

REVIEW

Li-ion batteries: basics, progress, and challenges

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Keywords

Anode, cathode, electrolyte, Li-ion batteries, rechargeable, separator

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Funding Information

The author appreciates Professor Simon Ng for comments on the manuscript and Wayne State University for support.

Received: 22 April 2015; Revised: 11 July 2015; Accepted: 12 August 2015

Energy Science and Engineering 2015; 3(5):385–418

doi: 10.1002/ese3.95

Abstract

Li-ion batteries are the powerhouse for the digital electronic revolution in this modern mobile society, exclusively used in mobile phones and laptop computers. The success of commercial Li-ion batteries in the 1990s was not an overnight achievement, but a result of intensive research and contribution by many great scientists and engineers. Then much efforts have been put to further improve the performance of Li-ion batteries, achieved certain significant progress. To meet the increasing demand for energy storage, particularly from increasingly popular electric vehicles, intensified research is required to develop next-generation Li-ion batteries with dramatically improved performances, including improved specific energy and volumetric energy density, cyclability, charging rate, stability, and safety. There are still notable challenges in the development of next-generation Li-ion batteries. New battery concepts have to be further developed to go beyond Li-ion batteries in the future. In this tutorial review, the focus is to introduce the basic concepts, highlight the recent progress, and discuss the challenges regarding Li-ion batteries. Brief discussion on popularly studied “beyond Li-ion” batteries is also provided.

Introduction

Li-ion batteries, as one of the most advanced rechargeable batteries, are attracting much attention in the past few decades. They are currently the dominant mobile power sources for portable electronic devices, exclusively used in cell phones and laptop computers [1]. Li-ion batteries are considered the powerhouse for the personal digital electronic revolution starting from about two decades ago, roughly at the same time when Li-ion batteries were commercialized. As one may have already noticed from his/her daily life, the increasing functionality of mobile electronics always demand for better Li-ion batteries. For example, to charge the cell phone with increasing functionalities less frequently as the current phone will improve quality of one's life. Another important expanding market for Li-ion batteries is electric and hybrid vehicles, which require next-generation Li-ion batteries with not only high power, high capacity, high charging rate, long life, but also dramatically improved safety performance and low cost. In the USA, Obama administration has set a very

ambitious goal to have one million plug-in hybrid vehicles on the road by 2015. There are similar plans around the world in promotion of electric and hybrid vehicles as well. The Foreign Policy magazine even published an article entitled “The great battery race” to highlight the worldwide interest in Li-ion batteries [2].

The demand for Li-ion batteries increases rapidly, especially with the demand from electric-powered vehicles (Fig. 1). It is expected that nearly 100 GW hours of Li-ion batteries are required to meet the needs from consumer use and electric-powered vehicles with the latter takes about 50% of Li-ion battery sale by 2018 [3]. Furthermore, Li-ion batteries will also be employed to buffer the intermittent and fluctuating green energy supply from renewable resources, such as solar and wind, to smooth the difference between energy supply and demand. For example, extra solar energy generated during the day time can be stored in Li-ion batteries that will supply energy at night when sun light is not available. Large-scale Li-ion batteries for grid application will require next-generation batteries to be produced at low cost.

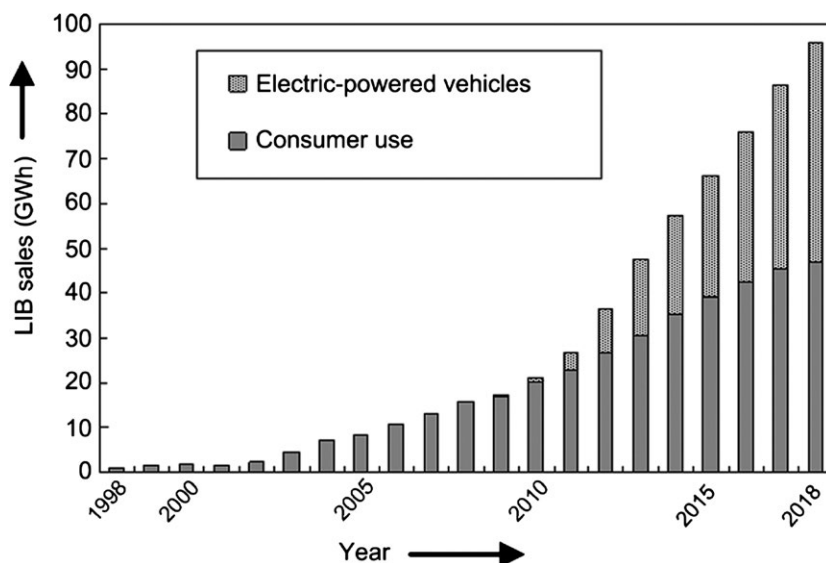


Figure 1. Demand for Li-ion batteries in two decades. Reproduced with permission [3].

Another important aspect of Li-ion batteries is related to battery safety. The recent fire on two Boeing 787 Dreamliner associated with Li-ion batteries once again highlights the critical importance of battery safety [4, 5]. This will trigger another wave of extensive research and development to enhance safety of Li-ion batteries, beyond pursuing high-energy density. In this tutorial review, I will try not to have a comprehensive coverage due to the limited scope, but instead I will highlight the basics, progress, and challenges regarding Li-ion batteries.

Li-ion batteries are highly advanced as compared to other commercial rechargeable batteries, in terms of gravimetric and volumetric energy. Figure 2 compares the energy densities of different commercial rechargeable batteries, which clearly shows the superiority of the Li-ion batteries as compared to other batteries [6]. Although lithium metal batteries have even higher theoretical energy densities than that of Li-ion batteries, their poor rechargeability and susceptibility to misuses leading to fire even explosion are known disadvantages. I anticipate that lithium metal batteries based on solid-state electrolytes with enhanced safety will be commercialized in the next decade. Recently, lithium-air and lithium-sulfur batteries regain wide interest, although the concepts have been proposed for a while. Promising progress has been achieved regarding Li-air and Li-sulfur batteries, but it may take another two decades to fully develop those technologies to achieve reliable performances that will be comparable to Li-ion batteries. It is expected that Li-ion batteries will still be dominant in rechargeable battery market, at least for the next decade, for advantages they offer. Li-ion batteries are design flexible. They can be formed into a wide variety

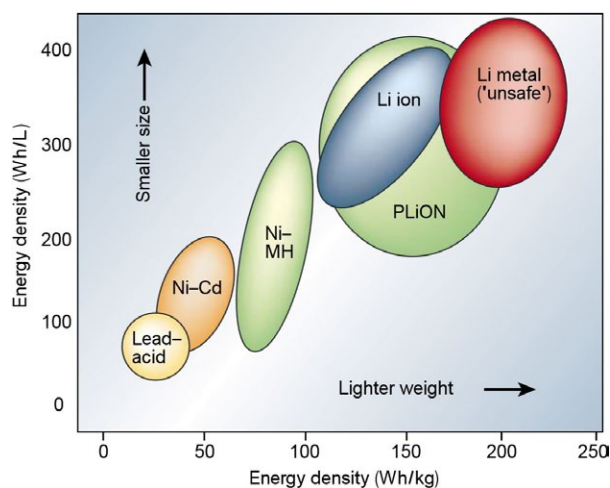


Figure 2. Comparison of energy densities and specific energy of different rechargeable batteries. Reproduced with permission [6].

of shapes and sizes, so as to efficiently fit the available space in the devices they power. Li-ion batteries do not suffer from the problem of memory effect, in contrast to Ni-Cd batteries. Li-ion batteries have voltages nearly three times the values of typical Ni-based batteries. The high single-cell voltage would reduce the number of cells required in a battery module or pack with a set output voltage and reduce the need for associated hardware, which can enhance reliability and weight savings of the battery module or pack due to parts reduction. The self-discharge rate is very low in Li-ion batteries – a typical figure is <5% per month which compares very favorably to 20–30% of Ni-based batteries.

It would be interesting to briefly review the history on the development of Li-ion batteries. The first rechargeable Li-ion batteries with cathode of layered TiS_2 and anode of metallic Li was reported by Whittingham while working at Exxon in 1976 [7]. Exxon subsequently tried to commercialize the Li-ion batteries, but was not successful due to the problems of Li dendrite formation and short circuit upon extensive cycling and safety concern [2]. Also in 1976, Besenhard proposed to reversibly intercalate Li^+ ions into graphite and oxides as anodes and cathodes, respectively [8, 9]. In 1981, Goodenough first proposed to use layered LiCoO_2 as high energy and high voltage cathode materials. Interestingly, layered LiCoO_2 did not attract much attention initially [10]. In 1983, Goodenough also identified manganese spinel as a low-cost cathode materials [11]. However, the lack of safe anode materials limited the application of layered oxide cathode of LiMO_2 ($M = \text{Ni}, \text{Co}$) in Li-ion batteries. It was discovered by Besenhard [8], Yazami [12], and Basu [13] that graphite, also with layered structure, could be a good candidate to reversibly store Li by intercalation/deintercalation in late 1970s and early 1980s. In 1987, Yohsino et al. [14] filed a patent and built a prototype cell using carbonaceous anode and discharged LiCoO_2 as cathode (Fig. 3). Both carbon anode and LiCoO_2 cathode are stable in air which is highly beneficial from the engineering and manufacturing perspectives. This battery design enabled the

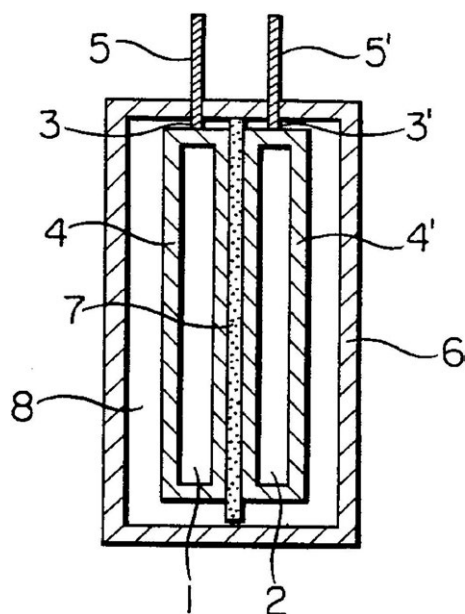


Figure 3. Illustration of first full cell of Carbon/ LiCoO_2 coupled Li-ion battery patterned by Yohsino et al., with 1-positive electrode, 2-negative electrode, 3-current collecting rods, 4-SUS nets, 5-external electrode terminals, 6-case, 7-separator, 8-electrolyte. Reproduced with permission [14].

large-scale manufacturing of Li-ion batteries in the early 1990s.

It should be highlighted that Yohsino also carried out first safety test on Li-ion batteries to demonstrate their enhanced safety features without ignition by dropping iron lump on the battery cells, in contrast to that of metallic lithium batteries which caused fire [3]. Yohsino's success is widely considered the beginning of modern commercial Li-ion batteries. Eventually Sony, dominant maker of personal electronic devices such as Walkman at that time, commercialized Li-ion batteries in 1991. It was a tremendous success and supported the revolution of personal mobile electronics. To acknowledge their pioneering contribution to the development of Li-ion battery, Goodenough, Yazami, and Yoshino were awarded the 2012 IEEE Medal for Environmental and Safety Technologies. Japan is still leading the share of global Li-ion battery market dominating 57% global market in 2010. In the past two decades, there is some notable progress in development of Li-ion batteries, particularly the introduction of low-cost cathode of LiFePO_4 by Goodenough in 1996 and high capacity anode of C-Sn-Co by Sony in 2005. The recent development of high capacity anode based on nanostructured silicon (theoretical-specific capacity of 4200 mAh/g) is also worthy to be highlighted [15–17]. In 1990s, Dahn and colleagues pioneered the exploration of composites of C/Si obtained from pyrolysis of silicon-containing polymers as promising candidate as anode materials for Li-ion batteries [18–21]. In 2008, Cui and colleagues [15] reported potential application of Si nanowires for Li-ion batteries. Deng et al. [22–25] studied a number of tin-based negative electrode materials with different compositions and structures to achieve improved electrochemical performances. Deng et al. recently also studied iron and copper oxides based nanostructures that could be used as potential carbon alternatives with much higher capacity than that of graphite [26, 27]. There are a large number of excellent scientific papers published in the past few years, achieving impressive good progress. Future research should focus on full-cell evaluation and standardization of battery testing procedures.

Basics of Li-Ion Batteries

A Li-ion battery is constructed by connected basic Li-ion cells in parallel (to increase current), in series (to increase voltage) or combined configurations. Multiple battery cells can be integrated into a module. Multiple modules can be intergrade into a battery pack. For example, the 85 kWh battery pack in a typical Tesla car contains 7104 cells. Typically, a basic Li-ion cell consists of a cathode (positive electrode) and an anode (negative electrode) which are contacted by an electrolyte containing lithium ions. The

electrodes are isolated from each other by a separator, typically microporous polymer membrane, which allows the exchange of lithium ions between the two electrodes but not electrons. In addition to liquid electrolyte, polymer, gel, and ceramic electrolyte have also been explored for applications in Li-ion batteries. Figure 4 illustrates the basic operating principle of a typical Li-ion battery cell. The basic design of Li-ion cells today is still the same as those cells Sony commercialized two decades ago, although various kinds of electrode materials, electrolyte, and separators have been explored.

The commercial cells are typically assembled in discharged state. The discharged cathode materials (e.g., LiCoO_2 , LiFePO_4) and anode materials (e.g., carbon) are stable in atmosphere and can be easily handled in industrial practices. Yohsino made a significant contribution to the commercial production of Li-ion batteries by using discharged electrode materials in full cells for the first time. During charging process, the two electrodes are connected externally to an external electrical supply. The electrons are forced to be released at the cathode and move externally to the anode. Simultaneously the lithium ions move in the same direction, but internally, from cathode to anode via the electrolyte. In this way the external energy are electrochemically stored in the battery

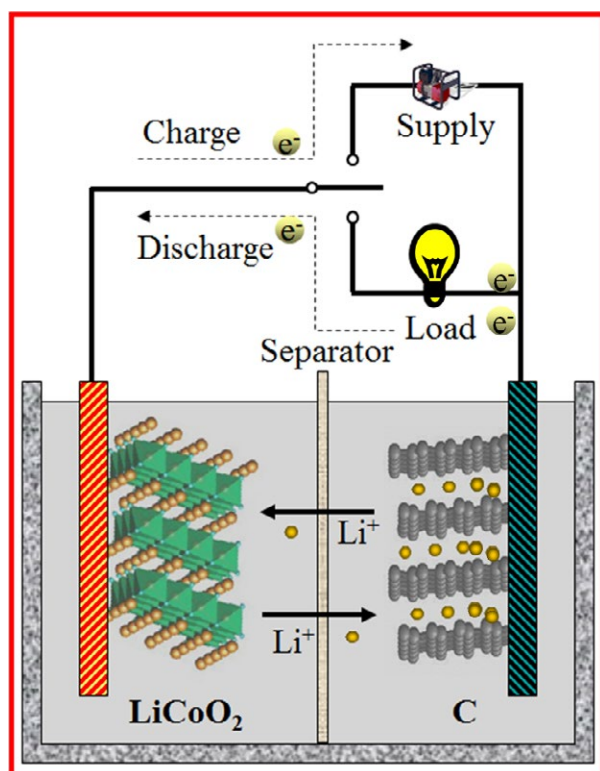


Figure 4. Illustration to show the basic components and operation principle of a Li-ion cell. Reproduced with permission [1].

in the form of chemical energy in the anode and cathode materials with different chemical potentials. The opposite occurs during discharging process: electrons move from anode to the cathode through the external load to do the work and Li ions move from anode to the cathode in the electrolyte. This is also known as “shuttle chair” mechanism, where the Li ions shuttle between the anode and cathodes during charge and discharge cycles.

Electrochemical reactions at the two electrodes released the stored chemical energy [1]. The total Gibbs free energy change due to the electrochemical reactions on the two electrodes is determined by the electrode materials selected. Given the overall electrochemical reaction and charges transferred, one can estimate the theoretical cell voltage ($\Delta E = -\Delta G/nF$). The performance of Li-ion batteries can be evaluated by a number of parameters, such as specific energy, volumetric energy, specific capacity, cyclability, safety, abuse tolerance, and the dis/charging rate. Specific energy (Wh/kg) measures the amount of energy that can be stored and released per unit mass of the battery. It can be obtained by multiplying the specific capacity (Ah/kg) with operating battery voltage (V). Specific capacity measures the amount of charge that can be reversibly stored per unit mass. It is closely related to number of electrons released from electrochemical reactions and the atomic weight of the host. Cyclability measures the reversibility of the Li-ion insertion and extraction processes, in terms of the number of charge and discharge cycles before the battery loses energy significantly or can no longer sustain function of the device it powers. Practically, the cycle life of Li-ion batteries is affected by depth of discharge (DOD) and state of charge (SOC), as well as operating temperature, in addition to the battery chemistry. Cycle life is enhanced with shallow DOD cycles and less SOC swing, and avoiding elevated temperature. Li dendrite formation on graphite anode can occur at low-temperature charge which should be avoided. Safety requirement is very high for Li-ion batteries with multiple cells. Battery management systems (BMS) are typically employed in battery cells/packs/modules to prevent any possible thermal runaway. For example, in the case of battery cell failure inside a battery pack, the BMS could detect and isolate the particular cell.

Abuse tolerance is a critical requirement for practical application of Li-ion batteries, especially in electric vehicles. Typically, mechanical, thermal, and electrical abuse evaluations are carried out on prototypes to evaluate abuse tolerance of the batteries. The mechanical abuse evaluation includes mechanical shock and drop, roll-over, nail penetration, and immersion in water tests. The thermal abuse evaluation includes radiant heat, thermal stability, overheat, and extreme cold tests. The electrical abuse evaluation includes short circuit, overcharge, over-discharge, and alternative current exposure tests. Those abuse tolerance

tests are extremely important for their applications in electric vehicles, as electric vehicles are expected to compete with existing internal combustion engine-powered vehicles that run well in rough conditions. The rate of charge or discharge measures how fast the battery can be charged and discharged, typically called C-rate. At 1 C, the battery is fully discharged releasing maximum capacity in 1 h. Common Li-ion batteries with carbonaceous anodes used in personal mobile devices take 1–4 h to return to the fully charged state. Li-ion batteries used in electric vehicles may take even longer, for example, overnight, to get fully charged, although it could be quickly charged to certain low SOC at high current with special charging devices. One of the active research directions in Li-ion battery community is to increase the rate performance so that the time consumed for charging a battery can be dramatically reduced, which is particularly crucial to the market acceptance of electric vehicles [28].

Theoretical capacity of active electrode materials can be estimated based on electrochemical reactions involved. For example, electrochemical reaction for the anode of graphite that can intercalate reversibly with lithium to form LiC_6 , the reaction is

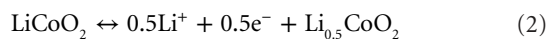


The theoretical specific capacity (mAh/g) of anode graphite can be estimated as the following:

$$\begin{aligned} C_{\text{specific}} &= xF/nM = 1 \times (96485 \text{ C/mol}) / 6 \times (12 \text{ g/mol}) \\ &= 372 \text{ mAh/g} \end{aligned}$$

where x is number of electrons transferred in reaction (1), $F = 96485 \text{ C/mol}$ is Faraday's constant, n is number of moles of a chosen electroactive component that take place in the reaction, and M is the molecular weight of the same electroactive component.

The cathode reaction for LiCoO_2 , with 0.5 as the practical number of electrons transferred, is



The theoretical specific capacity can be estimated similarly

$$\begin{aligned} C_{\text{specific}} &= xF/nM = 0.5 \times (96485 \text{ C/mol}) / 1 \times (98 \text{ g/mol}) \\ &= 137 \text{ mAh/g} \end{aligned}$$

In practice, to evaluate specific capacity of a Li-ion battery cell, one not only has to take into consideration of the integration of cathode and anode materials but also other essential components, such as binders, conductive enhancers, separators, electrolyte, current collectors, case, tabs, as well as battery management systems (BMS). Therefore, the practical energy density is always less than that estimated based the battery chemistry.

Progress in Li-Ion Batteries

Since the commercialization of Li-ion batteries by Sony, Li-ion batteries have been attracting much attention world widely [6, 29–32]. The global production of Li-ion batteries continuously increase in the past two decades, especially with popularity of personal mobile electronics devices, such as mobile phones and personal computers, and electric vehicles. Although Li-ion batteries are highly successful commercially, there are still noticeable disadvantages. (1) The cost of Li-ion batteries based on per unit of energy stored (\$/kWh) is still very high, although the price was decreasing over the past two decades. The Li-ion battery packs for electric vehicles could cost about \$600/kWh, and it is anticipated that the cost could be reduced to about \$200/kWh by 2020. In contrast, the average retail price of electricity to customers is about 0.1 \$/kWh in 2014 according to the U.S. Energy Information Administration. (2) The performances of Li-ion batteries degrade at high temperature. (3) At the same time, it may not be safe if rapidly charged at low temperature. Therefore, protective circuits are typically used avoid over-charge and thermal runaway. However, the protective circuits could add weight burdens and decrease energy density of the whole batteries. (4) Another disadvantage is the possible venting and fire when crushed, which requires critical safety enhancement. The recent accidents of fires in Li-ion battery packs upon crushed by metal objects in the promising Tesla Model S cars highlights the importance of battery safety. Therefore, active research is continuing in all aspects of batteries, from anode, cathode, separator, electrolyte, safety, thermal control, packaging, to cell construction and battery management. The electrode materials selected are critical to the performances of Li-ion batteries, as they generally determine cell voltage, capacity, and cyclability. There are a number of potential alternative electrode materials to replace carbon-based anodes and LiCoO_2 -based cathodes (Fig. 5). Composite alloys, Si, Sn-based materials and 3d-metal oxides materials have relatively higher specific capacities than graphite. However, they suffer from severe volume expansion during the process of lithiation, which causes the fracture of original structure upon lithium extraction, leading to bad electrical contact between particles and current collectors and poor cycling performance. Li metal has the issue of dendrite formation and is not safe as anode, which explained the failed commercialization of the Exxon's lithium ion batteries in the 70s. Given the high capacity of Li metal as anode, it should still be worthy for further exploration and research should focus on depressing the dendrite formation issues. In terms of cathode materials, a number of Co, Mn, Ni-based layered and spinel materials have been explored (mainly

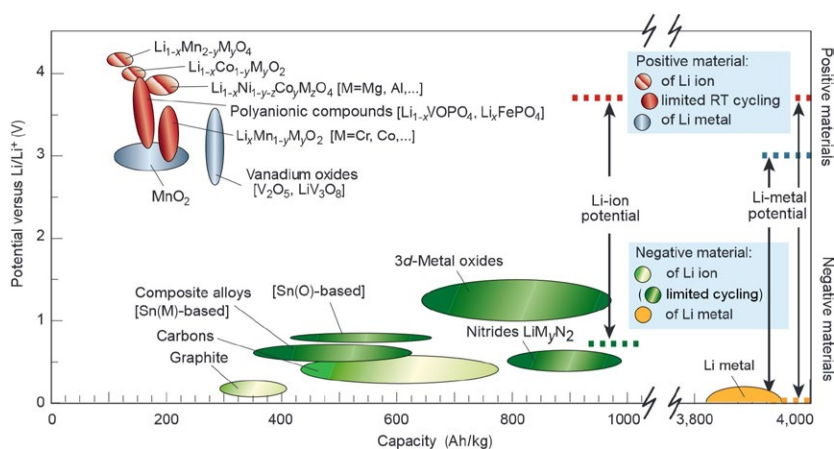


Figure 5. Voltage versus capacity for positive- and negative electrode materials presently used or under considerations for the next-generation of Li-ion batteries. Reproduced with permission [6].

concentrated in the left upper corner of Fig. 5). Recently, much effort is shifted to polyanionic components, such as LiFePO_4 and LiMnPO_4 . The main requirements for cathode materials are high free energy of reaction with lithium, incorporating large quantities of lithium and insoluble in electrolytes. Although various promising electrode materials have been proposed, the slow lithium ion diffusivity, poor electronic conductivity and high cost are limiting their practical applications.

To address those issues associated with alternative electrode materials, recent efforts are to employ nanostructured materials for Li-ion batteries. It is generally believed that size and shape tunable properties of those lithium-active materials at nanoscale can offer additional parameters for further optimization of their electrochemical performances [29–31, 33]. The fascinating size-shape-related properties of nanomaterials bring new opportunities for a potential breakthrough in the development of next-generation Li-ion materials. Nanostructured electrode materials can offer various advantages not available in conventional bulk materials, and are believed to be the material-of-choice for the next-generation Li-ion batteries [1, 34–46]. However, nanomaterials bring along with new problems as will be discussed. In this tutorial review, I will try to provide an introduction on four aspects of Li-ion batteries, including cathode materials, anode materials, electrolyte, and separators, with emphasized on the progress achieved and challenges faced in those areas. Battery management and monitoring and optimization and cell integration are out of the scope of this review.

Cathode materials

There are a number of candidates that have been explored as cathode materials for Li-ion batteries. The cathode

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

Currently LiCoO_2 and LiFePO_4 are most widely used in commercial Li-ion batteries because of their good cycle life (>500 cycles). LiCoO_2 can be easily manufactured in large scale and is stable in air. Its practical capacity is ~140 mAh/g and the theoretical capacity is 274 mAh/g upon full charge. In addition to its low practical capacity, other noticeable disadvantages of the LiCoO_2 are their high material cost and the toxicity of cobalt. On the other hand, LiFePO_4 -based cathode materials are attracting much attention in the past decade due to its low cost and low environmental impact. Compared to LiCoO_2 , LiFePO_4 also offers a number of advantages, such as stability, excellent cycle life, and temperature tolerance (–20 to 70°C). However, LiFePO_4 has a problem of poor electronic and ionic conductivity at 10^{-10} S/cm and 10^{-8} cm²/sec, respectively, as well as relatively low capacity [47]. The other issue is one-dimensional channels for lithium ion diffusion which can easily be blocked by defects and impurities. Modeling and calculation reveal that the lowest Lithium ion migration energy is in the channels along [010] direction (Fig. 6) [48]. It also suggests that diffusion constant depends on particle size with diffusion in bulk being much slower than in nanoscale. Therefore, LiFePO_4 in nanoscale have been explored for and employed in Li-ion batteries.

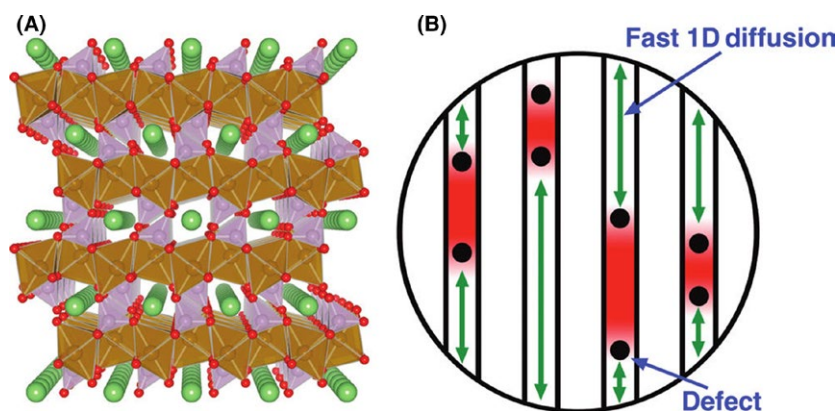


Figure 6. (A) Crystal structure of LiFePO₄ illustrating 1D Li⁺ diffusion channels along the [010] direction; (B) Illustration of Li⁺ diffusion impeded by immobile point defects in the channels. Reproduced with permission [48].

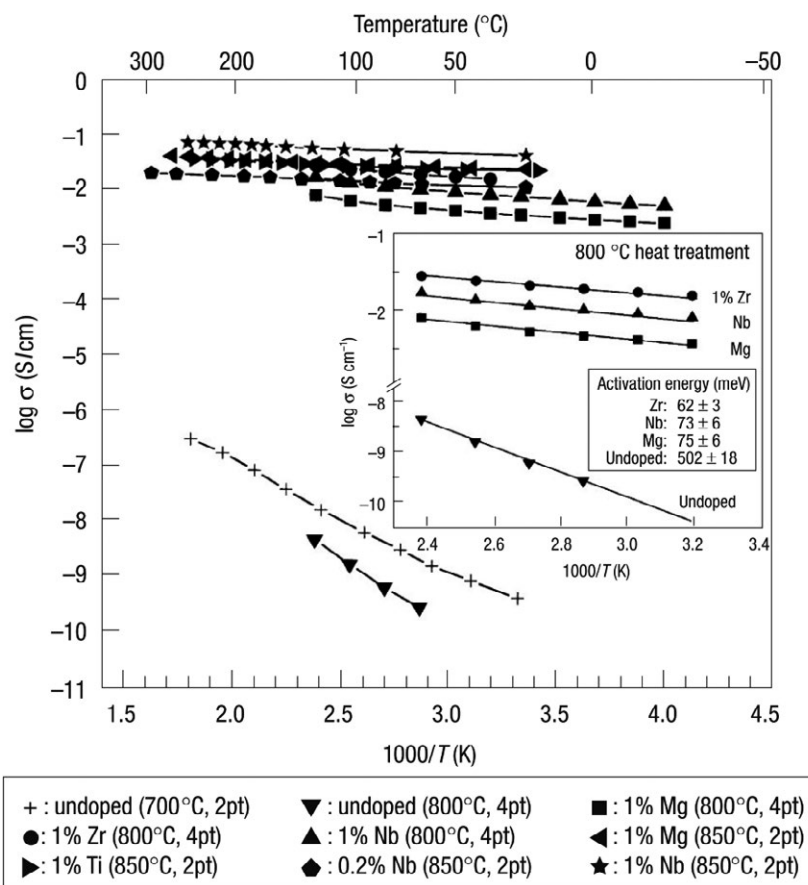


Figure 7. Electrical conductivity compared at different temperature with different cation doping for olivines of stoichiometry Li_{1-x}M_xFePO₄ versus undoped LiFePO₄. Reproduced with permission [47].

To enhance electronic and ionic conductivity of LiFePO₄, two common strategies are developed, namely doping by ions and coating by carbon [47, 49]. Chiang et al. reported that electronic conductivity of LiFePO₄ can be increased

by a factor of 10⁸ by cation doping (Fig. 7). The doped LiFePO₄ of stoichiometry Li_{1-x}M_xFePO₄ (M = Mg, Ti, Zr, Nb) could provide significant capacity with little polarization at rates as high as 6 A/g [47]. It was revealed by

structural and electrochemical analysis that doping could reduce the lithium miscibility gap, increase phase transformation kinetics during cycling, and expand Li diffusion channels in the structure [49]. Combined doping and nanoscale size, it was possible to produce high power Li-ion batteries based on LiFePO_4 . In fact, the start-up company A123 adopted the doping strategy to employ LiFePO_4 as cathode materials for making advanced Li-ion batteries with high power and was very successful initially and quickly established multiple manufacturing plants globally.

Recently, Kang and colleagues [50] reported that nanocrystalline $\text{LiFe}_{1-x}\text{Sn}_x\text{PO}_4$ ($0 \leq x \leq 0.07$) could be synthesized using Sn as dopant via an inorganic-based sol-gel method (Fig. 8). They noticed that under the synergetic effects between the charge compensation and the crystal distortion, the electrical conductivity first increases and then decreases with the increasing amount of Sn doping when tested at various rates. Their study suggested that a doping amount of about 3 mol% delivered the highest capacities at all rates attributed to the high electrical conductivity and the fast lithium ion diffusion velocity. It would be interesting to further understand the mechanism of change in specific capacity as a function of amount of Sn doped in LiFePO_4 , and why the 3 mol% is the optimized value.

Improved rate performance of LiFePO_4 by Fe-site doping was observed [51]. When evaluated at 10 C rate, the capacity of $\text{LiFe}_{0.9}\text{M}_{0.1}\text{PO}_4$ for ($\text{M} = \text{Ni}, \text{Co}, \text{Mg}$) could be maintained at 80–90 mAh/g with 95% capacity retention after 100 cycles. Without doping, only 70% capacity can be retained. The improved rate performance and cyclability were attributed to the enhanced conductivity and good mobility of Li^+ ions in the doped electrode. In addition to Fe-site doping, Ceder reported an interesting strategy by designing LiFePO_4 off-stoichiometry (e.g., $\text{LiFe}_{1-2y}\text{P}_{1-y}\text{O}_{4-\delta}$) as cathode materials to achieve high lithium bulk mobility [28]. The procedure for materials

preparation was impressively simple, suggesting the process could be easily carried out in manufacturing process. Precursors of Li_2CO_3 , $\text{FeC}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$ and $\text{NH}_4\text{H}_2\text{PO}_4$ in calculated amounts were ball-milled and heated to 350°C for 10 h and then heated at 600°C for 10 h under argon. The as-prepared nanoparticles are about 50 nm in size with poorly crystallized layer <5 nm thick (Fig. 9C). This two-stage heating was believed to provide the right conditions for construction of a fast ion-conducting surface phase of glassy lithium phosphate containing Fe^{3+} . The exceptionally high-rate performance (Fig. 9A and B) was attributed to the combination of nanoparticles with small size and the optimal coating with good lithium ion conductivity. It was estimated that a full battery discharge in 10–20 sec could be achieved. The very high-rate tests were carried out with 65 wt% carbon as conductive enhancer [28]. On the other hand, the ultrafast charging rate could require extremely high current up to 900 A for practically application, which is not recommended for safety consideration [52]. Similar to other fast charging batteries, more work is still needed to be done on addressing the issues of safety and heat generation.

In addition to doping, the other strategy of coating LiFePO_4 with carbon has also been demonstrated to improve electrochemical performance of LiFePO_4 as cathode for Li-ion batteries [53]. In fact, by a very simple procedure of dispersion of LiFePO_4 nanoparticles in a nanoporous carbon matrix, Guo and colleagues [54] demonstrated that LiFePO_4 -based cathode could achieve both high power and high energy. The improved electrochemical performance could be attributed to the presence of conducting 3D nanonetwork in carbon matrix which enhances both Li ions and electrons to migrate and reach each LiFePO_4 particle achieving full utilization of the active materials. The nanoporous carbon matrix could serve as an electrolyte container for high-rate operation and be employed to support other active materials as well (Fig. 10)

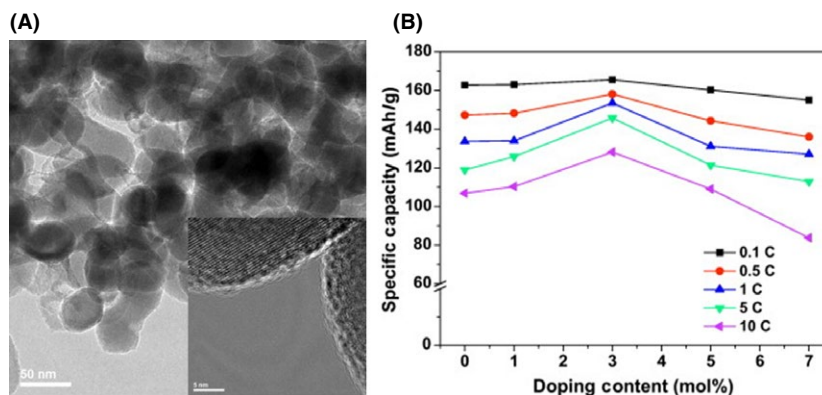


Figure 8. (A) The TEM image for the $\text{LiFe}_{1-x}\text{Sn}_x\text{PO}_4$ ($0 < x \leq 0.07$) nanoparticles and the inset shows the high-resolution TEM image. (B) The capability of the $\text{LiFe}_{1-x}\text{Sn}_x\text{PO}_4$ ($0 \leq x \leq 0.07$) samples as a function of the doping amount of tin and current rate (C-rate). Reproduced with permission [50].

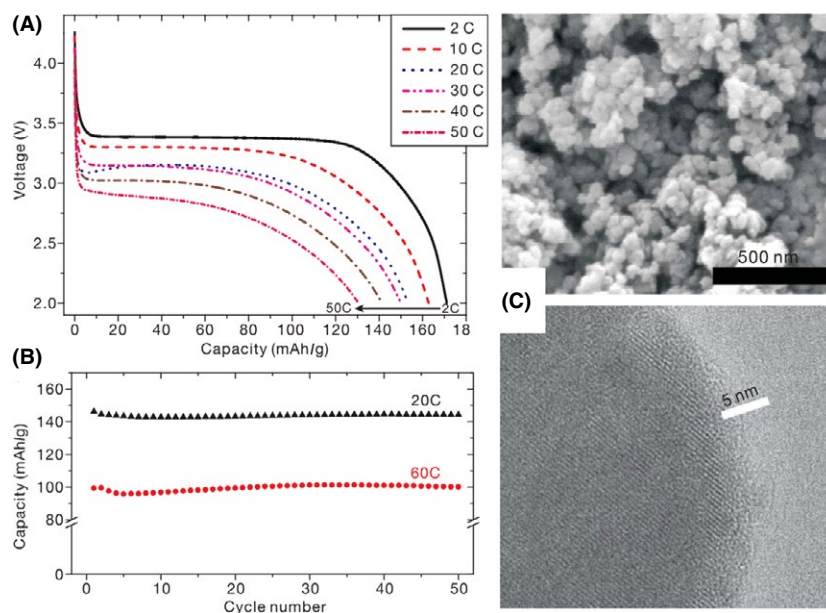


Figure 9. (A) Discharge rate capability and (B) capacity retention for $\text{LiFe}_{0.9}\text{P}_{0.95}\text{O}_{4-\delta}$ prepared by heating at 600°C under argon; (C) SEM (upper) and TEM (lower) images showing a particle size of ~ 50 nm and a poorly crystallized layer less than 5 nm thick on the edge of a particle, respectively. Reproduced with permission [28].

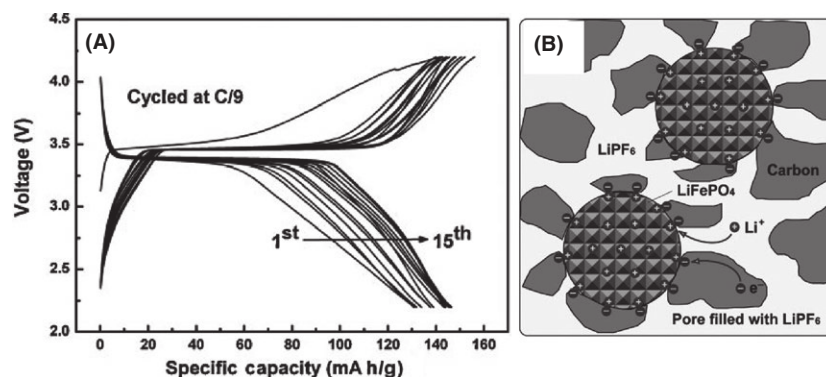


Figure 10. (A) First 15 cycles of galvanostatic charge/discharge profiles tested at a rate of C/9 of the composite of LiFePO_4 nanoparticles in a nanoporous carbon matrix; (B) Schematic illustration of the LiFePO_4 @nanoporous carbon matrix for Li storage. Reproduced with permission [54].

[54]. It also interesting to note that the preparation procedure using sol-gel method followed by a solid-state reaction is very simple and can be used for industrial scale production in the future.

Amine et al. explored the coating of LiFePO_4 with carbon by vapor deposition process to improve the rate performance in Li-ion batteries. The carbon coating was achieved by decomposition of propylene balanced with N_2 in a preheated furnace at 700°C containing the olivine material [55]. The coating process is considered a low-cost coating technique, which could be suitable for mass production. Interestingly, few monolayers of carbon film formed on

the surface of olivine particles and the carbon also was deposited inside the pores of the particles. With just 3.4 wt% carbon, impressive cycling performance over 70 cycles could be achieved with no capacity fade at either room temperature or at 37°C (Fig. 11). It is particularly interesting to note that, without addition of carbon black as the conductivity enhancer typically for LiFePO_4 , they could achieve specific capacity of 140 and 150 mAh/g when tested at room temperature and at 37°C , respectively. The improved performance was attributed to the network of carbon film on the surface of the olivine as well as the in the pores of the particles. The presence of carbon film dramatically

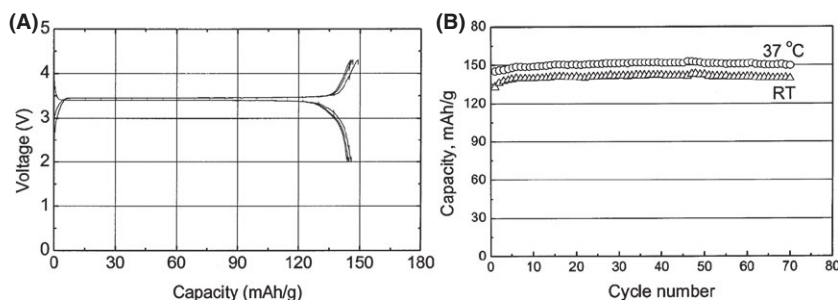


Figure 11. (A) The charge/discharge profiles of the carbon-coated olivine LiFePO_4 ; (B) Cycling performance of the carbon-coated olivine tested at room temperature and 37°C over 80 cycles of charge and discharge. Reproduced with permission [55].

improved the overall conductivity of the electrodes. It is believed the C- LiFePO_4 could be very promising to replace those toxic transition metal oxide-based cathodes.

In addition to carbon coating, other conductivity enhancers have been explored to improve the conductivity of LiFePO_4 as well. Chung and colleagues [56] explored the preparation of LiFePO_4 thin films with uniformly dispersed highly conductive silver to improve the conductivity of LiFePO_4 (Fig. 12). With a small fraction of dispersed silver at only 1.37 wt%, a superior electrochemical performance in terms of specific capacity, cyclability, and high charge–discharge rate has been achieved. The preparation

procedure for making this uniformly dispersed silver in LiFePO_4 thin films was remarkably simple. Pulsed laser deposition was employed to deposit $\text{LiFePO}_4\text{-Ag}$ on a $\text{Si}/\text{SiO}_2/\text{Ti}/\text{Pt}$ substrate using 248 nm laser beam with the substrate kept at 600°C . The conductivity of the as-prepared $\text{LiFePO}_4\text{-Ag}$ thin film is $1.29 \times 10^{-3} \text{ S/cm}$, which is dramatically higher than that of bare LiFePO_4 film at $0.25 \times 10^{-9} \text{ S/cm}$. The improved conductivity helped to achieve impressive electrochemical performances in terms of specific capacity, cyclability, and charging rate [56]. The thin film-based active materials deposited on Si substrate suggest that the Li-ion batteries eventually developed will

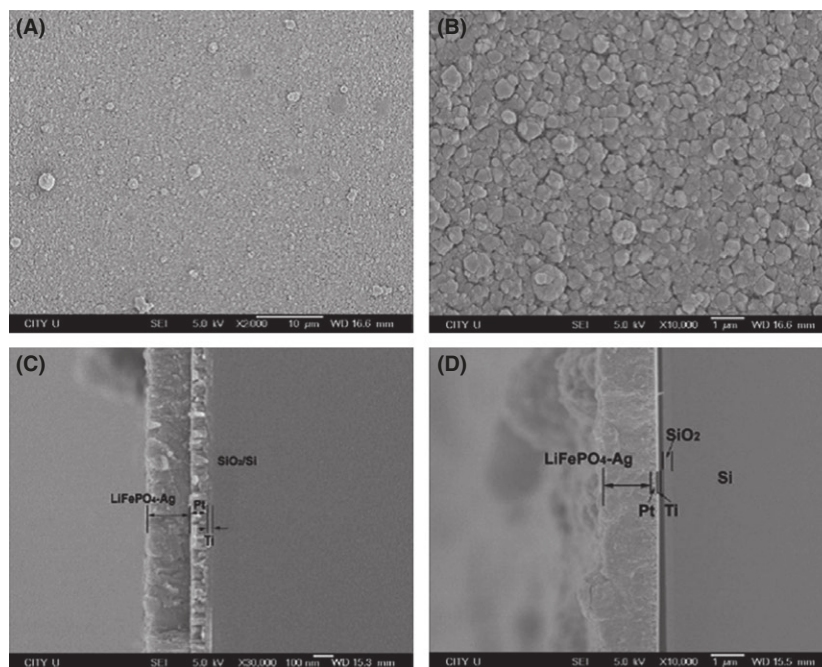


Figure 12. Planar view SEM images of the as-deposited $\text{LiFePO}_4\text{-Ag}$ thin film at (A) low and (B) high magnifications. (C) Cross-sectional SEM image of the typical $\text{LiFePO}_4\text{-Ag}$ film deposited on coated substrate. (D) Cross-sectional SEM image of the thick $\text{LiFePO}_4\text{-Ag}$ thin film ($1.4 \mu\text{m}$) with a PLD deposition time of 4 h showing the film delaminated from substrate due to large stress of the thick film on the substrate. Reproduced with permission [56].

be for certain niche applications, such as microscale batteries, but not for mobile electronics or electric vehicles. On the other hand, thin film analysis is always helpful to reveal certain fundamental electrochemical mechanisms. The understanding and results obtained can be used to design better cathode materials beyond thin films.

Although LiFePO_4 has been demonstrated to show huge potential to replace traditional LiCoO_2 as safe cathode materials in Li-ion batteries, there are still challenges. The relatively moderate specific capacity or energy (by mass) of LiFePO_4 associated with its chemistry does not provide much space for further improvement. On the other hand, its rate performance or power can be further increased by the introduction of nanoscale structures. However, the introduction of nanoscale LiFePO_4 has two issues, namely the low volumetric density of the nanomaterials and the difficulty in preparation of nanoscale LiFePO_4 at low cost. The low packing density issue of nanoscale LiFePO_4 makes it difficult to produce batteries with high-energy density (by volume). Given that the interfacial behavior between LiFePO_4 with electrolyte plays critical roles in electrochemical performance, which is even more critical at nanoscale, it is crucial to gain better in-depth understanding of the interfacial phenomena involved. In situ investigation to monitor the interface during charge–discharge process may reveal the fundamental mechanisms involved in the interfacial electrochemical reactions. This kind of understanding will help to design better coating for LiFePO_4 , and achieve better rate and cycling performance. Further study to address those challenges will enhance their electrochemical performance and generate big impact on energy storage.

Additional to layered compounds LiMO_2 (e.g., LiCoO_2) and olivine compounds LiMPO_4 ($M = \text{Fe, Mn, Ni, Co}$ or combinations, e.g., $\text{LiMn}_{1-x}\text{Fe}_x\text{PO}_4$) discussed above, 5-Volt cathode materials of olivine LiMnPO_4 , LiCoPO_4 , and spinel $\text{Li}_2\text{MxMn}_{4-x}\text{O}_8$ ($M = \text{Fe, Co, Ni}$) are also being actively pursued. High voltage cathode materials could help to increase the energy density but demand for alternative stable electrolyte instead of conventional electrolyte. Another family of emerging polyanionic cathode is Li_2MSiO_4 , ($M = \text{Mn, Fe, Co, Ni}$, e.g., $\text{Li}_2\text{MnSiO}_4$), which could offer much high capacity of 330 mAh/g. The obstacles to adopt those high-capacity Li_2MSiO_4 (Fig. 13) are their poor electronic conductivity, poor rate capability and fast capacity fading upon cycling [58].

Another notable progress was made recently by a team from the Argonne National Laboratory based on innovatively designed layered lithium nickel cobalt manganese oxide (with average composition of $\text{Li}[\text{Ni}_{0.68}\text{Co}_{0.18}\text{Mn}_{0.18}]\text{O}_2$) microparticles [59]. The cathode materials is unique in the way that the microparticles have concentration gradient, where the core is rich in Ni, and the outer layer is rich in Mn with decreasing Ni concentration and

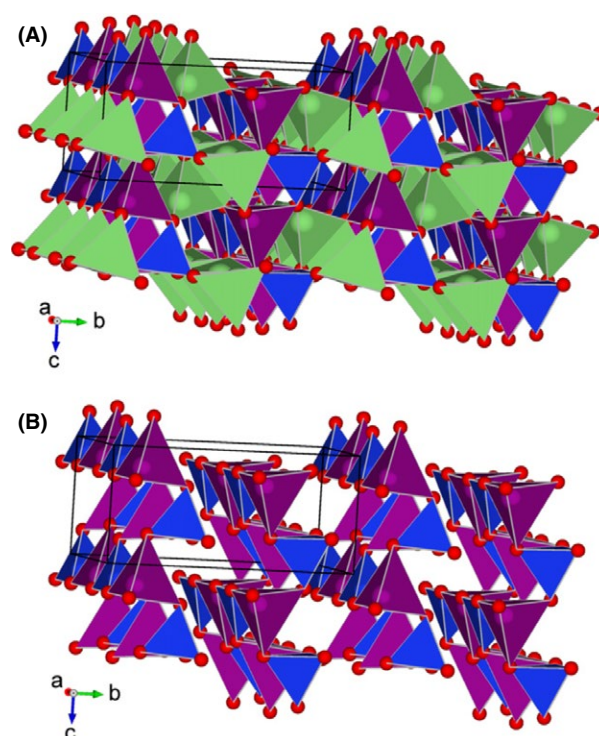


Figure 13. The crystal structure of (A) a typical form of $\text{Li}_2\text{MnSiO}_4$ (Pmnb) and (B) the hypothetical structure of the fully delithiated MnSiO_4 with SiO_4 shown in blue, LiO_4 in green, and MnO_4 in purple. Reproduced with permission [57].

increasing Mn and Co concentrations at the surface (Fig. 14). The bulk core of Ni-rich cathode provides high capacity. The concentration-gradient outer layer and the surface improve the thermal stability. The cathode materials demonstrated impressive high reversible capacity of 209 mAh/g and good safety characteristics. It should be noted that the materials preparation procedure based on coprecipitation in aqueous solution followed by calcination at 780°C is very simple and scalable, which is suitable for industrial scale production. This high-capacity concentration-gradient cathode material is promising to be produced on a large scale and used in next-generation commercialized Li-ion batteries. NCM cathodes are expected to play increasing roles in commercial Li-ion batteries.

Anode materials

Anode materials are extensively investigated and there is a bigger pool of candidates and materials. The electrochemical performances, including cyclability, charging rate, and energy density, of Li-ion batteries are significantly affected by anode materials selected. Since the first commercialization of carbonaceous anodes, carbon is still dominant in commercial Li-ion batteries today. Graphitic carbon with

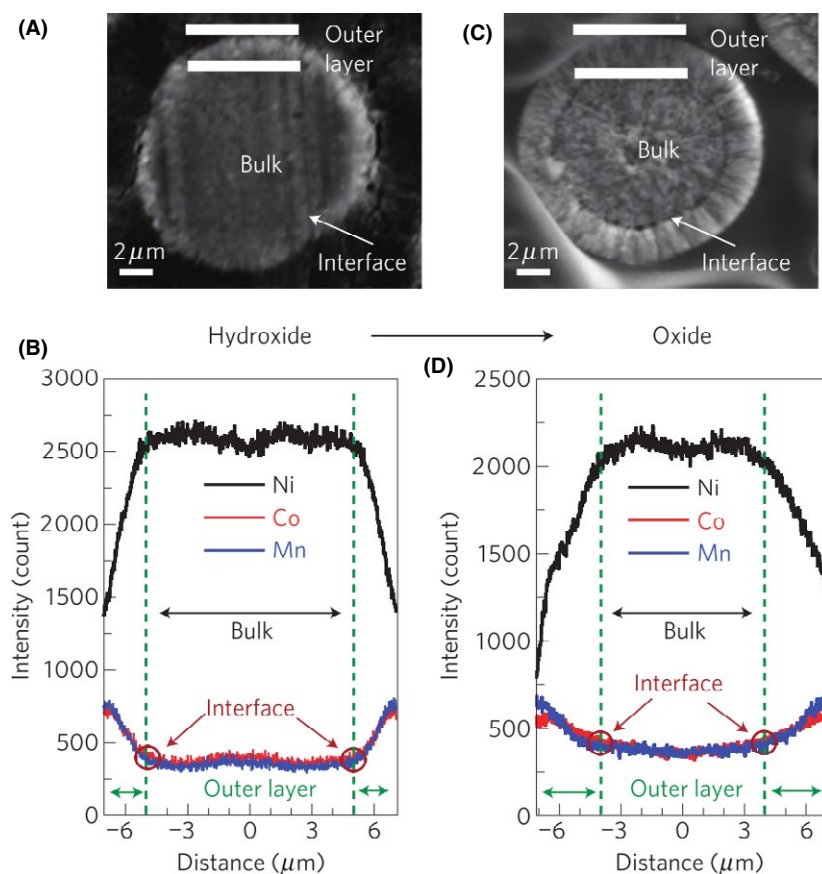


Figure 14. SEM images of (A) the precursor hydroxide obtained by coprecipitation, and (B) the final concentration-gradient lithiated NCM oxide; (C) and (D) are the corresponding electro-probe X-ray microanalysis line scans for (A) and (B), respectively. Reproduced with permission [59].

layered structure can facilitate the movement of lithium ions in and out of its lattice space with minimum irreversibly, resulting in an excellent cyclability [60]. However, the carbon anodes are soon approaching their theoretical maximum capacity of 372 mAh/g over the past two decades of development. Carbon alternatives with high-energy density and enhanced safety are required to meet the demands for increases in energy and power densities, especially to meet the demands from electric vehicles [61]. Fuji Film introduced tin composite oxide (TCO) as a carbon alternative in 1997 but was not very successful due to the poor cycling performance [62]. Sony Cooperation announced new-generation Li-ion batteries with the trade name of Nexelion in 2005. The anode of Nexelion is based on a carbon–tin–transition-metal composite (e.g., Sn–Co–C), and the compound is mainly amorphous or microcrystalline aggregates. Those efforts have rekindled another wave of interest in anode materials for Li-ion batteries [63].

Besides Sn, many other elements that are known to alloy with lithium, including silicon, are good candidates to replace carbon for lithium storage. These elements could alloy and de-alloy with lithium electrochemically

at room temperature. However, the alloying/dealloying process during charging/discharging is accompanied by substantial variations in the specific volume of the material. The induced huge mechanical stress could lead to the destruction of the crystal structures and disintegrate the active materials and current collectors within a few cycles, or the so-called “pulverization” issue. The resulting poor cyclability has significantly limited their usability in practical situations. The engineering approach to solve the poor cyclability problem is to introduce composites. In such a composite material, one component (usually carbon) functions as a stress absorber whereas the other (such as silicon or tin) provides the boost in capacity. Through this approach a composite with capacity higher than carbon and cyclability better than Sn or Si can be achieved. A number of combinations involving carbon have been explored, among them Si/C [64] and SnO₂/C [65] have attracted much interest.

Carbons that are capable of reversible lithium ion storage can be classified as graphitic and nongraphitic (disordered) carbon. Graphitic carbons have a layered structure. Natural graphite, synthetic graphite, and

pyrolytic graphite which consist of aggregates of graphite crystallites are commonly named graphite as well. The lithium insertion into graphite follows a stepwise occupation of the graphene interlayers at low concentrations of the lithium ions, known as stage formation [30]. Disordered carbons consist of carbon atoms that are arranged in a planar hexagonal network without an extended long-range order. There are amorphous domains cross-linking the crystalline graphitic flakes. Disordered carbon normally demonstrate high-specific capacity ($x > 1$ in Li_xC_6), but with issues of huge first-cycle irreversible capacity loss and capacity fading [66].

The excess charge consumed in the first cycle is generally attributed to the formation of a passivating solid-electrolyte interphase (SEI) on the carbon surface [30]. The SEI is caused by electrolyte decomposition at low potentials on fresh carbon surfaces. A poorly formed SEI

would continue to grow with time, leading to the increase in cell internal resistance and preventing full reversibility of lithium ion insertion into carbon. Subsequently the energy density of the cell decreases with the number of charging cycles. It is also known that some organic solvents would promote the insertion of lithium ions together with the solvent molecules. The solvated intercalation is accompanied by extreme expansion of the graphite matrix ($\sim 150\%$), which gradually deconstructs the graphite structure resulting in reduced charge storage capability [30]. The disordered carbons are normally synthesized by heat treatment of various carbon precursors under inert atmosphere. Recently, much effort is focused on disordered carbon, although the exact mechanism by which the high-specific capacity is achieved has not been fully understood [67–69]. Other carbon-based materials that have been extensively studied are buckminsterfullerene, carbon

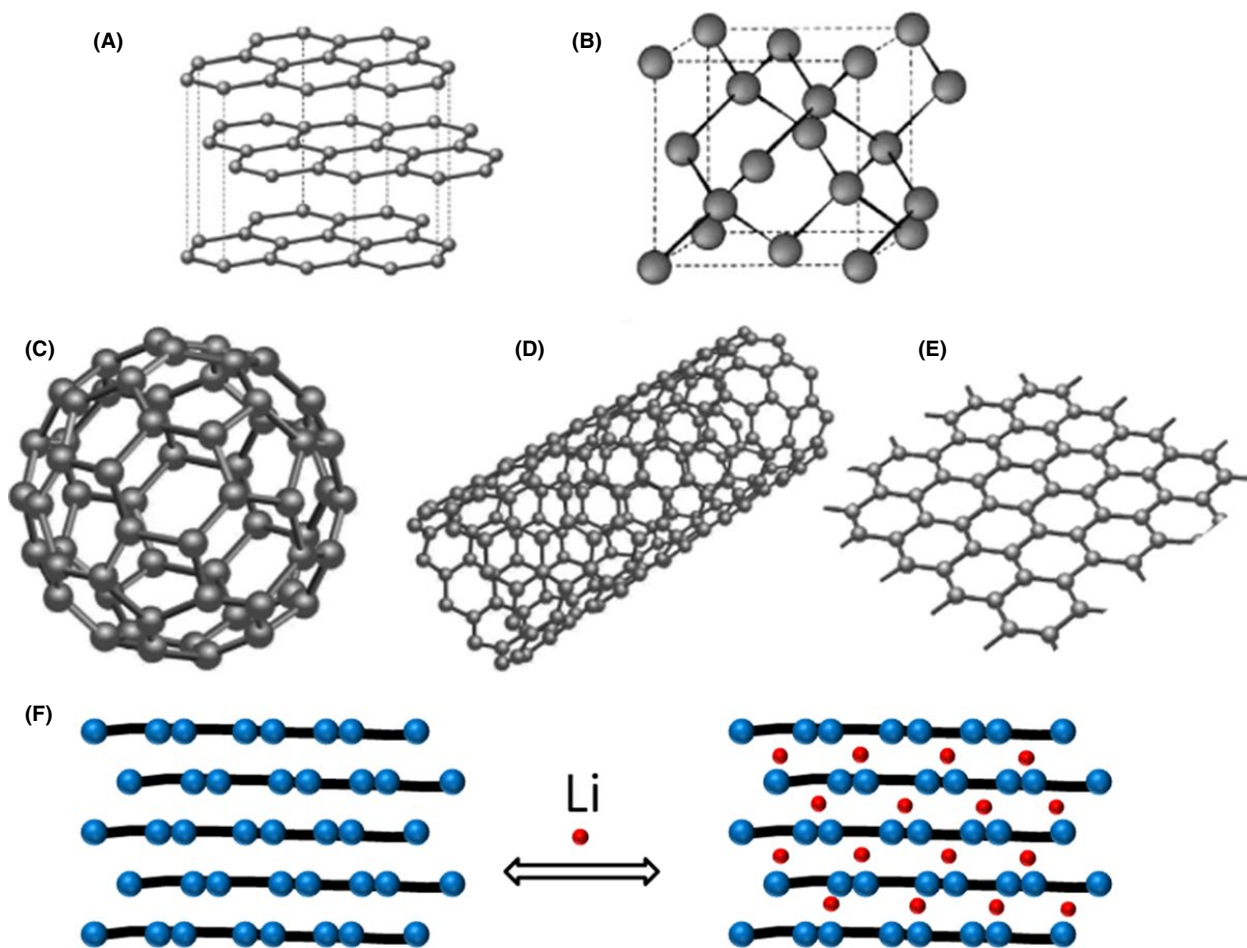


Figure 15. A family of carbon-based materials with different structure: (A) graphite with a stack of graphene layers, (B) diamond with carbon atoms arranged in a FCC structure, (C) buckminsterfullerene (C_{60}) with consisting of graphene balled into a sphere, (D) carbon nanotube with rolled-up cylinder of graphene, and (E) graphene of a single layer carbon, (F) the schematic of lithium intercalation and deintercalation between graphene layers in graphite. (A–E) were reproduced with permission [74].

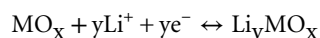
nanotubes, and graphane (Fig. 15). Carbon nanotubes, in particular, can be a good lithium host on grounds of their excellent electronic conductivity and other properties associated with their linear dimensionality [70, 71]. However, current interest is focused on CNT- and graphene-based composites instead of pristine CNTs or graphene to achieve much higher capacity than that of pristine carbon [72, 73].

Another family of anode materials with high capacity is metal oxides, which have been widely studied since the first report by Tarascon's group [31]. Although metal oxides are generally poor in conductivity, properly tailored metal oxides at nanoscale have demonstrated promising characteristics. The reaction mechanism of lithiation and delithiation in metal oxides can be generally classified into three main types (Fig. 16): (1) the insertion/extraction, (2) the alloying/dealloying, and (3) the conversion mechanisms. The first mechanism is observed in different kinds of anode materials, including anatase TiO_2 [75]. In fact, most of cathode materials with layered or spinel structures also follow the insertion-extraction mechanism as discussed previously. Alloy reaction exists in some main-group elements, including Si, Sb, Ge, Bi and Sn, which can alloy with lithium forming Li_xM providing high-specific capacity. However, the lithium alloying and dealloying processes are typically associated with huge volumetric expansion (as high as 300%) and shrinkage, or pulverization, leading

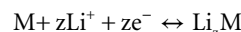
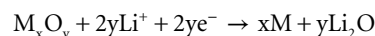
to capacity fading upon cycling. The third mechanism of conversion is typically observed in transition metal oxides (M_xO_y , $\text{M} = \text{Mn, Fe, Co, Ni, Cu, etc.}$). Those conversion-type materials have relatively high theoretical capacities for they can incorporate more than one Li per metal. Metal grains and Li_2O will form during the process of lithiation. In many cases, the metals can reversibly alloy with lithium. Metal oxides also have the issue of pulverization, huge first-cycle irreversible capacity loss, as well as poor conductivity. To overcome those problems, much effort is focused on the preparation of nanoscale metal oxides and $\text{M}_x\text{O}_y/\text{carbon}$ composites.

The electrochemical reactions of three types of reaction are listed.

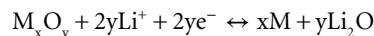
1. Insertion/extraction mechanism:



2. Li-alloy reaction mechanism:



3. Conversion reaction mechanism:



TiO_2 -based anode materials have been extensively explored, although its practical capacity is not comparable to that of carbon anodes. In contrast to carbon where the

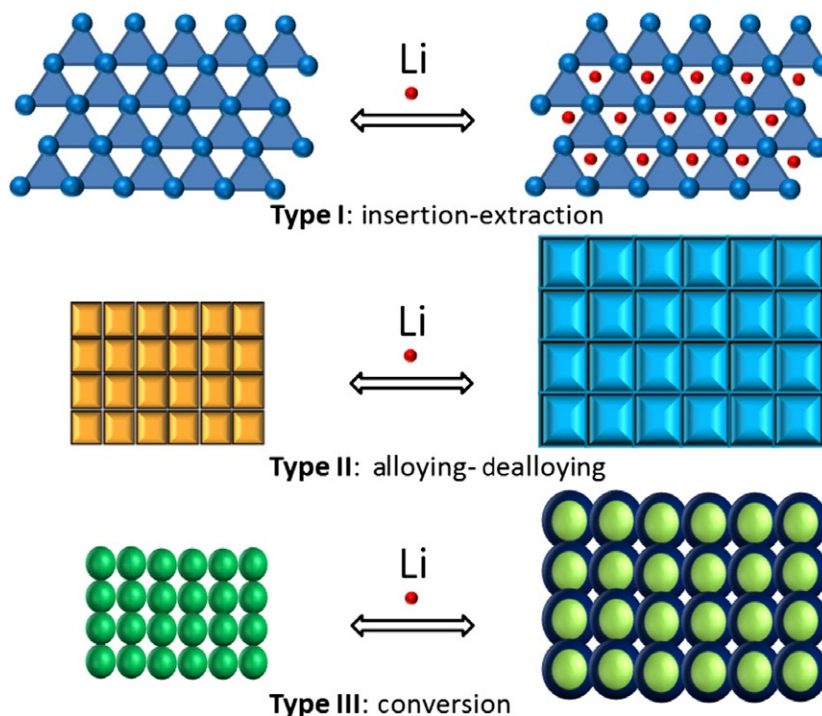


Figure 16. Schematic of different mechanisms of reversible lithium ion storage in metal oxides. The illustrate was drawn based on literature [76].

insertion of lithium into carbon takes place at a low voltage close to 0 V versus Li/Li⁺ couple, the Li-ion insertion into TiO₂ is at about ~1.5 to 1.8 V versus Li/Li⁺ couple. The electrochemical characteristics suggest that the potential risk of metal lithium deposition and dendrite formation, battery short circuit and thermal runaway in carbon-based batteries can be avoided if TiO₂ is used. Additionally, no surface electrolyte interphase (SEI) could form on TiO₂ in the potential window. In contrast, SEI formation on carbon causes the first-cycle irreversible capacity loss issue which would demand for additional supply of expensive cathode materials. Therefore, TiO₂-based anodes can find some niche applications where safety is the number one priority, for example, in aviation and aerospace applications. Among the four different phases of TiO₂, namely anatase, rutile, brookite and TiO₂(B), anatase TiO₂ is the most attracting one with theoretical specific capacity of 168 mAh/g based on the following electrochemical Li insertion-extraction reactions: TiO₂ + x(Li⁺ + e⁻) → Li_xTiO₂ where x = 0.5 for anatase TiO₂.

A facile gram-scale preparation of anatase TiO₂ high-order structures with subunits of tunable nanoparticle

aggregates from one precursor for Li-ion batteries has been reported [75]. The nanoparticles were formed by basic building units aggregated controlled by calcination temperature (Fig. 17). Interestingly, the size of the basic building units of TiO₂ nanoparticles can significantly affect their electrochemical characteristics. When the crystallite size was at 17 nm, the anatase TiO₂ aggregates achieved an impressive high capacity 170 mAh/g, which is close to the theoretical value of 168 mAh/g. When charged at higher currents, good capacity retention was achieved indicating good rate performance. After 120 cycles, a reversible capacity of 160 mAh/g was still achieved at rate of ~C/3. However, when the crystallite size was at 33 nm, the amount of lithium insertion and extraction is very small. Electrochemical analysis revealed that the storage capacity was mainly in the form of pseudocapacity. Therefore, in the preparation of nanoparticles for Li-ion batteries, one has to control basic crystallite size to optimize their electrochemical performances.

Recently, much research focus of anode materials has been shifted to silicon-based anode. Silicon has the high theoretical capacity of 4200 mAh/g (lithiated to Li_{4.4}Si) or 3572 mAh/g (based on Li_{3.75}Si) which is about 10 times

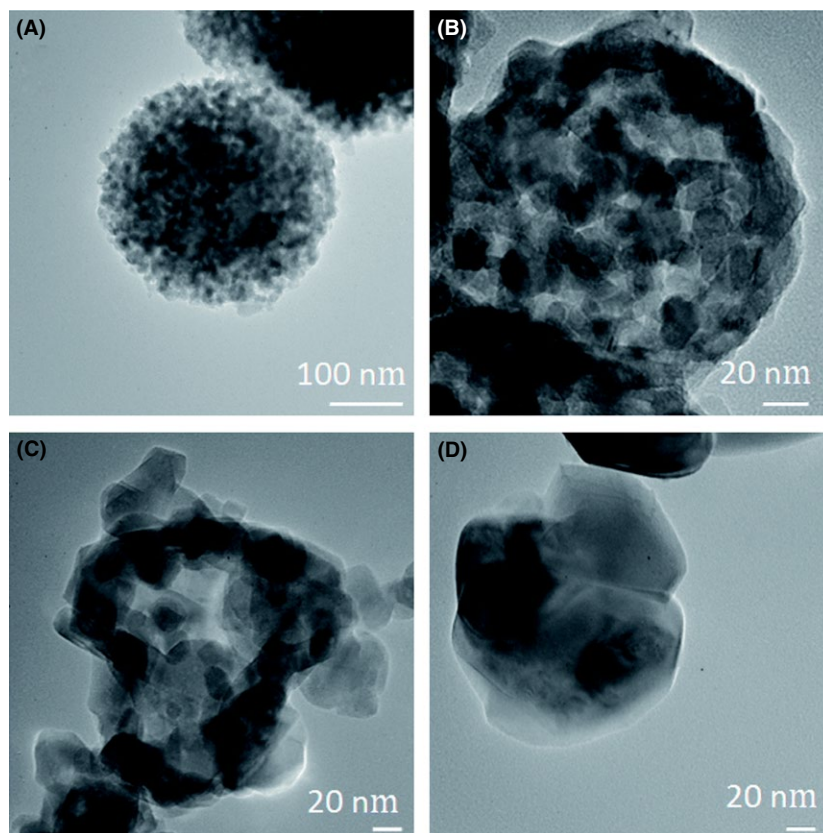


Figure 17. Anatase TiO₂ nanoparticle formed by nanoparticle aggregates with different unit size obtained from the same precursor by calcination at (A) 400, (B) 550, (C) 700 and (D) 900 °C characterized by TEM. Reproduced with permission [75].

of that graphite and almost four times of many metal oxides. However, silicon suffers two main drawbacks, namely poor conductivity and huge volume variation (400%) upon cycling, which makes it practically difficult to use bulk silicon anode. The silicon nanostructured anode materials are very attractive. However, unlike metallic anodes, Si is a semiconductor and is more difficult to produce Si particles at nanoscale by simple cost-effective approaches on a large scale. Recently silicon nanowires have been reported to demonstrate promising reversible lithium storage properties [15]. Cui and colleagues [15] proposed and demonstrated that silicon nanowires were superior in lithium ion storage as compared to silicon thin film and particles (Fig. 18). The silicon nanowires could avoid the issue of pulverization and contact loss due to facile strain relaxation and efficient electron transport along each nanowire.

Bogart et al. [77] also demonstrated that silicon nanowires with carbon skin could enhance the cycling and rate performances of silicon nanowires in lithium storage. Recently, in another attempt, Ti@Si core-shell coaxial nanorods were proposed to further improve the electrochemical performances of Si nanorods (Fig. 19). As compared to pristine

Si nanorods, the benefit of metallic core is that the axial resistance observed in solid Si nanorods could be dramatically reduced. The electrons released/acquired on electrochemical reactions of dealloying/alloying for Li_xSi could be transferred to the Ti foil current collectors easily via the metallic Ti core, in contrast to the solid semiconductor Si nanorod. The incorporation of metallic Ti core could dramatically reduce the Li diffusion distances from the radius of the solid Si nanorod to just the thickness of the shell of the core-shell Ti@Si nanorod. Additionally, the longitudinal direction charge transfer of the semiconductor solid Si nanorod with length of a few micrometers is reduced to thickness of the shell in the case of Ti@Si core-shell coaxial nanorods. Besides, the contact surface of Si with Ti increases, which could improve the connection between active materials and the collector. However, the capacity fading was still observed, suggesting further efforts should be put to optimize the core-shell materials. The concept should be extended to the preparation of other core-shell materials as well.

The author believes that silicon nanomaterials could potentially replace carbon anodes in the next 10 years,

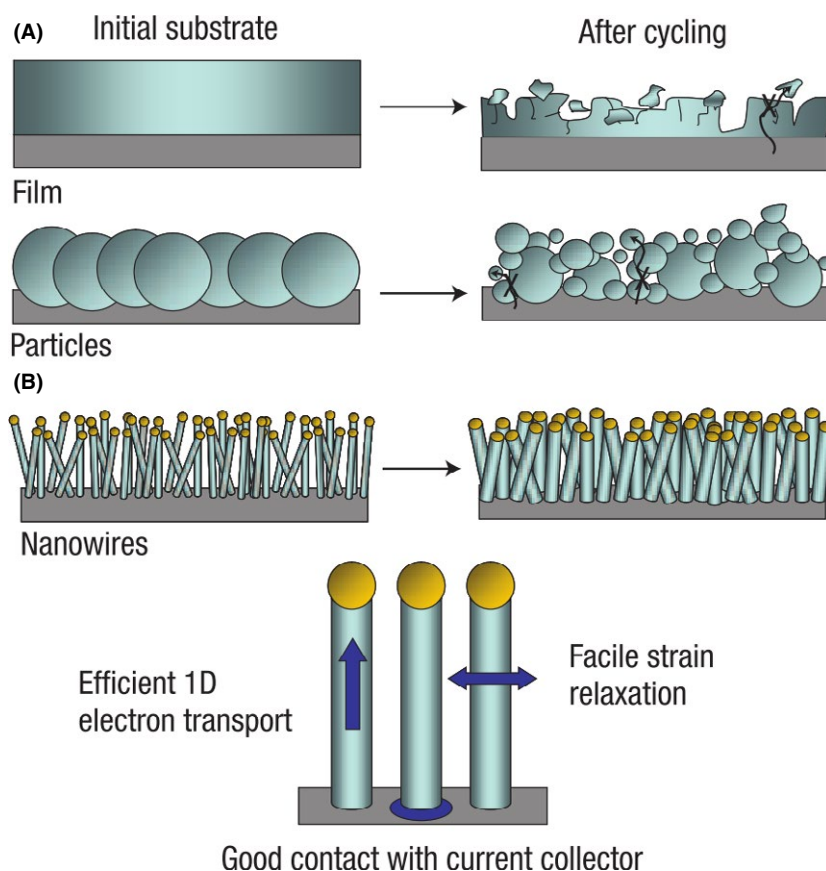


Figure 18. Schematic comparing the stability of (B) silicon nanowires with (A) thin film and particles upon repeated lithiation and delithiation. Reproduced with permission [15].

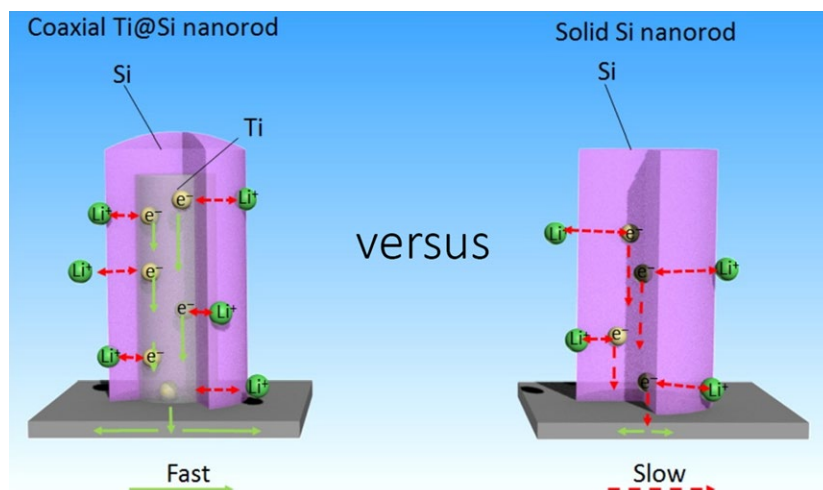


Figure 19. Illustration to compare (left) Ti@Si core-shell coaxial nanorod to that of (right) solid Si nanorod from the perspective of ion and electron transfer. Reproduced with permission [78].

provided that if the cost of production could be reduced significantly. Their application could be limited to devices that have no space restriction, for example, in smart energy grids, where high tap density is not the top priority. The production of nanostructured Si anodes must be scaled up to industrial level, which is also challenging. On the other hand, the volumetric density (mAh/cc) may be sacrificed in the adoption of silicon nanomaterials which have very low tap densities, typically in the order of 0.1 g/cc. Volumetric density (based on volume) has relatively less explored as compared to that of specific density (based on mass). Dahn and colleagues [79] has argued that although Si has the highest theoretical specific capacity (mAh/g), its energy density based on unit volume (Wh/cc) is just about the same as other materials (Fig. 20).

If one takes into consideration of low tap density of Si nanomaterials as compared to bulk Si, the future Si nanomaterials based Li-ion batteries will have even lower energy density. Therefore, a tradeoff between specific capacity and energy density should be considered, which is true for many other kinds of nanomaterials based electrodes. Similar to the problem faced in the preparation of silicon nanostructures, the fabrication of Si/C nanocomposites requires extensive studies as well. Mostly likely, the commercial Si-based electrode will be a composite containing a significantly high percentage of carbon and a small percentage of Si.

As one of the intensively studied anode candidates, SnO_2 -based anodes are promising to replace carbon anodes. In its first cycle of lithiation, SnO_2 is converted to Sn, and

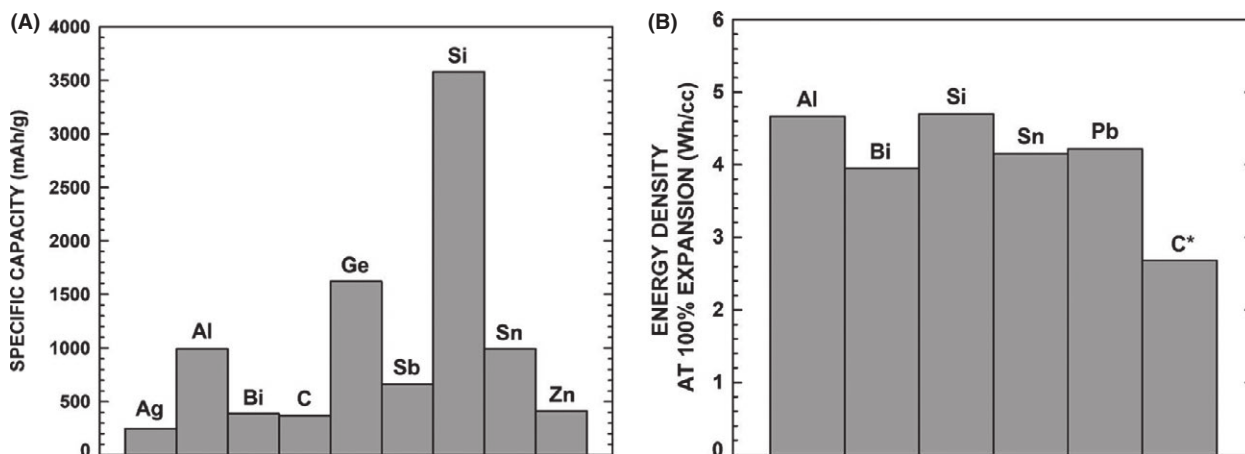


Figure 20. (A) Specific capacity (mAh/g) of a number of materials; (B) the volumetric energy density of the materials at a 100% volume expansion. Reproduced with permission [79].

subsequently, the Sn phase could store and release Li ions according to the Li-Sn alloying and dealloying reactions. SnO_2 has a theoretical capacity of 781 mAh/g, which is about two times higher than graphite. However, its poor cyclability is not acceptable from the perspective of cycling performance. Nanostructured SnO_2 has been proposed as a possible solution [25, 72, 80–84]. One dimensional (1-D) SnO_2 nanotubes could be prepared by template-assisted method using an anodic alumina oxide membranes with 1-D tunnels as the template [83]. In another study, polycrystalline hollow SnO_2 spheres could be prepared by deposited the precursor on hollow carbon nanospheres as the template and subsequent calcination in air at 800°C could remove the hollow carbon spheres and compacted the SnO_2 nanoparticles into hollow spheres. However, capacity fading was generally observed in SnO_2 -based anodes [81].

Another interesting SnO_2 -based anode material is electro-spray deposited thin films of particles with unique porous spherical multideck-cage morphology (Fig. 21). The reversible capacity was reported to be as high as 1158 mAh/g, which is even higher than theoretical value. The improved electrochemical performance was attributed to the unique structure and the presence of Li_2O and CuO phases in the composite film [85]. Interestingly, even higher capacity of 2050 mAh/g with excellent capacity retention (97% upon 60 cycles) has also been reported for Sn-Si/C anode materials [86]. Additional effort should put to reveal the unusually high capacity observed. Besides metallic Sn- or SnO_2 -based anodes, other Sn-based compounds, including tin phosphate [87, 88], SnO_2 filled mesoporous tin phosphate [87], teardrop-shaped SnP, [89] AlPO_4 -coated SnO_2 [90], and Zn_2SnO_4 [91] have been reported, achieving certain degree of success in terms electrochemical characteristics.

Iron oxides have been considered as promising carbon alternative anode materials for high-capacity Li-ion batteries. It has advantages of low cost, nontoxicity, and

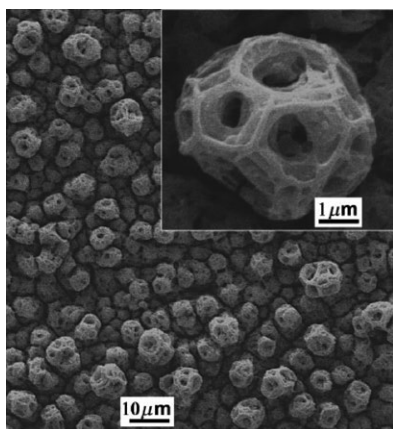


Figure 21. SEM images of the as-deposited film of nanostructured SnO_2 on copper current collector. Reproduced with permission [85].

environmental benignity. Iron is the fourth abundant element in the earth crust. It is abundant and has much lower cost than other 3d metal oxides, such as Co and Ni. However, similar to other metal oxides, iron oxides also suffer from poor conductivity and large volume change during the charge/discharge processes, which limits their practical use in commercial Li-ion batteries. Again, one popular strategy is to prepare iron oxide materials in nanoscale with tailored morphologies and synthesize iron oxide/carbon composites to accommodate the volume changes as well as improve conductivity. Various iron oxides with different nanostructures have been synthesized, including nanoparticles [92], nanowires [93–95], nanobelts [94, 96], nanorods [97–99], nanotubes [100, 101], nanoflakes [102], nanodisks [103] and nanorings [104], nanocubes [105–107], nanospheres [108–111], nanospindles [108, 112], nanourchins [113], and nanoflowers [103, 108, 114–119]. Hollow structured iron oxides are of great interest as the space could, ideally, accommodate the volume expansion during Li insertion [108, 115–119].

Popular routes to prepare iron metal oxides are template-assisted, hydrothermal, sol-gel and thermal oxidizing methods. Wen et al. [94] reported the preparation of vertically aligned iron oxide nanobelt and nanowire arrays by direct thermal oxidation of iron substrates under the flow of O_2 . Nanobelts were produced in the low-temperature region ($\sim 700^\circ\text{C}$) and cylindrical nanowires tens of nanometers thick were formed at relatively higher temperatures ($\sim 800^\circ\text{C}$). Both nanobelts and nanowires are mostly bicrystallites with a length of tens of micrometers which grow uniquely along the [110] direction [94]. In another study, nanoflakes of $\alpha\text{-Fe}_2\text{O}_3$ on Cu foil were achieved by thermal treatment method. The as-prepared $\alpha\text{-Fe}_2\text{O}_3$ nanoflakes exhibited a stable capacity of 680 mAh/g, with no noticeable capacity fading up to 80 cycles when cycled in the voltage range 0.005–3.0 V at a rate of 65 mA/g [102]. Xu et al. reported the preparation of spindle-like porous $\alpha\text{-Fe}_2\text{O}_3$ from an iron-based organic framework template, MIL-88-Fe. MIL-88-Fe was prepared by a modified solvothermal method using $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ and 1,4-benzenedicarboxylate (BDC) as starting materials. The as-prepared spindle-like porous $\alpha\text{-Fe}_2\text{O}_3$ exhibited very high charge capacity of 911 mAh/g after 50 cycles at current rate of 0.2C (1C = 1000 mA/g). Meanwhile, the capacity of commercially available bulk Fe_2O_3 ($< 5 \mu\text{m}$; Sigma-Aldrich, Missouri, USA) quickly faded to < 630 mAh/g. The spindle-like porous $\alpha\text{-Fe}_2\text{O}_3$ also show a superior rate performance as compared to bulk Fe_2O_3 (Fig. 22) [112].

Chen et al. [103] reported a top-down approach to fabricate uniform single-crystal $\alpha\text{-Fe}_2\text{O}_3$ nanodisks and melon-like $\alpha\text{-Fe}_2\text{O}_3$ microparticles through selective oxalic acid etching, using phosphate ions as capping agent to

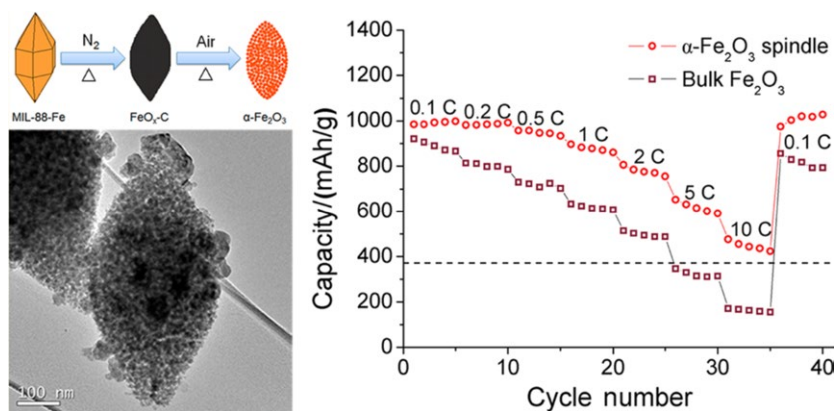


Figure 22. Schematic of the formation and TEM image of spindle-like porous $\alpha\text{-Fe}_2\text{O}_3$ and its electrochemical performances compared to bulk Fe_2O_3 . Reproduced with permission [112].

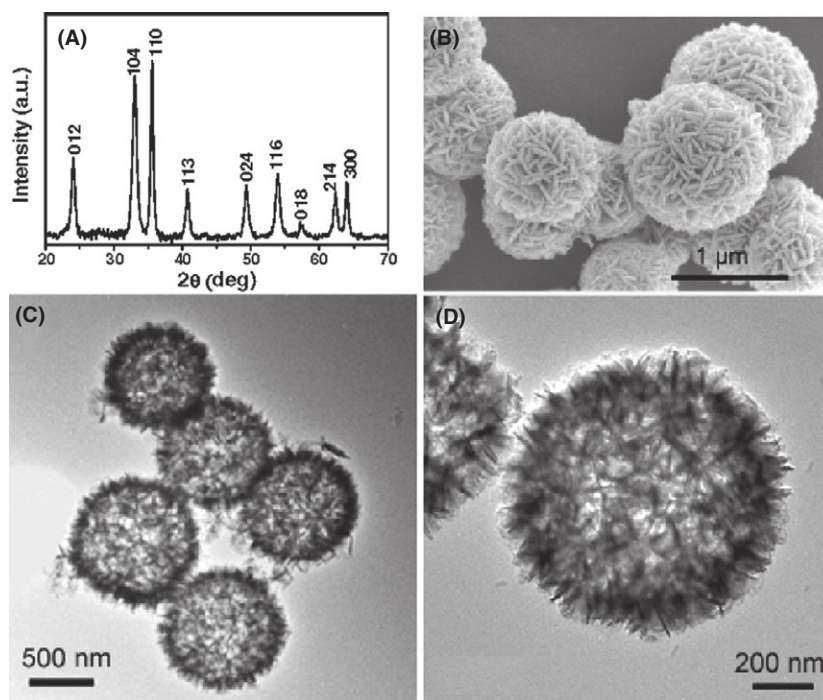


Figure 23. (A) XRD, (B) SEM, and (C, D) TEM images of Fe_2O_3 hollow spheres for Li-ion batteries. Reproduced with permission [111].

control the etching along [001] direction. The capacities of 662 and 341 mAh/g were retained after 100 cycles, for porous and solid melon-like $\alpha\text{-Fe}_2\text{O}_3$ microparticles, respectively. Wang et al. reported the preparation of hollow $\alpha\text{-Fe}_2\text{O}_3$ sphere with sheet-like subunits with quasiemulsion-templated methods (Fig. 23). The capacity of as-prepared hollow spheres around 1 μm faded very slowly from ~ 900 to 710 mAh/g after being charge/discharge from 2nd to 100th cycle, at testing rate of 200 mA/g. In contrast, the capacity of $\alpha\text{-Fe}_2\text{O}_3$ microparticles faded from ~ 900 to 340 mAh/g, which was less

than one half of the capacity retained of hollow spheres [111]. Other hollow $\alpha\text{-Fe}_2\text{O}_3$ has also been reported demonstrating advantages of hollow structures [120]. Beside spherical hollow materials, other structured Fe_2O_3 anode materials have been reported. For example, cocoon-like Fe_2O_3 mesoparticles of nanoparticle aggregates have also been reported [120]. Microscale single crystals of hematite with nearly 100% exposed {104} facets have been synthesized with a fast hydrothermal method [121].

Addition to nanostructures, carbon coating was used to improve the electrochemical performances of iron

oxides. It is generally believed that the carbon coating layer can enhance the conductivity of each single units as well as improve the better electrical contact between each single units. The carbon layer can also act as a buffer layer to alleviate the stress caused by huge volume expansion and prevent the structure from collapsing or improved cyclability. Additionally, given that nanomaterials are more active than bulk materials, the high contact area between electrode and electrolyte may lead to more

significant side reactions. The carbon-coated layer can act as a protective layer to prevent the direct contact between the active nanomaterials and the electrolyte. Wang et al. [122] reported a novel hierarchical nanostructure composed of carbon-coated α - Fe_2O_3 hollow nanohorns grafted on CNT backbones by bottom-up assembly of β - FeOOH nanospindles on CNTs and subsequent in-situ transformation and further modification with carbon nanocoating (Fig. 24). The specific capacity of carbon-coated CNT@

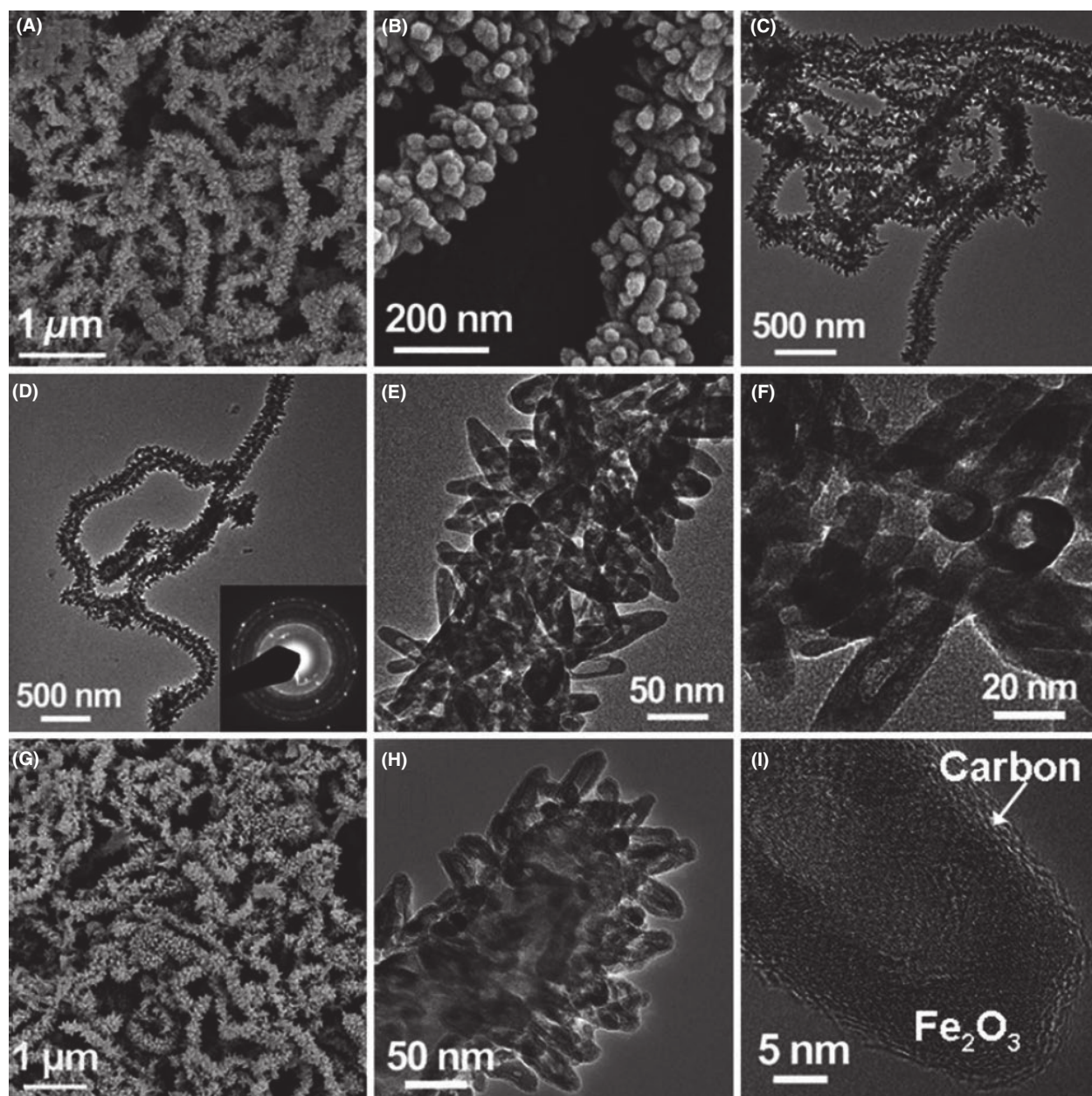


Figure 24. CNT@ Fe_2O_3 hierarchical structures characterized by (A and B) FESEM and (C and D) TEM at different magnification; (E and F) TEM images revealing the formation of hollow nanohorns on CNT; (G) FESEM image and (H) TEM image of carbon-coated CNT@ Fe_2O_3 hierarchical structures; (I) HRTEM image of uniform carbon coating on α - Fe_2O_3 hollow nanohorns. Reproduced with permission [122].

Fe_2O_3 hollow nanohorns gradually rose from 660 to 820 mAh/g from 2nd to 100th cycle at current density of 500 mA/g, while the capacity of uncoated CNT@ Fe_2O_3 slowly faded from 1200 to around 500 mAh/g, from 1st to 100th cycle. Both materials show superior performance compared to $\alpha\text{-Fe}_2\text{O}_3$ nanoparticles, which had a capacity of 300 mAh/g after 100 cycles. The results evidenced that properly tailored structure with designed coating could further improve their electrochemical performances.

Another family of iron oxide, magnetite Fe_3O_4 , which has a theoretical capacity of 927 mAh/g, has been attracting much attention due to its low cost, abundance, environmental friendliness, and especially the high electrical conductivity at room temperature of about 2.5×10^2 S/cm [123]. High electrical conductivity is rarely observed in other metal oxides explored for application in LIBs (e.g., $\alpha\text{-Fe}_2\text{O}_3$ has an electrical conductivity of $\sim 10^{-4}$ S/cm which is six order of magnitude or $\times 10^{-6}$ lower than electrical conductivity of magnetite). High conductivity is highly desirable for electrodes in LIBs to facilitate charge transfer [124, 125]. Carbon-coated magnetite nanospindles prepared by in situ partial reduction in hematite nanospindles with carbon shells was reported [126]. The specific capacity of Fe_3O_4 spindle/carbon composites remained 530 mAh/g after 80 cycles, while the specific capacities of bare $\alpha\text{-Fe}_2\text{O}_3$ spindles and the commercial Fe_3O_4 particles faded to 105 and around 152 mAh/g, respectively. In another study, Yang et al. reported a facile, scalable emulsion polymerization technique for synthesizing Fe_3O_4

nanoparticles around 20 nm embedded in a porous carbon matrix [127]. The as-prepared materials had specific capacities around 600 and 450 mAh/g with little fading after being discharged/charged at current rates of 1C and 0.2C, respectively. In another interesting study, Wang et al. [128] successfully synthesized $\text{Fe}_3\text{O}_4@\text{C}$ core-shell nanorings by a synchronous reduction and carbon deposition process from the reduction in the Fe_2O_3 nanoring precursor with the assistance of acetylene (Fig. 25). The specific capacity of $\text{Fe}_3\text{O}_4@\text{C}$ core-shell nanorings was about 900 mAh/g after 160 cycles at charge rate of 200 mA/g. It was proposed that the shorter pathways for diffusion, nanospace in the structures and conductive carbon shells all contributed to the superior electrochemical performances.

Carbon-decorated Fe_3O_4 also demonstrated interesting electrochemical performance, even in the absence of carbon black additives, PVDF binders [129]. It is particularly interesting to highlight that a new procedure in making electrode using centrifugation-assisted deposition (CAD) was demonstrated, where the active materials of $\text{Fe}_3\text{O}_4/\text{C}$ were directly fabricated on Cu disk which can be used as an electrode without any further process. In contrast, traditional electrode preparation involves multiple steps of slurry preparation, coating, drying in a vacuum oven and additives (e.g., PVDF binder, carbon black conductivity enhancer and NMP solvent) are used. The as-prepared additive-free porous $\text{Fe}_3\text{O}_4/\text{C}$ -based electrode exhibited superior electrochemical performance. Excellent cycling

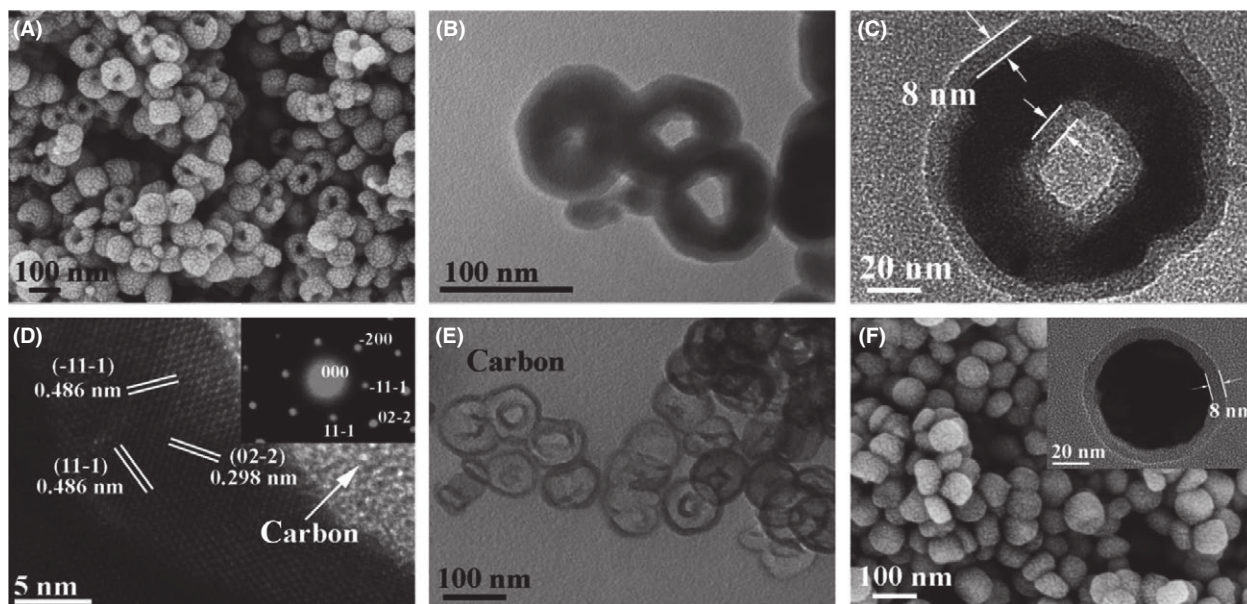


Figure 25. Characterization of $\text{Fe}_3\text{O}_4@\text{C}$ core-shell nanorings: (A and B) SEM and TEM images, (C) high magnification TEM image and (D) HRTEM image and (inset) SAED patterns; (E) TEM image of the carbon shell; (F) SEM and (inset) TEM images of erythrocyte-like $\text{Fe}_3\text{O}_4@\text{C}$ nanoparticle. Reproduced with permission [128].

performance was achieved with a specific capacity at ~ 800 mAh/g for more than 200 cycles. Impressive rate performance was accomplished when tested under different currents: a specific capacity of 730 mAh/g could be maintained at current of 1500 mA/g (Fig. 26). It is interesting to highlight that new techniques or procedures in the preparation of electrodes and their effects on materials performance are relatively less studied as compared to the large number of publications on materials designs. Future studies should try to define the optimized electrode preparation procedure for individual electrode materials.

Electrolyte

Electrolyte must be carefully chosen to withstand the redox environment at both cathode and anode sides and the voltage range involved without decomposition or

degradation. Additionally, electrolyte should be inert and stable in an acceptable temperature range. In commercial Li-ion batteries, typically a liquid electrolyte is a solution of lithium salts in organic solvents. However, the existing organic liquid electrolyte can potentially catch fires under conditions of thermal runaway or short circuit due to volatile and flammable nature of the solvents which are highly toxic. Ideally, the electrolyte should also be environmentally benign and can be produced at low cost in the future. Polar aprotic organic solvents, such as carbonate solvents with high dielectric constant, are selected to solvate lithium salts at a high concentration (1 M typically). On the other hand, solvents with low viscosity and low melting point are required to meet the requirement for high ionic mobility in the operating temperature range. Various organic solvents have been explored, including dimethyl carbonate, diethyl carbonate, ethyl methyl carbonate, propylene carbonate, ethylene carbonate, diethoxyethane,

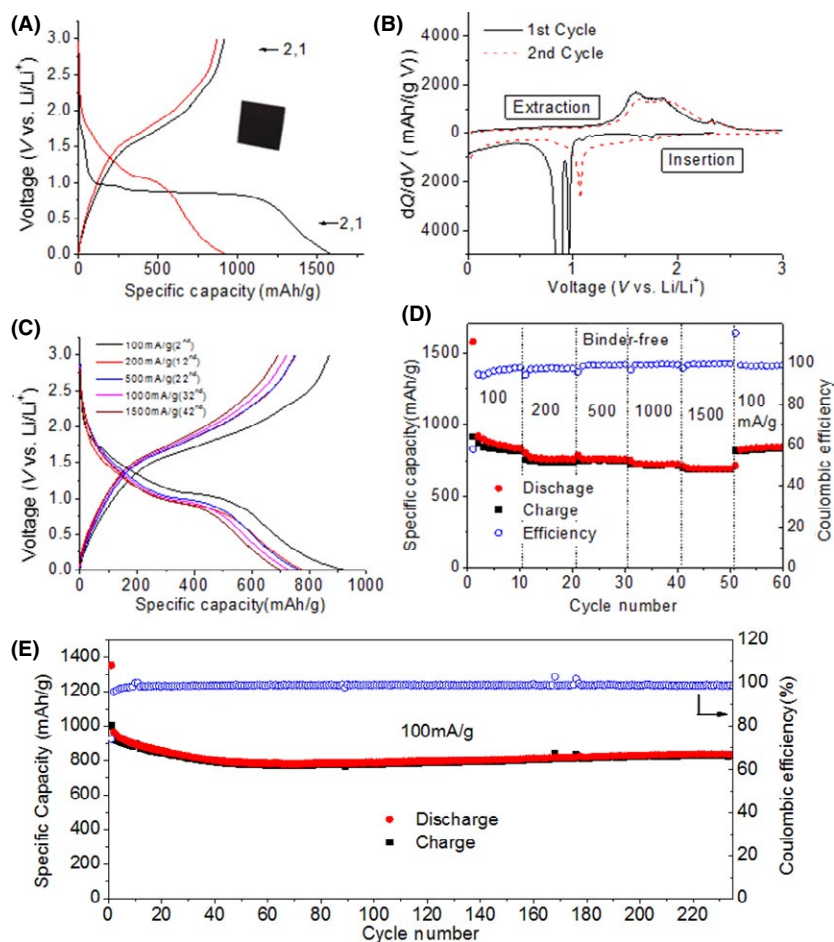


Figure 26. Electrochemical measurement of additive-free carbon decorated Fe_3O_4 fabricated directly on a copper current collector by centrifugation assisted electrode preparation: (A) first two cycle charge–discharge profiles; the inset of (A) shows the optical image of black additive-free Fe_3O_4 on a copper disk as a ready electrode; (B) differential capacity profiles for first two cycles; (C) charge–discharge voltage profiles and (D) rate performances and Coulombic efficiency at different currents from 100 to 1500 mA/g; (E) cycling performance at rate of 100 mA/g. Reproduced with permission [129].

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

The solvents are typically formulated and mixed to address the requirements on viscosity, conductivity and stability and to match with the lithium salts selected. For example, high dielectric solvents with high viscosity are typically mixed and balanced with solvents with low viscosity to achieve a liquid state electrolyte within a required temperature window. The commonly used electrolyte is 1M LiPF_6 in a 50:50 w/w mixture of ethylene carbonate (EC, melting point of 34°C and boiling point of 260.7°C) and diethyl carbonate (DEC, melting point of $2-4^\circ\text{C}$ and boiling point of 90°C) or dimethyl carbonate (DMC, melting point of 2°C and boiling point of 90°C) (Fig. 27). Generally, the EC can bind Li^+ ions more strongly than DEC or DMC [130]. The formulated electrolyte offer reasonably good stability over a wide potential range. Additives to further enhance the electrolyte stability and improve the formation of good solid-electrolyte interphase (SEI) are also added in many cases. The various formulated additives in terms of chemical compositions and percentages used by different companies in making Li-ion

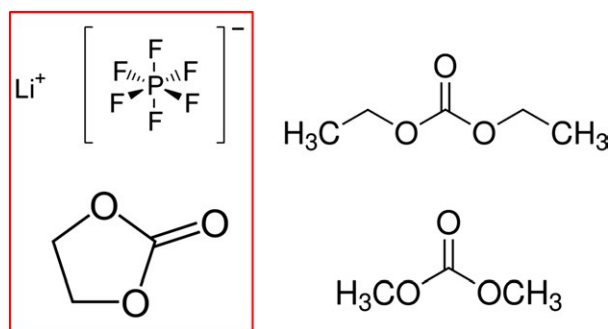


Figure 27. Chemical structures of common components in commercial electrolyte: LiPF_6 as the lithium salt and ethylene carbonate as the solvent are present in almost all commercial electrolyte; whereas diethyl carbonate or dimethyl carbonate are also present to reduce viscosity to promote ion transfer.

batteries could be considered business secrets. Generally, SEI formed in the first cycle is essential to isolate the electrode and electrolyte to avoid further electrolyte decomposition upon cycling. It is generally believed that the SEI is electrically insulating but ionically conductive. Although the chemical composition of SEI is relatively well characterized, the formation mechanism of SEI is still poorly understood and various SEI formation models have been proposed. SEI formation is a hot topic in battery community and the knowledge obtain could help to design better Li-ion batteries with improve abuse tolerance capability. A very informative review by Xu is an excellent source of information regarding liquid electrolyte in Li-ion batteries [131].

Other types of electrolyte have also been developed and proposed for Li-ion batteries, such as polymer, gel and ceramic electrolyte. Polymer electrolytes are solvent-free using high molecular weight-based polymers with dissolved lithium salts [132]. One should be aware that polymer electrolyte is not considered polyelectrolyte. The obvious advantages of polymer electrolyte over liquid electrolyte are (1) improved safety properties due to low volatility, (2) design flexibility, and (3) potential to eliminate separators. Arguably, polymer electrolyte could be more conveniently processed as compared to that of liquid electrolyte. Simplified processes could reduce the cost significantly. Similar to other electrolyte, polymer electrolyte must be stable under the operating conditions of Li-ion batteries from electrochemical, thermal and mechanical perspectives. One of the widely studied polymer is poly(ethylene oxide) which has been coupled with various lithium salts, such as LiCF_3SO_3 and LiClO_4 . The ion conduction in poly(ethylene oxide) mainly occurs at amorphous phases. The ions can be transported by the semirandom motion of short polymer segments. In order to maintain a good mechanical stability, ionic conductivity will be sacrificed. The conductivity is typically about 10^{-8} S/cm, which is significantly less than that of liquid electrolyte. Li-ion batteries based on polymer electrolyte are design flexible and can be fabricated as cylindrical, coin, prismatic, flat cells and other configurations. There are good reviews on polymer electrolyte in literature [133, 134].

Another type of electrolyte is based gels in which both lithium salts and polar solvents are dissolved and added into inactive networks of high-molecular-weight polymers. LiPF_6 and carbonate solvents are typically used similar to those in liquid electrolyte discussed above. The liquid phases are fully absorbed within the polymers which can avoid the leakage issue in contrast to that of pristine liquid electrolyte. Meanwhile, the ionic conductivity of gel electrolyte could be dramatically increased as compared to that of polymer electrolyte. There are a number of polymers explored as the hosts, including polyacrylonitrile,

polyvinyl chloride, polyvinylidene fluoride and Poly(methyl methacrylate). In the preparation of gel electrolyte, one can simply increase the viscosity of liquid electrolyte by adding soluble polymers. Alternatively, one can soak the microporous polymer matrix into the electrolyte.

Recently, ceramic electrolyte is also re-attracting much attention. Ceramic electrolyte has long been explored for fuel cells, and their application in Li-ion batteries is attracting increasing interest. The obvious advantage to use ceramic electrolyte is safety, for example, no more flammable organic solvents needed. Those batteries with ceramic electrolyte can find applications in high-temperature environment, including handheld orthopedic tools and other batteries powered medical devices that need to be sterilized in autoclaves under high temperature and high pressure conditions. The batteries autoclaved should be able to withstand for at least 130°C and are impermeable up to 30 psi in heated water, and importantly, deterioration in performance should be minimum after sterilization. Another interesting advantage to use ceramic electrolyte for high-temperature applications is that the ionic conductivity of ceramic electrolyte increases with increasing temperature. This is because the creation and movement of ionic point defects, which determines the ionic conductivity, requires energy. One area of intensive research is to achieve ceramic electrolyte with reasonably high conductivity at room temperature. Various sulfides, oxides and phosphates have been explored. The author would anticipate that ceramic electrolyte will eventually be used in next-generation Li-ion batteries in electric vehicles, mainly for its excellent safety performance which can enhance the customer confidence and acceptance. Fergus provided a good review on various ceramic electrolyte explored for Li-ion batteries [135].

Separators

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

microporous polyolefin materials based polymer membranes are dominantly used in commercial Li-ion batteries with liquid electrolyte.

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

For the development of future Li-ion batteries for high-temperature applications, inorganic membranes as separators are highly attractive. The all-solid Li-ion batteries should also be further investigated to meet those niche markets of high-temperature applications. Another parameter that determines the commercial success of a separator is cost. The cost of the existing polymer separator in a Li-ion battery could be as high as one-fifth of the total cost of the battery. Therefore, intensified research on the development of highly improved separators at reasonably low price for Li-ion batteries is required. Zhang wrote a good review article on the separators of liquid electrolyte Li-ion batteries [136].

Challenges in Li-Ion Batteries

Li-ion batteries have been commercialized for about two decades. The technology is considered relatively mature based on the current battery chemistry. Li-ion batteries have been dominantly used in mobile electronic devices, including cell phones and laptop computers, and are starting to play increasing role in electric vehicles. Li-ion batteries will also be considered in sustainable energy grids to store sustainable energy generated from renewable sources. The increasing demand for energy storage requires further improvements in the existing Li-ion batteries and

the development of next-generation Li-ion batteries, in particular, to reduce the cost of Li-ion batteries. It is still colossally challenging to develop new battery chemistry to replace the existing Li-ion battery technology.

In order to increase energy density Li-ion batteries, it is desirable to find electrode couples with both high-specific capacities and high operating cell voltage. As discussed previous, there are a large number of anode candidates that could dramatically increase the specific capacities, in particular, with highly attractive Si- and Sn-based anodes. It is still challenging to prepare Si nanomaterials on a large scale with low cost. Sn-based anodes suffer from the issue of poor cycling performance due to pulverization. Therefore, one of the possible future anodes could be Si-Sn-based composites [137]. In contrast to that of anode candidates, the cell capacity is mainly limited by the low capacity of cathode candidates. The existing cathode material of LiCoO_2 is expensive and highly toxic. The increasingly popular LiFePO_4 has a low capacity. The facilely prepared Ni-Co-Mn-based cathodes developed by Argonne National Laboratory are highly attractive, especially from industrial prospective. However, the specific capacity is still considered moderate, and both Co and Ni are expensive and toxic. Future cathode materials should try to avoid the use of either Co or Ni, or other toxic elements, from environmental perspectives. Additionally, the ideal cathode should be able to reversibly insert/extract multiple electrons per 3d metal. The future low-cost cathode materials could be Mn- and/or Fe-based. The issue of intrinsically low conductivity should be creatively addressed, most likely by nanotechnology and nanocomposites. There is relatively no much room to increase the operating cell voltages with the current known cathode candidates under exploration. Composite cathodes with two or three 3d metals and polyanions are highly promising. New cathode chemistry may be developed in the next 10 years. The new cathode chemistry may require for new electrolytes as well.

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

about those electrode materials in terms of stability and interaction with electrolyte. Instead of intensively pursuing of high-energy density, there should be increasing emphasis on battery safety as well. Standardized battery safety testing procedures should be widely employed.

It is still challenging to develop electrode materials with low carbon footprint, or the so-called “green batteries”. Ideally, future Li-ion batteries should use biologically derived organic or inorganic electrodes, using aqueous electrolyte. Carbon and silicon can be derived from biomasses. The recent attempts to explore virus-assisted synthesis of electrode materials for Li-ion batteries attracted much enthusiasm [138]. It will be interesting to explore large-scale synthesis at room temperature using biological templates, including genetically modified virus. Organic electrodes that will not be easily dissolved by electrolyte can be further developed for sustainable Li-ion batteries [139]. Therefore, one area of future research could be focusing on “sustainable” and “green” Li-ion batteries.

Additionally, future batteries research should keep in mind the life cycle assessment (LCA) of the technologies to evaluate whether the batteries are truly green or not. The existing materials involved in commercial Li-ion batteries (typically, LiCoO_2 , LiMn_2O_4 , LiNiO_2 , LiFePO_4 as cathodes; Graphite, $\text{Li}_4\text{Ti}_5\text{O}_{12}$ as anodes; Ethylene carbonate, diethyl carbonate, LiPF_6 , LiBF_4 , LiClO_4 as electrolytes/salts; Polypropylene, polyethylene as separator) still require further studies from the perspectives of LCA. Little is known about the environmental impacts of the production, use and disposal of next-generation Li-ion batteries [140]. Mass production of Li-ion batteries for electric vehicles will result in large volumes of contaminated waste and places. It could reduce agricultural productivity near mine sites, decrease air quality near processing facilities, and increase energy cost near factories. Furthermore, additional fossil fuel use may be required to meet factory demand in production of Li-ion batteries. LCA may provide the full scenarios of their environmental aspects and potential environmental impacts of throughout their life cycle from raw minerals acquisition through production, use, end-of-life treatment, recycling, and final disposal. Therefore, LCA is an important tool for the development of truly “green” Li-ion batteries in the future, which can contribute to future sustainability. Another important area that should attract deserved attention is techno-economic analysis (TEA) of Li-ion batteries. TEA will help to determine whether a new Li-ion battery system developed is technically and economically feasible for large-scale production. The combination of LCA and TEA studies will help to develop next-generation Li-ion batteries achieving optimized social, environmental and economic impacts.

There are increasing worldwide interests in preparation of “nano” materials to increase the storage capacity for next-generation Li-ion batteries. The development of nanomaterials could offer tremendous opportunities, as it is known that electrochemical properties of nanomaterials are size and shape dependent. “Nano” has been attracting much attention in the battery community in the past two decades. However, the challenging issue rarely mentioned is that the energy density (by volume) of “nano” materials is very low due to the low volumetric density of nanomaterials. This critical issue of low tap density is most vividly illustrated by the following example: the tap density of intensely pursued graphene is 0.03 g/cc, as compared to that of MCMB graphite power at 1.3 g/cc, or about 40 time difference by volume for a given weight. Other issues associated with electrode materials at nanoscale are poor electrical properties of the electrode due to interparticle resistance and low Coulombic efficiency attributed to large surface area induced side reactions between the electrode and electrolyte. The author would like to suggest the use of microstructures of nanoparticles as the building units, instead of random “nano” particles, to simultaneously overcome the issues discussed above, in particular, achieving electrode materials with high packing density, while preserving certain beneficial features of nanomaterials. We have been working on the preparation of micromaterials of nanoparticle aggregates to increase volumetric density for a while [27, 91, 120, 121, 129, 141]. For example, the microscale cubes of Zn_2SnO_4 & Sn@C of nanoparticle aggregates have a tap density of 0.98 g/cc which is nearly eight times higher than that of commercial P25 TiO_2 nanoparticles [91]. Additionally, it seems that the electrochemical performances of micromaterials are comparable to that of nanomaterials. In many cases, the devices powered by Li-ion batteries have restricted space to hold the batteries, such as in cell phone and electric vehicles. In other words, electrode materials with high tap density are required in the future. Therefore, the author would dare to anticipate that further Li-ion batteries will be based on micromaterials with features of nanomaterials, from the perspective of volumetric density. Future battery research should enable the preparation of next-generation batteries with smaller size but better performances as compared to the existing ones (Fig. 28).

In addition to specific technical challenges discussed above, the other less disclosed challenge is the limitation of lithium reserves to meet future 100 million 40 kWh Li-based batteries for electric vehicles annually. The limited or inaccessible lithium resources could make it very challenging to reduce the cost of Li-ion batteries in the future. Of course, Li-ion batteries should be recycled as much as we can. We still have to intensify the research on

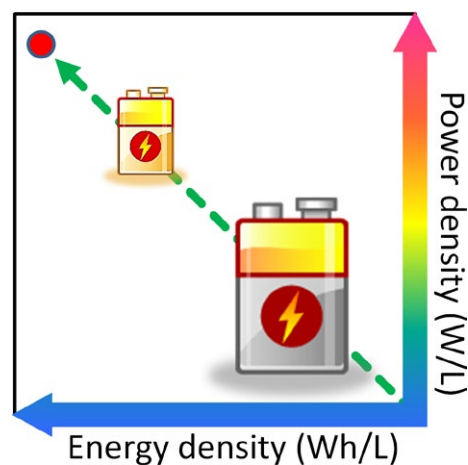


Figure 28. The illustration to demonstrate that future Li-ion batteries should be light and small without any compromise on energy and power.

alternative Li-ion batteries or beyond Li-ion batteries, including Na-ion, Mg-ion, Ca-ion, Al-ion, and F-ion batteries. Learning from the experience on the development of Li-ion batteries, with access to increasingly powerful computational tools, future development of batteries beyond Li-ion batteries must leverage the simulation and modeling power of modern computers to guide and accelerate electrode discovery and synthesis. Therefore, the time required for the development of those advanced batteries beyond Li-ion batteries will be significantly shorter than that used in the development of Li-ion batteries.

Beyond Li-Ion Batteries

In line with the aim to develop batteries with even higher energy, Li-air (Li-O_2) and Li-sulfur (Li-S), achieving impressively high-energy density theoretically, have again attracted much attention recently. Although Zn-air and high-temperature Na-sulfur have been commercialized for a while, the development of rechargeable Li-O_2 and Li-S batteries still have technical barriers. On the anode side, the critical understanding of and control over Li-electrolyte interface must be thoroughly studied. In fact, Exxon had tried to commercialize the Li metal-based batteries more than 40 years ago without a success, which was partially attributed to the poor Li-electrolyte interface and dendrites. Then Li-ion batteries were developed later to avoid the Li-electrolyte interface by completely taking out the lithium metal. We have to revisit the issue of Li-electrolyte interface in the development of Li-O_2 or -S batteries now. On the cathode side, the designing oxygen electrodes, which has been “a nightmare for fuel cells” [142], for Li-air batteries is colossally difficult. The good news is that the knowledge accumulated over the past few decades

on electrodes for fuel cells can be used as a good source of references for development of Li-O₂ batteries. Another notable issue is the high overpotential and low electrical efficiency observed, which make Li-O₂ or -S less attractive from the perspective of energy efficiency and sustainability. Currently, many efforts are focused on the development of efficient catalysts for the cathodes, but mainly based on trial and error. Computer assisted modeling and simulation must be employed to predict and design the catalysts with exposed highly active facets, similar to those have been done in the field of fuel cells, for those catalysts-based cathodes. However, the solid phases formed in the Li-O₂/-S batteries are different from that of fuel cells at either gas or liquid phases. In other words, the challenges faced in the development of Li-O₂ batteries are even more difficult to overcome than that in fuel cells. Another issue is associated with the volatile electrolyte, which can be evaporated into gas phases leading to death of the battery. For Li-S batteries, the formation of soluble polysulfide (LiS_x) species is another critical problem, in addition to its poor conductivity. Confining sulfur into voids of mesoporous nanostructures is a popular strategy to overcome the solubility of LiS_x. It is believed that rechargeable Li-O₂ or Li-S batteries will eventually be commercialized in the future, which will require intensified studies. The good news is that increasing number of research groups and battery companies are starting to investigate Li-O₂ or Li-S batteries, which should help to accelerate their development. However, due to the problems with Li-O₂ or Li-S batteries, Li-ion batteries will not be replaced by them in the next decade.

Sodium-ion batteries (SIBs) are outstanding candidates that could potentially replace Li-ion batteries. With respect to large-scale stationary energy storage systems for energy grids in sustainable energy networks of wind and solar energy, low-cost SIBs are expected to be produced at lower cost than that of Li-ion batteries in the future [143–146]. Mass produced SIBs with comparable performances with those existing rechargeable batteries can significantly impact our environment and society [147]. Additionally, due to the lower standard half-reaction potential of sodium (2.714 V for Na/Na⁺) as compared to that of lithium (3.045 V for Li/Li⁺), electrolyte degradation will be reduced and safe electrolyte with low decomposition potential can be used in SIBs to enhance safety [148]. In other words, not only low cost, SIBs will be good candidates as safe rechargeable batteries. The performances of the highly attractive reemerging SIBs will be strongly dependent on electrode materials developed [149–152]. A number of positive electrode materials have been explored [147]. For example, cathode materials: carbon-coated NaVPO₄F could deliver a reversible capacity of 98 mAh/g; [153] Na_{0.44}MnO₂ particles delivered

65 mAh/g; [154] Na_xCo[Fv(CN)₆]_{0.90}·2.9H₂O delivered 135 mAh/g; [155] layered Na_{0.71}CoO₂ delivered 80 mAh/g; [156] KFe_(II)Fe_(III)(CN)₆ delivered 100 mAh/g; [157] and Na₂FePO₄F exhibited high voltage of 3.5 V [144]. In terms of anode materials, the widely used graphite in Li-ion batteries, however, cannot reversibly store significant amount of Na, typically <5 mAh/g due to lack of Na intercalation [147, 151, 158, 159]. On the other hand, disordered nongraphitic carbons can reversibly store more Na as compared to graphite [147, 151]. Carbon nanowires prepared by pyrolyzation of polyaniline demonstrated impressive performance in Na storage [160]. Nanocellular carbon foams delivered 152 mAh/g [161]. Furthermore, metals, metal oxides, and phosphorus have been investigated as anode as well [162–171]. Interestingly, for both Na- and Li-active materials of Sn@C nanospheres, it would be broken in SIBs but well preserved in Li-ion batteries tests [172]. Therefore, in the selection of materials for SIBs, the knowledge learned from Li-ion batteries may not always be applicable.

There are many other promising battery technologies under development. The new battery technologies may not be necessary to directly compete with Li-ion batteries in market share due to their unique characteristics in terms of performance, cost and size. Redox flow batteries using solutions of redox complexes or ions, or so-called catholyte and anolyte, are good options for stationary applications, such as in energy grids based on sustainable sources. Mg-ion batteries have the advantages of no dendrite formation and therefore enhanced safety, and high-energy density comparable to Li-ion batteries but at significantly lower cost. Therefore, Mg-ion batteries are highly attractive for electric vehicles. Toyota is leading the industrial efforts to commercialize Mg-ion batteries which are expected to power electric vehicles by 2020. Al-ion batteries, with three-electron transfer, could achieve three times higher energy density than that of Li-ion batteries. However, the use of expensive ionic liquids will limit Al-ion batteries to mainly special applications. Rechargeable Zn-air batteries may be more promising as compared to Li-air batteries. Primary Zn-air batteries were invented more than 100 years ago. The recent efforts are mainly focusing on the development of rechargeable Zn-air batteries. Rechargeable Zn-air batteries can find applications in electric vehicles.

Summary

In summary, Li-ion batteries have affected almost everyone in the world. The success of commercial Li-ion batteries was a result of intensive research and contribution by many great scientists over few decades. Recently, much effort was put into further improvement on the

performances of Li-ion batteries, achieving certain level of success. There are still notable issues. Intensified research is required to achieve next-generation Li-ion batteries. Private companies are investing significantly into the research and development of Li-ion batteries which could lead to incrementally advanced products achieving significant direct impacts to our society. Academic sections could make contributions by generating out-of-the-box ideas and concepts, especially those beyond Li-ion batteries that could be commercialized in the next few decades. Battery safety and sustainable batteries should receive their deserved emphasis and attention in the future. New battery concepts have to be further developed to go beyond Li-ion batteries in the future. LCA and TEA are good tools for evaluation next-generation Li-ion batteries and beyond Li-ion batteries.

Acknowledgment

The author appreciates Professor Simon Ng for comments on the manuscript and Wayne State University for support.

Conflict of Interest

None declared.

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