> alloys by mechanical milling process and their properties as anode materials in all-solid-state lithium batteries. *Solid State Ionics* 2004; 175 (1-4): 177-80.
- [136] Takada K, Inada T, Kajiyama A, et al. Solid state batteries with sulfide-based solid electrolytes. *Solid State Ionics* 2004; 172 (1-4): 25-30.
- [137] Zhang SS. A review on the separators of liquid electrolyte Li-ion batteries. *J Power Sources* 2007; 164 (1): 351-64.
- [138] Kim SS, Lim GBA, Alwattari AA, Wang YF, Lloyd DR. Microporous membrane formation via thermally-induced phase-separation. 5. Effect of diluent mobility and crystallization on the structure of isotactic polypropylene membranes. *J Membr Sci* 1991; 64 (1-2): 41-53.
- [139] Vadalia HC, Lee HK, Myerson AS, Levon K. Thermally-induced phase-separation in ternary crystallizable polymer-solutions. *J Membr Sci* 1994; 89 (1-2): 37-50.
- [140] Matsuyama H, Yuasa M, Kitamura Y, Teramoto M, Lloyd DR. Structure control of anisotropic and asymmetric polypropylene membrane prepared by thermally induced phase separation. *J Membr Sci* 2000; 179 (1-2): 91-100.
- [141] Venugopal G, Moore J, Howard J, Pendalwar S. Characterization of microporous separators for lithium-ion batteries. *J Power Sources* 1999; 77 (1): 34-41.
- [142] Arora P, Zhang ZM. Battery separators. *Chem Rev* 2004; 104 (10): 4419-62.
- [143] <http://www.celgard.com/>.
- [144] Chung YS, Yoo SH, Kim CK. Enhancement of meltdown temperature of the polyethylene lithium-ion battery separator via surface coating with polymers having high thermal resistance. *Ind Eng Chem Res* 2009; 48 (9): 4346-51.
- [145] Yoo SH, Kim CK. Enhancement of the meltdown temperature of a lithium ion battery separator via a nanocomposite coating. *Ind Eng Chem Res* 2009; 48 (22): 9936-41.
- [146] Cho TH, Tanaka M, Onishi H, et al. Silica-composite nonwoven separators for lithium-ion battery: Development and characterization. *J Electrochem Soc* 2008; 155 (9): A699-703.
- [147] Prosini PP, Villano P, Carewska M. A novel intrinsically porous separator for self-standing lithium-ion batteries. *Electrochim Acta* 2002; 48 (3): 227-33.
- [148] Augustin S, Hennige V, Horpel G, Hyring C. Ceramic but flexible: new ceramic membrane foils for fuel cells and batteries. *Desalination* 2002; 146 (1-3): 23-8.
- [149] Hennige V, Hyring C, Hörpel G. Pyrogenic oxidic powder, production thereof and use thereof in a separator for electrochemical cell. US7759009B2, July 20, 2010.
- [150] Kim M, Shon JY, Nho YC, Lee TW, Park JH. Positive effects of e-beam irradiation in inorganic particle based separators for lithium-ion battery. *J Electrochem Soc* 2010; 157 (1): A31-4.

Received: January 18, 2011

Revised: May 17, 2011

Accepted: June 23, 2011

© Tao et al.; Licensee Bentham Open.

This is an open access article licensed under the terms of the Creative Commons Attribution Non-Commercial License (<http://creativecommons.org/licenses/by-nc/3.0/>) which permits unrestricted, non-commercial use, distribution and reproduction in any medium, provided the work is properly cited.