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Chapter 19: Li-ion batteries and beyond/future design challenges

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1 Introduction

Selecting electrode materials is very important for battery design, because the theoretical cell voltage is determined by the standard redox potentials of the active materials, and the specific capacity of a cell (ampere-hour capacity per gram of electrode material, Ah g⁻¹) strongly depends on the atomic weight (or molecular weight) of the active material and the number of electrons involved in the electrochemical redox reaction. Including lithium (Li), the light metals have been widely using as electrode materials for batteries due to their highly negative redox potential, their low equivalent weight, large specific capacity, and great abundance, as shown in Table 19.1.

Element	Atomic weight	Standard potential, (25 °C, V)	Valence change	Melting point (°C)	Density (g cm ⁻³)	Capacity	
						Ah g ⁻¹	Ah cm ⁻³
Li	6.94	□ 3.01	1	180.5	0.54	3.86	2.04
Na	22.99	□ 2.71	1	97.8	0.97	1.16	1.13
Mg	24.31	□ 2.38	2	648.7	1.74	2.20	3.83
Al	26.98	□ 1.66	3	660.3	2.69	2.98	8.02
K	39.10	□ 2.92	1	63.3	0.86	0.69	0.59
Ca	40.08	□ 2.84	2	839.0	1.54	1.34	2.06

Table 19.1 Characteristics of light metals

Many kinds of light metals have been employed in primary cells such as Li (or Mg, Ca)/MnO₂, Li/SO₂, Li/LiI/I₂ and the water-activated Mg battery. Those are widely used for various electrical devices, toys, portable lighting, military equipment and memory backup.^[1]

Despite the fact that primary batteries are still widely used, the battery industry has been focusing mainly on secondary (rechargeable) batteries, because the scale of the emerging market for advanced applications demanding rechargeable batteries such as electric vehicles (EVs), high performance portable electronics and large scale electrical energy storage systems has been getting much larger. Since the idea for the Li ion battery was proposed by M. S. Whittingham in the 1970s,^[2] Sony released the first commercial Li ion battery in 1991^[3] and the Li ion battery has become one of the most viable candidates for advanced rechargeable battery applications due to its high specific power, high energy density and ambient temperature operation. Not only has the Li ion cell been employed for small portable electronic devices, but it has also been considered for large systems, especially for EVs. However, because the performance of current Li ion cells is not high enough to satisfy the emerging market demands, intensive effort is necessary to develop the next generation of cells with even higher specific energy, and low cost.

In this chapter, the limitations of current Li-ion cells and various advanced materials for each component of the cell are discussed. Other candidate materials for the next generation of rechargeable cells using light metals as electrode materials such as magnesium, and sodium, are also discussed.

2 Li ion batteries

2.1 Introduction

Li ion batteries are primarily being used for small portable devices such as laptop computers, cellular phones, tablets and cameras because those cells are light and compact with a high operating voltage of ~ 4 V and a high specific energy of 100-200 Wh kg⁻¹.

Conventional Li ion cells contain a graphite anode, a layered transition metal oxide cathode and non-aqueous Li-ion-containing organic electrolyte. Because of the reversible Li ion intercalation reaction at both anode and cathode in an appropriate electrolyte, a long cycle life of the cell with stable power can be achieved.

Despite the merits of conventional Li ion batteries, they are facing tough challenges to satisfy the market demands such as low cost, much improved safety, larger energy density, faster charge/discharge rates and longer service life. H. J. Sohn et. al.^[4] suggested three types of next generation Li ion batteries based on different needs: high specific energy Li rechargeable cells, high specific power Li rechargeable cells and Li rechargeable thin film and flexible cells. To meet these requirements, replacing battery materials is preferentially considered because the characteristics of cells definitely depend on the materials employed in the cells. For example, the energy density is mainly determined by the theoretical specific capacity and operating voltage of the active materials, which are directly related to the reaction chemistry of the active materials.

$$\text{Specific Energy (Wh kg}^{-1}\text{)} = \text{operating voltage (V)} \times \text{specific capacity (Ah kg}^{-1}\text{)}$$

Therefore, developing larger specific capacity electrodes, higher operating voltage cathodes and appropriate electrolytes are required for high specific energy battery applications.

In the case of a high specific power cell, how rapidly large quantities of energy can be stored and released are very important, because the cell specific power is given by

$$\text{Specific Power (W kg}^{-1}\text{)} = \text{Operating voltage (V)} \times \text{Current generated by the cell (A)} / \text{mass of the cell (kg)}$$

Since $I=V/R$ from Ohm's law, power can be expressed as $P = V^2/R$ which indicates that maximizing the operating voltage and minimizing the internal resistance are key points. Therefore, materials that can accept and release lithium ions very quickly are mainly considered for high specific power battery applications.

Thin film and flexible cells are required for emerging applications such as flexible (or rollable) displays, wearable electronic devices and microelectronics that require special shapes of power sources. Because the morphology of those devices can be changed while they are in use, this type of battery must be able to supply stable electrical power even if it is bent or stretched. For this type of application, unique cell designs such as the cable-type battery^[5] and the all-solid-state battery with solid electrolyte are required.

2.2 Anode materials

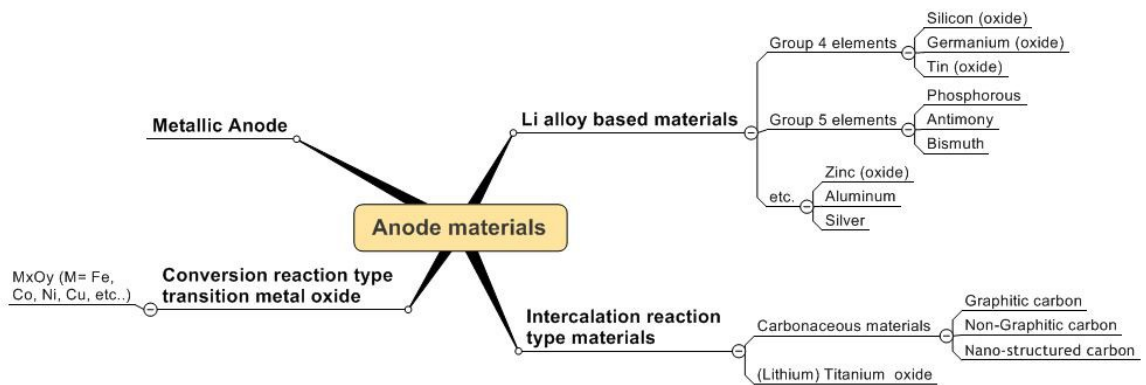


Figure 19.1 Candidates for lithium-ion cell anode materials.

To select anode materials, a low operating voltage, a large specific capacity, low cost and safety should be considered. Figure 19.1 shows candidate anode materials for Li ion

cells. Each material has its own advantages, however, three types of materials are considered to be promising candidates to replace the graphite anode: Li metal, intercalation type materials and Li alloy based materials.

2.2.1 Lithium metal anode

The graphite anode was employed in Li ion cells because the Li metal anode has proven to be much less safe. During cycling, dendritic growth of Li on the Li metal electrode surface occurs, which can cause internal shorts, resulting in degradation of the self-discharge rate and thermal stability.^[6] Commercialized Li/TiS₂ and Li/MoS₂ cells in 1980s could not be used widely due to this safety issue, despite of their relatively high specific energy and relatively long cycle life.^[7]

However, the large theoretical specific capacity and low operating voltage of lithium metal are still very attractive, so many attempts have been made to overcome the safety issue. A review article written by H. J. Sohn et. al.^[8] discussed the key factors for the Li metal anode and introduced various kinds of approaches for protecting the Li metal. The morphology of the electrodeposited lithium must be controlled. The morphology is affected by the composition of the electrolyte and the magnitude of the current density. Most metal electrodes showed dendritic growth of the electrodeposited metal as the current density approaches the limiting current density, which indicates that the electrodeposition morphology strongly depends on the current distribution on the electrode.^[9] M. Arakawa et al.^[10] and M. Z. Mayers et al.^[11] successfully demonstrated that the amount of needle-like Li increased significantly when the deposition current density increased.

Another possible reason for dendrite formation is the solid electrolyte

interphase (SEI)^[12] that is a by-product of reaction between the electrolyte (or salt) and the Li. Because this SEI is not mechanically strong, the SEI can become cracked due to the volume change of lithium metal during cycling. Li can be preferentially deposited through the cracks in the SEI, resulting in dendrite formation. For these reasons, the stability of the interphase between the Li electrode and the electrolyte could be a central issue for the Li metal anode. Many approaches have been taken to overcome this problem: finding appropriate organic solvents and salts as electrolyte, which determine the nature of the SEI; finding effective additives to modify SEI formation; using a solid-state-electrolyte, and surface modification of the Li electrode with lithium ion conducting materials.^[8]

Since the Li/S cell and the Li/air cell have been considered as candidates for the next generation rechargeable cell, researchers are paying more attention to the Li metal electrode.^[13] Apart from the dendrite formation problem, the Li/air and Li/S cells suffer from other issues. A major issue of the Li anode in the Li/air cell is protection from water and gases such as oxygen and carbon dioxide that can cause performance degradation and safety problems. Because Li metal is highly reactive with water, Li metal should be separated from the aqueous electrolyte by a solid membrane that allows Li ion transfer. In the case of the Li/S cell, the polysulfide shuttle and deposition of insoluble sulfur products on the Li metal is a critical issue that can degrade the performance of the Li/S cell.

2.2.2 Lithium Intercalation type anodes

The intercalation reaction, which involves the penetration of Li into a host structure without a structural change of the host material, is generally reversible resulting in

stable cycling. Carbonaceous materials and titanium-based oxide electrodes are representative intercalation anodes. A review article written by M. Winter et al.^[14] covers the subject of intercalation materials for the Li ion battery electrodes.

Carbonaceous materials are used as the anode materials for commercial Li ion cells due to its relatively negative intercalation potential and mechanical stability during cycling. There are hundreds types and qualities of carbon and those carbons can be classified as graphitic and non-graphitic carbons.^[14] Graphitic carbon has a continuous layered structure in the c-direction with a certain stacking order depending on its crystal structure (for example, the stacking order of AB in the case of hexagonal graphite) while non-graphitic carbon materials have a lack of stack ordering in the c-direction. Non-graphitic carbon is characterized by a random mixture of amorphous and small graphitic regions, which strongly depend on both the precursor of the carbon and the manufacturing temperature. Non-graphitic carbon can be divided into 'soft' carbon and 'hard' carbon according to the development of graphitic structure at high temperature.^[15] When soft carbon is heat treated at high temperatures between 1500 °C and 3000 °C , a graphite-like structure is developed during the process.

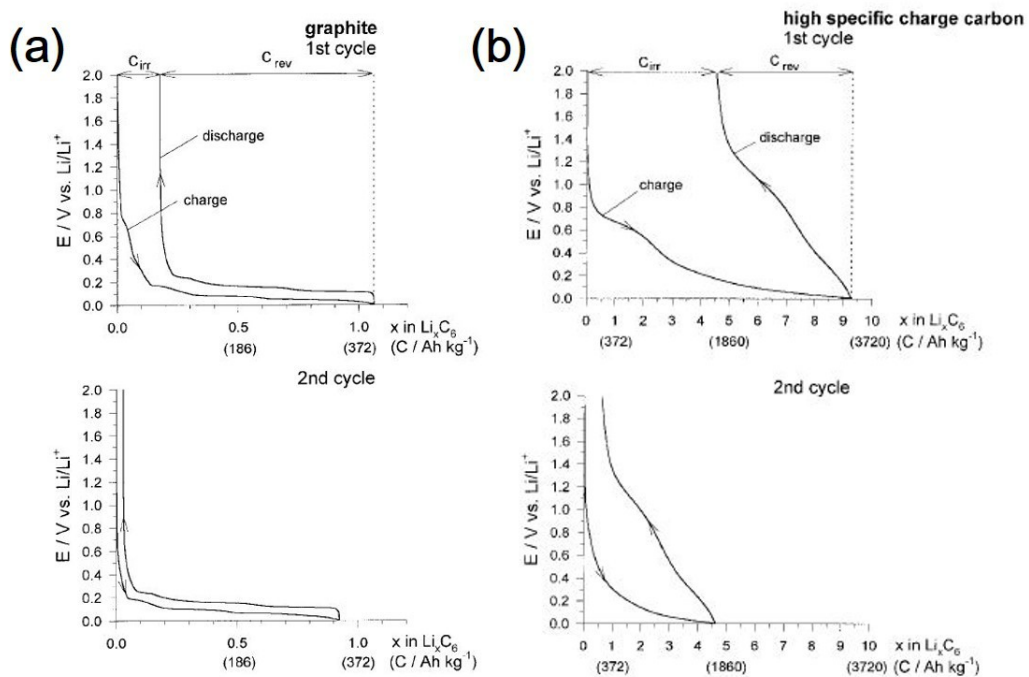


Figure 19.2 Voltage profiles of (a) graphitic and (b) non graphitic carbon. (License is needed)^[14].

Because of structural differences between graphitic and non-graphitic carbon, their electrochemical characteristics are different as shown in Figure 19.2. The voltage profile of the graphite electrode has a characteristic shape associated with Li intercalation which shows a significant plateau near 0.1 V. On the other hand, the non-graphitic hard carbon electrode exhibits a hysteresis wherein Li insertion occurs close to 0 V and Li deinsertion occurs at much higher voltages. The hysteresis behavior is related to hydrogen in the carbon, which might have a chemical interaction with Li. Interestingly, the hard carbon electrode showed much larger specific capacity than that of the graphite electrode. Several lithium storage models have been proposed to explain the larger amount of lithium storage in the carbon structure, such as Li located at the surface (or edge) of graphite,^[16] Li interaction with hydrogen in carbon^[17] and Li storage in pores (or defects).^[18] However, despite the large specific capacity of hard carbon electrodes, their large irreversible capacity and more positive reaction voltage range for the delithiation

process are still important issues to be dealt with in using hard carbon as anode material for commercial lithium ion cells.

Recently various carbon nano-structures such as carbon nanotubes, graphene (oxide) sheets and mesoporous (or hollow) carbons have been reported as high performance anode materials^[19] however, they not only suffer from a large irreversible capacity but also exhibit a wide voltage range between 0.1 V and 3.0 V during de-lithiation, which is not appropriate for battery applications. Although the open structure of carbon can provide larger surface area for storing significant amounts of Li and providing shorter diffusion distances for Li in the carbon structure, a large amount of SEI can be formed during cycling, which leads to a large irreversible capacity. N. A. Kaskhedikar et al.^[19] suggested ways to overcome this dilemma by providing closed cavities to which lithium but not the electrolyte has access, or preforming the passivation layer on the anode material before use. Adding an additional Li source such as stabilized Li metal powder (SLMP) in the anode also can compensate for the irreversible capacity loss caused by SEI layer formation during the discharge process.^[20]

Besides carbonaceous materials, titanium (Ti) based oxide materials such as $\text{Li}_4\text{Ti}_5\text{O}_{12}$ and TiO_2 represent another group of intercalation type anode materials.^[4, 14, 21] Although $\text{Li}_4\text{Ti}_5\text{O}_{12}$ (LTO) has a theoretical capacity of only 175 mAh g^{-1} and shows relatively positive redox potential between 1.2 V ~ 2.0 V, it has strong advantages for some battery applications; high cycling stability due to a very low volume change during cycling, only slight electrolyte decomposition because of the less-reducing voltage being within the stability window of common organic electrolytes, thermal stability and excellent rate capability.

TiO₂ also has gained attention because it has similar advantages to those of Li₄Ti₅O₁₂ but a theoretical specific capacity of 335 mAh g⁻¹ which is larger than that of LTO. This theoretical specific capacity corresponds to LiTiO₂ formation, associated with a complete Ti⁴⁺ → Ti³⁺ reduction. The practical capacity of the TiO₂ electrode is 168 mAh g⁻¹ which corresponds to orthorhombic Li_{0.5}TiO₂. Many kinds of TiO₂ polymorphs such as anatase, rutile, brookite and TiO₂-B and their modifications have been researched. Nano-structured anatase TiO₂^[22] and TiO₂-B^[23] anodes showed the most promising electrochemical performance among the various TiO₂ materials.

2.2.3 Li alloy based anodes

Because many metallic or semi-metallic elements such as group IV elements, group V elements, zinc, silver and aluminum can electrochemically alloy with a relatively large amount of Li at low potentials, these elements and their compounds have been investigated as anode materials.^[24] However, they suffer from large volume changes due to Li accommodation in their structure during cycling, which causes a large irreversible capacity at the first cycle and poor cycling stability. Many elements are still being considered for anode applications, however silicon (Si) and tin (Sn) show the most promise among the Li alloy based anodes due to their large theoretical specific capacity, relatively low operating voltage, low cost and low environmental impact.

Si has the largest theoretical gravimetric and volumetric capacity (Li₂₂Si₅, ~ 4200 mAh g⁻¹ and ~ 2400 mAh cm⁻³) among the alloy based anode materials and a low operating voltage (~ 0.4 V vs. Li/Li⁺). Besides, Si is the eighth most common

element on Earth by mass, which is a great advantage for industry. The detailed reaction and failure mechanism of the Si electrode are introduced in the review article written by H. J. Sohn et al.^[24] and in short, the main issue of the Si electrode is a large volume change of the silicon particles, which leads to the cracking or pulverization of Si particles (or electrode) resulting in loss of electrical contact between the Si and the current collector.^[25] Various approaches have been attempted to improve the performance of Si electrodes and the key issues are how to suppress the volume change of the electrode and how to maintain good electrical contact to each Si particle. Nano-structured Si (Si nano-wire, meso-porous Si, Si nano particles, etc.),^[26] Si-C composites (or silicon-M-carbon composites, M: active or inactive matrix),^[27] Si-polymer composites^[28] and SiO_x (0 < x < 2)^[29] were proposed to achieve mechanical stability and better electrical conductivity of the electrode which lead to improvement of the electrochemical performance of the Si electrode.

Sn is also competitive as an anode material for Li ion cells due to its large theoretical capacity of 991 mAh g⁻¹ (Li₂₂Sn₅). Although the theoretical gravimetric capacity of the Sn electrode is much lower than that of silicon electrode, its theoretical volumetric capacity is about 2000 mAh cm⁻³ which is comparable to that of the Si electrode. The anode material called Nexelion, which is commercialized by the Sony Company is composed of a Sn-Co-C nano-composite.^[30] The Sn anode also suffers the same mechanical degradation as Si due to a large volume change associated with the formation of a Li-Sn intermetallic phase. To overcome this mechanical issue, various forms of nano-structured Sn and its composites were proposed and some achieved better cycling performance. However, the cycling stability is still not enough because nano-sized Sn particles show a tendency to

aggregate into large Sn particles upon cycling which causes capacity degradation of the electrode.^[24] For this reason, one of the promising approaches to achieve stable cycling performance is the isolation of Sn nano-particles within other matrix materials to suppress the aggregation of Sn atoms during cycling. SnO₂ (or SnO) anode material is representative of materials for which the matrix concept has been employed. The irreversible formation of a Li₂O phase during the first lithiation process ($\text{SnO}_2 + 4\text{Li}^+ \rightarrow \text{Sn} + 2\text{Li}_2\text{O}$) can act as a matrix where the reduced Sn phase from SnO₂ can be finely dispersed in the Li₂O matrix. Many nanostructured SnO₂ materials and nano-composite electrodes have successfully achieved a good cycling performance, however, the irreversible capacity of the SnO₂ electrode associated with Li₂O formation is still a problem for employing SnO₂ in commercial Li ion cells.

2.3 Cathodes

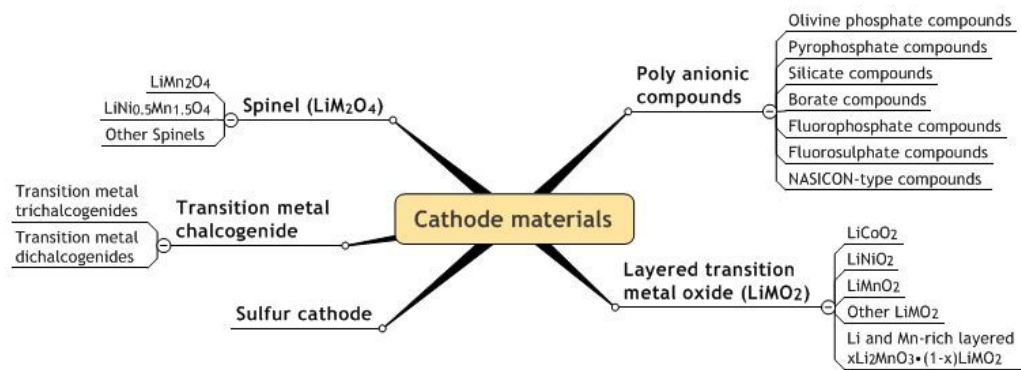


Figure 19.3 Candidates for lithium ion cell cathode materials.

For developing advanced cathode materials, a large specific capacity, a high redox potential, a good rate capability, a low cost and good safety need to be considered. In particular, the working voltage of Li ion cells could only be enhanced by employing

higher voltage cathodes because the operating voltage of the anode cannot be lower than 0 V (vs. Li/Li⁺), which has already been achieved by Li metal (~ 0 V) or carbonaceous anodes (~ 0.1 V). As shown in Figure 19.3, many kinds of cathode materials have been proposed in the past several decades and among them, three types of cathode materials are mainly considered for Li ion cells in recent years: layered transition metal oxides, spinel type materials and poly anionic compounds. Figure 19.4 shows the crystal structures of cathode materials and their voltage profiles. Based on their crystal structures, they show characteristic shapes of their voltage profiles as well as different operating voltages.

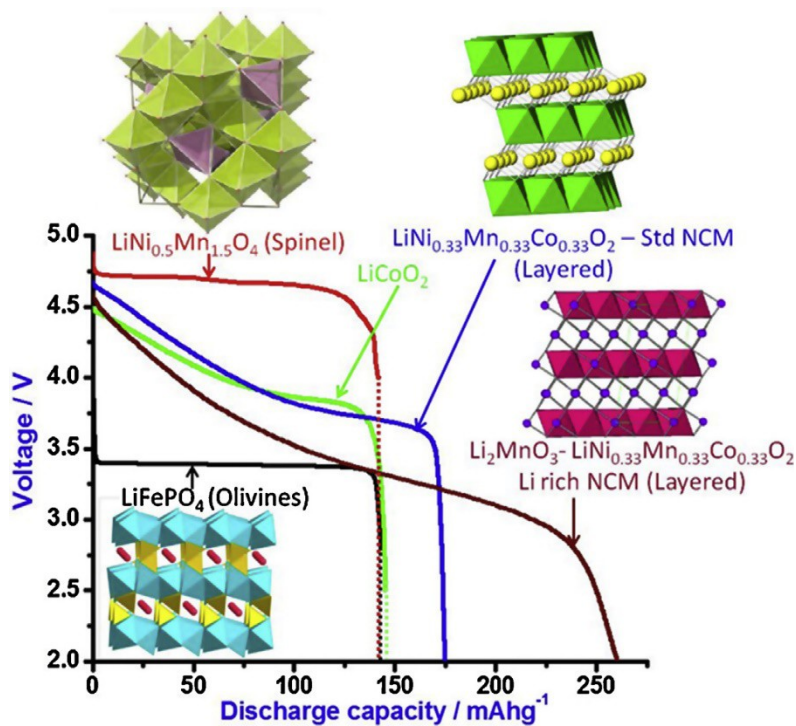


Figure 19.4 Crystal structure and voltage profiles of representative cathodes for lithium ion battery. (Copyright is needed)^[31]

The sulfur based cathode is a strong competitor for advanced Li rechargeable cells due to its high theoretical specific capacity of 1672 mAh g⁻¹ (approximately six times higher than that of LiCoO₂ cathode (272 mAh g⁻¹)), abundance and low environmental impact. The gaseous O₂ cathode is another important candidate for

advanced Li rechargeable cells, but it will be discussed in the section for metal-air batteries. In this section, representative cathode materials and their reaction and failure mechanism are discussed briefly. Detailed reaction and failure mechanisms of these materials were well-explained in review articles.^[31-35]

2.3.1 Layered lithium metal oxides

The first Li ion battery proposed by M. S. Whittingham used layer structured TiS_2 as the cathode material.^[2] Because the layered structure of TiS_2 allows mechanically stable insertion/de-insertion of Li ion between the layers, the TiS_2 cathode showed good cycling stability. However, its low working voltage of only ~ 2.5 V was not appropriate for high voltage Li ion cells. In the 1980s, J. B. Goodenough et al. suggested LiCoO_2 which has similar crystal structure as that of LiTiS_2 but exhibits a higher redox potential of ~ 4.1 V and a theoretical capacity of 274 mAh g^{-1} .^[36] The first commercialized Li ion cell by Sony employed layered LiCoO_2 as cathode material.^[3]

However, although LiCoO_2 cathodes have been successfully employed in commercial Li ion cells, its low practical specific capacity of $\sim 140 \text{ mAh g}^{-1}$ and poor rate capability cannot satisfy the market demands for advanced Li ion cells. Unfortunately, the theoretical capacity of the LiCoO_2 cathode cannot be used completely, because if more than half of the Li is extracted from its structure, oxygen evolution and Co dissolution occur, which causes electrolyte oxidation and material crumbling resulting in capacity fading during cycling.^[37, 38] Besides, the toxicity and relatively high price of Co have made the LiCoO_2 cathode more difficult to use in commercial Li ion cells. To overcome these problems, other layered

transition metal oxides such as LiNiO_2 and LiMnO_2 have been studied as cathode materials due to their similarly high operating voltage, relatively lower price than Co and lower environmental impact, however, several problems such as limited reversible Li insertion/de-insertion and difficulty of pure LiNiO_2 synthesis have to be overcome.^[32]

Recently, substituted or mixed transition metal oxide compounds such as a layered $\text{LiNi}_{0.5}\text{Mn}_{0.5}\text{O}_2$, layered Li–Co–Ni–Mn–O compounds (NCM) and Li–Ni–Co–Al–O compounds (NCA) cathode materials have been studied to achieve a better material stability, good rate capability and a larger reversible capacity.^[39, 40] Among them, Li and Mn-rich layered cathode materials, $x\text{Li}_2\text{MnO}_3 \cdot (1-x)\text{LiMO}_2$ (M = Mn, Ni, Co) show much higher specific capacity of $\sim 250 \text{ mAh g}^{-1}$ than that of conventional transition metal oxide cathodes.^[41-43] Basically, Li_2MnO_3 by itself cannot deliver high capacity, but a composite with LiMO_2 on a nanometric scale induces a reversible reaction of the excess Li. However, these Li and Mn-rich layered cathodes must still overcome drawbacks such as a large irreversible capacity at the first charging and a gradual decrease of the lithiation voltage during cycling.

2.3.2 Spinel type materials

Spinel is representative of three-dimensional framework structures that allow Li diffusion through three-dimensional pathways with a small degree of volume change of the structure during cycling. The structure of LiM_2O_4 spinel is composed of the same oxygen framework as layered LiMO_2 but 1/4 of the transition metal cations are located in the Li layer instead of the octahedral site, so those vacancies at octahedral sites are available for Li storage. Since the spinel LiMn_2O_4 was demonstrated by J.

B. Goodenough et al.,^[44, 45] it attracted much attention due to its low environmental impact, the large abundance of manganese and good rate capability because of the three-dimensional Li diffusion pathway. However, it suffers from a large capacity fade during cycling which is caused by the dissolution of Mn ions or the formation of a new, less symmetric and more disordered phase during the first cycle.^[46]

To improve the electrochemical performance of the spinel cathode, substituting Mn with other metal ions such as Co, Ni, Fe, Ti, Cr, Al and Mg has been investigated and $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ showed the most promising electrochemical performance among the above.^[47] In principle, Ni ions in $\text{LiMn}_{1.5}\text{Ni}_{0.5}\text{O}_4$ spinel are located in the same position as the Mn ions originally. As shown in Figure 19.4, this material shows a relatively high operating voltage of about 4.7 V with a flat voltage profile. Although its theoretical capacity is only about 147 mAh g^{-1} , the $\text{LiMn}_{1.5}\text{Ni}_{0.5}\text{O}_4$ spinel electrode exhibits good cycling stability and rate capability due to its three-dimensional spinel structure, so low capacity is balanced by the higher operating voltage and good rate capability. However, better cycle stability of the $\text{LiMn}_{1.5}\text{Ni}_{0.5}\text{O}_4$ spinel cathode is still required to be employed into commercial Li ion cells.

2.3.3 Poly-anion compounds

Poly-anion compounds which have an open three dimensional framework for Li diffusion, have been extensively investigated in recent decades due to their advantages such as cycling stability, low environmental impact and lower oxygen loss than transition metal oxides.^[48] Among many poly-anion compounds, olivine LiFePO_4 is one of most attractive due to its excellent cycling stability, potentially

low production cost and low environmental impact. In 1997, J. B. Goodenough et al. first proposed olivine LiFePO_4 ^[49] and further computational^[50] and experimental^[51] studies confirmed that the one dimensional Li ion pathway along the (0 1 0) direction is much more favored than other paths. However, although the olivine LiFePO_4 cathode exhibits excellent cycling stability, its low redox potential (~ 3.4 V) and poor rate capability that is limited by the one dimensional Li ion path have been critical issues for employing olivine LiFePO_4 cathode into commercial Li ion cells. Recent work has significantly improved the rate capability of this material.^[52]

On the other hand, silicate compounds and other compounds have recently attracted a lot of interest as cathode materials. When two Li atoms are extracted from the structure, the Li_2MSiO_4 cathode (M = Mn, Fe, Co and Ni) can exhibit a high theoretical specific capacity of $\sim 330 \text{ mAh g}^{-1}$ ($\text{Li}_2\text{FeSiO}_4$). However, poor cycling stability, poor rate capability and a practical specific capacity of only about 140 mAh g^{-1} should be overcome.^[54] Another interesting cathode material, LiMPO_4F called tavorite is a derivative class of the olivine structure, so their characteristics are similar as those of olivine materials.^[55] The main different characteristic of tavorite from typical olivine materials is a multidimensional Li pathway due to the fluorine in the structure resulting in better rate capability. Tavorites also exhibit good thermal stability and cycle retention, however, their low specific energy should be considered.

2.3.4 Sulfur cathode for the Li/S system

Since sulfur cathodes were investigated for high temperature Li/S cells in the 1960s,

^[56] S has been considering to be a strong candidate for Li rechargeable cells due to its large theoretical specific capacity (Li_2S , 1675 mAh g^{-1}), low cost and abundance. Although its redox potential is lower ($\sim 2.1 \text{ V}$) than other conventional cathodes, its larger theoretical specific energy of 2600 Wh kg^{-1} can more than compensate for the lower working voltage. However, despite its great advantages, the early Li/S cells showed low utilization and poor cycling stability due to several major problems of the S cathode: the insulating nature of S and Li_2S , a large volume change of the S due to formation of Li_2S , dissolution of polysulfides (Li_2S_n , $2 \leq n \leq 8$) into liquid electrolytes and their shuttle process between anode and cathode.

Several review articles are available on Li/S cells that provide the detailed reaction chemistry of the sulfur electrode,^[13, 57-59] and they suggested that the key factors to improve the electrochemical performance of the S cathode are suppression of the polysulfide dissolution, the polysulfide shuttle effect, the volume change of the S, and how to increase the electronic and ionic conductivity of the S electrode. To overcome these difficulties, researchers not only have focused on the S cathode, but also have tried to modify the anode and electrolyte as well. For example, employing LiNO_3 as an additive,^[60] using an ionic liquid based electrolyte,^[61] employing a solid electrolyte^[62] and using an elastomeric binder^[63] are well-known approaches that showed significant performance improvement. From the point of view of cathode materials, synthesizing nanostructured S and its carbon composites, and surface coatings of conductive polymers or transition metal sulfides (or oxides) on S particles to inhibit direct contact between S and the electrolyte have been intensively investigated, and many of them have exhibited promising electrochemical performance.

Composite	S in the cathode (wt%)	Electrolyte	Binder	Discharge rate (C)	Discharge capacity (mAh g ⁻¹ S ⁻¹)	
					Initial	n th cycle
CTAB modified S/GO ^[63]	~ 55	1 M LiTFSI and 0.1 M LiNO ₃ in DOL/DME/PYR1 4TFSI (1:1:2 v/v)	SBR/CMC	1.0 C	~ 800	~ 800 (100 th)
S/CMK-3 (mesoporous carbon) ^[64]	58.8	1.2 M LiPF ₆ in ethyl methyl sulphone	PVDF	0.1 C	~ 1320	~ 1100 (20 th)
S/hollow carbon nanofiber ^[65]	~ 1 mg	1 M LiTFSI and 1 wt% LiNO ₃ in DOL/DME (1:1 v/v)	N/A	0.5 C	~ 828	~ 650 (300 th)
S/PANI ^[66]	49.6	1 M LiTFSI in DOL/DME (1:1 v/v)	PVDF	1.0 C	~ 460	~ 432 (500 th)
S/TiO ₂ ^[67]	~ 53	1 M LiTFSI and 1 wt% LiNO ₃ in DOL/DME (1:1 v/v)	PVDF	0.5 C	~ 1030	~ 690 (1000 th)
Li ₂ S/C ^[68]	41.4	1 M LiTFSI and 1.0 wt% LiNO ₃ in DOL/DME/PYR1 4TFSI (1:1:2 v/v)	PVP	0.2 C	~ 1394	~ 1056 (100 th)

Table 19.2 Electrochemical performance of S based composite cathodes.

Table 19.2 shows various approaches that have achieved significant improvement of cell performance. Previous studies on employing porous (or hollow) carbon or graphene oxide demonstrated that those carbon materials not only can improve the electrical conductivity but also can act as an immobilizer of polysulfides resulting in improvement of Coulombic efficiency as well as cycling stability.^[64, 69] The formation of a shell layer on S particles is another promising approach to protect S from polysulfide dissolution or mechanical pulverization of S particles due to the volume change of ~ 80 % during cycling. The other notable approaches, using prelithiated sulfur: i.e., Li₂S as the starting cathode material instead of S also showed excellent test results. Because Li₂S particles already occupy the maximum volume resulting from reaction with lithium, better mechanical stability of the electrode can be obtained during cycling. The Li₂S electrode can be coupled with a carbonaceous anode instead of Li metal, which can

provide better safety.^[68]

2.4 Electrolytes

Although battery researchers have been mainly focused on the electrodes, the electrolyte is also an important component that influences cell performance and safety. Even when both an anode and a cathode can provide a desirable high operating voltage, they cannot be employed in the cell unless an appropriate electrolyte that is stable at the potentials of both electrodes. In addition, the ionic conductivity, lack of reaction with all cell components, toxicity, price and thermal stability of the electrolyte are also very important for commercialization of Li ion cells.

Because aqueous electrolytes exhibit a narrow voltage window of only ~ 1.3 eV, non-aqueous electrolytes or polymer electrolytes are employed to achieve higher voltage cells. Once the electrolyte is determined, both anode and cathode can be selected based on their working potential which must lie within the voltage window of the electrolyte. Li salts (or additives) must be added to the electrolyte solvent to provide the ionic conductivity and/or to provide a stable SEI layer on the electrode.

Electrolytes	Example of classical electrolytes	Ionic conductivity ($\times 10^{-3}$ s/cm) at room temp	Electrochemical window (V) vs Li^+/Li^0		Remark
			Reduction	Oxidation	
Liquid organic	1M LiPF_6 in EC:DEC (1:1) 1M LiPF_6 in EC:DMC (1:1)	7^3 10^3	1.3 ⁷	4.5 ⁶	Flammable
			1.3 ⁷	> 5.0 ³	
Ionic liquids	1M LiTFSI in EMI-TFSI 1M LiBF_4 in EMI- BF_4	2.0 ¹⁵ 8.0 ¹⁵	1.0 ¹⁵	5.3 ¹⁵	Non-flammable
			0.9 ¹⁶	5.3 ¹⁶	
Polymer	$\text{LiTFSI-P(EO/MEEGE)}$ $\text{LiClO}_4\text{-PEO}_8$ + 10 wt % TiO_2	0.1 ²⁴ 0.02 ²⁶	< 0.0 ²⁴	4.7 ²⁴	Flammable
			< 0.0 ²⁶	5.0 ²⁶	
Inorganic solid	$\text{Li}_{4-x}\text{Ge}_{1-x}\text{P}_k\text{S}_4$ ($x = 0.75$) $0.05\text{Li}_4\text{SiO}_4 + 0.57\text{Li}_2\text{S} + 0.38\text{SiS}_2$	2.2 ²⁸ 1.0 ³⁰	< 0.0 ²⁸	> 5.0 ²⁸	Non-flammable
			< 0.0 ³⁰	> 8.0 ³⁰	
Inorganic liquid	$\text{LiAlCl}_4 + \text{SO}_2$	70 ²⁰	-	4.4 ²⁰	Non-flammable
Liquid organic + Polymer	0.04 LiPF_6 + 0.2EC + 0.62DMC + 0.14PAN $\text{LiClO}_4 + \text{EC} + \text{PC} + \text{PVdF}$	4.2 ³⁸ 3.0 ³⁹	-	4.4 ³⁸	Flammable
			-	5.0 ³⁹	
Ionic liquid + Polymer	1M $\text{LiTFSI} + \text{P}_{13}\text{TFSI} +$ PVdF-HFP	0.18 ⁴³	< 0.0 ⁴³	5.8 ⁴³	Less flammable
Ionic liquid + Polymer + Liquid organic	56 wt % $\text{LiTFSI-Py}_{24}\text{TFSI} +$ 30 wt % $\text{PVdF-HFP} +$ 14 wt % EC/PC	0.81 ⁴⁴	1.5 ⁴⁴	4.2 ⁴⁴	Less flammable
Polymer + Inorganic solid	2 vol % $\text{LiClO}_4\text{-TEC-19} + 98$ vol% 95 (0.6 $\text{Li}_2\text{S} + 0.4\text{Li}_2\text{S}$) + 5 Li_4SiO_4	0.03 ⁴⁶	< 0.0 ⁴⁶	> 4.5 ⁴⁶	Non-flammable
Ionic liquid + Liquid organic ¹⁹		-	-	-	Non-flammable

Table 19.3 Nonaqueous electrolytes for Li ion batteries (Copyright is needed)^[70]

The detail chemistry of organic (or inorganic) liquid electrolytes and solid state electrolytes as well as additives have been discussed in review articles^[35, 71-79] and they refer to four major types of nonaqueous electrolytes such as organic liquids with Li salts,

gel polymer electrolytes, solid electrolytes and ionic liquids. Table 19.3 shows the properties of each type of electrolyte and their combinations. Organic liquid electrolytes comprise the most common electrolyte group for Li ion cells. Alkyl carbonates, esters, ethers and nitriles can be employed, but alkyl carbonates have been widely used due to their wide voltage window and relatively low viscosity resulting in a low activation energy for Li ion diffusion. Ethylene carbonate (EC), propylene carbonate (PC), diethyl carbonate (DEC), dimethyl carbonate (DMC) and ethyl methyl carbonate (EMC) are employed in Li ion cells alone or in mixtures. LiPF_6 is commonly employed as the electrolyte salt in carbonate electrolytes. However, carbonate electrolytes are highly flammable and the LiPF_6 salt can decompose to PF_5 and LiF ; acidic impurities, especially HF can be formed when PF_5 reacts with any water.^[72]

Solid electrolytes have obvious advantages and disadvantages: they have excellent chemical and physical stability but low ionic conductivity, limited contact area with nanostructured electrode materials and suffer from interfacial stress due to volume changes of the electrodes during cycling. Because of their physical stability, they can be employed in thin film form in flexible batteries and micro batteries. Moreover, they suffer less from side reactions due to their chemical stability, they can provide better safety, which is very important for portable electronics. Ether-based polymers and their block copolymers such as polyethylene oxides (PEOs) and polypropylene oxide (PPO) are representative polymer solid electrolytes.^[76] Inorganic glass (or ceramic) electrolytes such as perovskite-type, lithium nitrides and sulfides have also been considered as the solid electrolyte in all-solid-state Li ion cells.^[77, 78, 80]

Gel polymer electrolytes are intermediate between liquid and solids, and are composed of a polymer solid electrolyte and an organic liquid electrolyte (or ionic

liquid). With this concept, two different types electrolytes could complement each other; for example, achieving better physical and chemical stability with good ionic conductivity.^[73] On the other hand, ionic liquids, especially room temperature ionic liquids (RTIL) are structurally composed of anions and cations, which interact with each other due to Coulombic forces. Because of strong Coulombic forces, they typically exhibit high viscosity, high anodic stability and low vapor pressure resulting in lack of flammability. However, their high viscosity causes wetting problems in composite structures, and low ionic conductivity at low temperatures making them hard to be employed in commercial batteries.^[75]

2.5 Future challenges

As the desire for the convenience achieved through battery-powered devices increases, the dependence on advanced rechargeable batteries will dramatically increase. Although the Li ion battery is facing tough challenges in satisfying market demands, it is still regarded as the front runner of rechargeable batteries due to its high working voltage and high energy density. Many scientists and engineers are devoted to advancing Li ion batteries, and there are several remarkable accomplishments such as nanostructured Si- and Sn-based high capacity anodes, titanium-based oxide high power anodes, Li- and Mn-rich layered high capacity cathodes, $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ spinel high voltage cathodes and various types of electrolytes as well as additives. Based on these results, the energy density or power density of Li ion cells can be significantly improved, however, it is still necessary to transfer these material technologies from laboratory to industry. This requires not only the high performance of cells under test conditions but also high cell performance under various practical conditions, safety in the hands of the user, feasibility of large scale material production, and low cost. Although many challenges remain for

commercialization of advanced Li ion cells, we believe that the current worldwide efforts will continue to provide Li ion cells that satisfy market demands.

3 Sodium and magnesium batteries

3.1 Sodium ion batteries

Sodium (Na), which is located below Li on the periodic table, exhibits similar chemical properties in many regards. Although its theoretical specific capacity is lower and its redox potential is more positive than those of Li (shown in Table 19.1), Na is obviously competitive due to its abundance and low cost of about \$135/ton (cost of Li is about \$5000/ton).^[81] Because of these advantages and some desirable electrochemical properties of Na, several Na-based battery systems such as ambient temperature Na ion cells and high temperature cells (Na/S cells and Zebra cells (Na/NiCl₂)) have been intensively studied and developed.

The Na-ion cell was also investigated from the 1970s to the 1980s in parallel with the Li ion cells,^[82, 83] although it barely received attention over the past few decades due to the steep growth of Li ion cells. But recently researchers have started to pay attention again to Na-ion cells because of the abundance and low cost of Na that are important for lowering the production cost of batteries. The fundamental chemistry of Na ion cells is basically same as that of Li ion cells, but Na ion cells exhibit somewhat different thermodynamic and electrochemical behavior, such as insertion/extraction mechanisms, ionic transport and kinetics in the active materials or through the SEI layer due to a relatively positive standard potential (≈ 2.7 V) and a larger ionic radius of the Na ion (1.06 Å) than that of the Li ion (0.76 Å).^[84] For these reasons, some electrode materials

used in Li ion cells do not electrochemically react with the Na ion or exhibit different reaction mechanisms from those of Li, resulting in poor electrochemical performance. Therefore, it is necessary to discover the new redox couples that can be used as anode and cathode materials as well as appropriate electrolytes for Na ion cells.

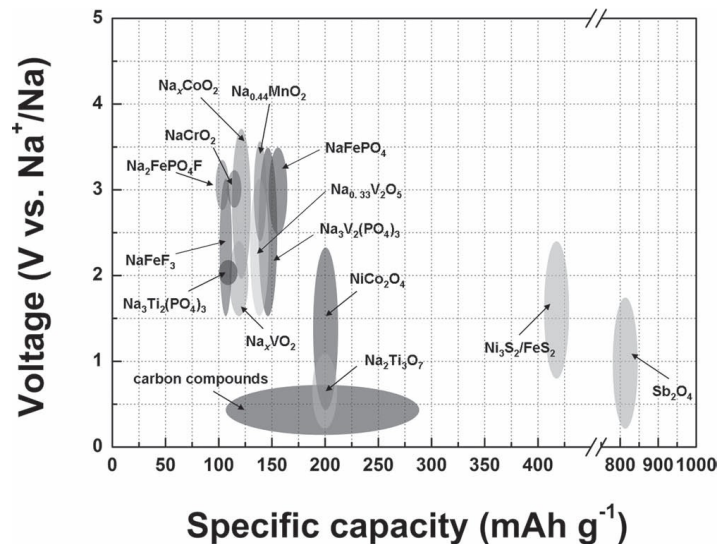


Figure 19.5 Electrode materials and corresponding electrochemical performances in current NIB technologies. (Copyright is needed^[85])

Detailed discussions about the materials for Na ion cells are available in several review articles,^[81, 86-88] and they will be just briefly discussed here. Figure 19.5 shows the practical specific capacities and working voltages of electrode materials. In case of anode materials, non-graphitic carbon and non-carbonaceous materials such as metal oxides and Na alloy based materials have been considered instead of Na metal due to its low melting temperature (98 °C), high reactivity with the organic solvents and the dendritic growth of Na during cycling. Interestingly, the graphite anode which is mainly being used for Li ion cells showed very poor electrochemical performance in organic electrolytes due to solvent cointercalation.^[89] Instead, Na exhibits much better reactivity with non-graphitic carbon materials such as carbon black,^[90] cokes,^[91] and templated carbon^[92] although many of those materials were tested under limited conditions such as

relatively low applied current or elevated temperatures. Like the TiO_2 (or LTO) anodes for Li ion cells, layered NaTiO_2 and $\text{Na}_2\text{Ti}_3\text{O}_7$ anodes showed a reversible intercalation reaction of 0.3–0.5 Na ions at around 1 V^[83] and 178 mAh g⁻¹ at 0.3 V,^[85] respectively. In the case of alloy-based materials, Sn,^[93] Sb,^[94] P^[95] and their composites showed similar advantages (large specific capacity) and disadvantages (pulverization due to a large volume change) as the Li alloy based anode materials. Therefore, the approaches to suppress the volume change during lithiation/delithiation might be effective for Na alloy based materials.

On the other hand, there are many kinds of cathode materials for Na ion cells such as chalcogenides, fluorides, polyanion compounds and oxide compounds. Among them, layered metal oxides have been studied more extensively than any others. As mentioned above, although the material concept of layered NaMO_2 (M = Co, Fe, Mn, Cr and their complexes) is similar as that of LiMO_2 , layered NaMO_2 materials have subtly different structures due to the larger size of the Na ion that limits cation disorder and prevents the accommodation of Na ions at the tetrahedral sites in the structure of NaMO_2 . Layered NaMO_2 cathodes can be categorized into two main groups according to O-type and P-type,^[96] in which the Na ions occupy the octahedral and the prismatic sites in their structures, respectively. The number that follows the letter P or O means the number of transition metal layers in the stacking repeat unit. Various Na_xMO_2 (or quaternary $\text{Na}_x\text{M}_y\text{M}'_{1-y}\text{O}_2$, M = Co, Ni, Fe, Cr, Mn, etc.) have been investigated and they exhibited the reversible intercalation reaction of Na ($x \leq 0.5$) at an average potential of 3.5 V, e.g. the O3-type NaFeO_2 cathode exhibits a specific capacity of about 80 mAh g⁻¹ with a significant plateau in the voltage profile at 3.4 V.^[97] Another structural type of oxide, tunnel type oxides, especially orthorhombic $\text{Na}_{0.44}\text{MnO}_2$ showed interesting

electrochemical behavior due to its three dimensional tunnel structure for Na ion diffusion. Nanowire $\text{Na}_{0.44}\text{MnO}_2$ reported by Cao et al. showed a specific capacity of 128 mAh g^{-1} at 0.1 C in the voltage range of 2.0 \square 4.0 V and 77 % capacity retention for 1000 cycles at 0.5 C^[98]

Another typical type of cathode material, polyanion compounds, have some advantages owing to their open channel for Na ion diffusion. Na super-ionic conductor (NASICON, $\text{A}_x\text{MM}'(\text{XO}_4)_3$) that is generally used as a solid electrolyte for Na/S cells has been investigated as a cathode material for Na ion cells. Typical $\text{Na}_3\text{V}_2(\text{PO}_4)_3$ exhibits reversible electrochemical reactions with two distinct plateaus near 1.6 V and 3.4 V (vs. Na/Na^+) associated with the $\text{V}^{3+}/\text{V}^{2+}$ and $\text{V}^{4+}/\text{V}^{3+}$ redox couples, respectively, which delivers a reversible capacity of 140 mAh g^{-1} in the voltage range of 1.2 \square 3.5 V. Using these two distinct reaction voltages, symmetric cells can be constructed, which are composed of a $\text{Na}_3\text{V}_2(\text{PO}_4)_3$ anode and cathode. Recently, it was demonstrated that combining this material with carbon significantly improves the cycling stability of the $\text{Na}_3\text{V}_2(\text{PO}_4)_3$ electrode.^[99] Another typical polyanion compound, olivine structured NaMPO_4 exhibits different properties from LiMPO_4 ($\text{M} = \text{Fe}, \text{Mn}, \text{Co}, \text{etc.}$) due to its thermodynamic instability. Instead of olivine NaMPO_4 , maricite NaMPO_4 is the stable phase, but unfortunately, maricite NaMPO_4 is electrochemically inactive due to the lack of Na ion diffusion channels in the structure. Therefore, synthesis of the olivine NaMPO_4 was one of challenges for research on cathode materials for Na ion cells. Recently, metastable olivine NaFePO_4 was obtained through electrochemical insertion into FePO_4 that is obtained by electrochemical delithiation of LiFePO_4 ^[100] and its reaction mechanism was investigated. Interestingly, the reaction mechanism of olivine NaFePO_4 with Na ion did not follow the conventional behavior of olivine LiMPO_4 . Unlike the two-

phase reaction between Li-deficient Li_xMPO_4 and Li-rich $\text{Li}_{1-x}\text{MPO}_4$, formation of an intermediate phase ($\text{Na}_{0.7}\text{FePO}_4$) is observed, which corresponds to a voltage plateau near 2.95 V in the discharge profile.

Selecting and optimizing the electrolyte are also very important for achieving good performance of Na-ion cells. Recently, Palacin et al. reported on the ionic conductivity, viscosity, voltage stability window and thermal stability of the three Na salts (NaClO_4 , NaTFSI , NaPF_6) in various solvents (PC, EC, DMC, DEC, DME, THF, triglyme and their mixtures).^[101] Based on these results, NaClO_4 or NaPF_6 in an EC/PC mixture shows the best performance for the hard carbon anode. NaFSI ^[102] and fluoroethylene carbonate (FEC)^[103] were recently proposed as additives that can provide a more stable SEI layer on the electrode. Solid-state electrolytes such as NASICON^[104] and a super ionic glass-ceramics^[105] are also proposed to achieve better safety and allow a variety of cell designs.

3.2 High temperature sodium batteries

Although ambient temperature rechargeable batteries have mainly been the focus of attention in recent years, special types of Na batteries that operate at high temperature also have been investigated owing to their high energy density, long cycle life and potential low cost.^[8, 106] Unlike conventional ambient temperature Na cells, high temperature Na cells are composed of liquid electrodes and an ionically-conducting solid electrolyte which not only acts as electrolyte but also acts as a separator that prevents direct contact of the two liquid electrodes. The operating temperature of high temperature Na cells has been between 270 and 350 °C to maintain the liquid state of the electrode materials (e.g. Na or S) and their reaction products (e.g. Na polysulfides in case of Na/S

cell) and to obtain a good conductivity of the solid electrolyte. However, the cell design of high temperature Na cells is very important in order to provide safety, considering the liquid state of the electrodes and the high operating temperature. For instance, because the corrosion of cell cases or seals can occur due to the highly corrosive properties of the liquid electrodes (or Na polysulfides), the cell container must be corrosion resistant under these conditions. Besides, if the solid electrolyte is broken due to mechanical forces, a large amount of liquid Na can react with liquid cathode, which causes the elevation of cell temperature to more than 1000 °C.

The representative high temperature Na cell system, the Na/S cell, is composed of a molten Na anode, a molten S cathode (commonly it is absorbed in a sponge-like carbon to improve the electrical conductivity) and a solid electrolyte. The Na/S cell was first developed by the Ford motor company in 1968.^[107] During the discharge process, molten Na loses an electron and produces Na ion, which transfer to the S electrode through the solid electrolyte forming a Na₂S₄ phase, which exhibits cell voltage of 2 V. Because both electrodes are liquid, the development of a solid electrolyte material is essential. β -Al₂O₃ (Na₂O•11Al₂O₃) is one of the most common solid electrolyte materials due to its high level of Na⁺ ionic conductivity among ceramic based electrolyte.^[108] Stabilizing agents such as MgO and Li₂O are commonly added in order to stabilize the crystal structure, because the β -Al₂O₃ is not thermodynamically stable. The ionic conductivity of the Na⁺ ion and the mechanical strength of β -Al₂O₃ are influenced by the purity of the β -Al₂O₃ phase (β -Al₂O₃ and β -Al₂O₃ mixtures can easily be formed), particles size and porosity of the electrolyte. Because those properties are very sensitive to the fabrication method of β -Al₂O₃, various synthesis methods including conventional solid-state reaction,^[109] sol-gel method,^[110] co-precipitation^[111] and spraying methods^[112] were

investigated to improve the cell performance.

There is another popular high temperature Na battery composed of same materials as Na/S cells except the solid NiCl_2 cathode is used instead of the molten S cathode. This cell is called the ZEBRA cell derived from the name of research group (Zeolite Battery Research Africa Project) that invented this system in 1985.^[113] The reaction chemistry of the anode is the same as for the Na/S cell but that of the cathode is different: $\text{NiCl}_2 + 2\text{Na}^+ + 2\text{e}^- \rightarrow \text{Ni} + 2\text{NaCl}$. Compared to the Na/S cell, the ZEBRA cell has advantages such as a relatively less corrosive nature of the solid state metal halides as compared to the Na polysulfides, and a higher operating voltage (2.58 V at 300 °C). In order to enhance the stability of the β - Al_2O_3 electrolyte or the ionic conductivity of the cells, molten NaAlCl_4 and Na salts (NaBr and NaI) can be added between the electrolyte and the cathodes and into the electrode.^[114]

3.3 . Magnesium rechargeable batteries

For rechargeable cell applications Magnesium (Mg) has advantages such as a highly negative standard potential of – 2.37 V, low environmental impact and abundance. Although the atomic weight of Mg is more than three times larger than that of Li, bivalency and a relatively high density of Mg (1.74 g/cc) provide a high theoretical volumetric capacity of 3.83 Ah cm^{-3} which is higher than that of the Li anode (2.04 Ah cm^{-3}). Mg is also chemically less reactive than Li (or Na), therefore, the large scale production of Mg is simpler and safer than that of Li (or Na). However, because of the divalent nature of Mg ions, the fundamentals of the chemistry of Mg rechargeable cells are very different from those of Li and Na based cells. Above all, the rapid formation of

passivating layers on the surface of the Mg metal anode completely blocks the conduction of Mg ions, so the reversible Mg dissolution/deposition reaction is prohibited. Furthermore, solid-state diffusion of Mg^{2+} ions in the electrode materials is sluggish due to its divalent nature.^[115, 116]

For these reasons, since the Mg rechargeable cell was proposed by Gregory et al.^[117] and the first prototype of a Mg ion cell was reported by Aurbach et al.,^[118] most research on Mg rechargeable cells has mainly focused on developing high capacity cathodes and appropriate organic electrolytes, which are strongly emphasized in the recent review articles.^[115, 116, 119] In the historical development of Mg rechargeable cells, there were two significant breakthroughs;^[116] (1) the report of solutions containing Mg organo-borate moieties that provide an environment for reversible Mg deposition/dissolution, even in the absence of highly reducing Grignard reagents, (2) finding an electrolyte system such as the Mg organo-haloaluminate complex (denoted as dichloro-complex (DCC)) obtained by the reaction between $\text{AlCl}_{3-n}\text{R}_n$ Lewis acid with R_2Mg Lewis base in ethers (THF or glymes), which can exhibit a 100% reversible Mg redox reaction and high anodic stability of ~ 2.4 V (vs. Mg/Mg^{2+}).

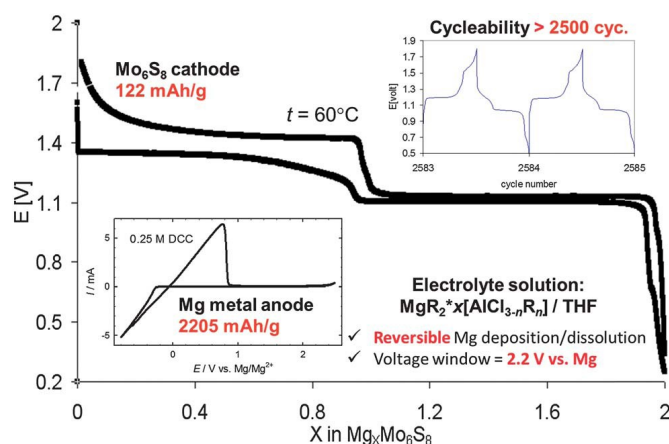


Figure 19.6 Operation scheme of the first working Mg-rechargeable cell prototype. (copyright is needed)^[116]

Since the DCC family of electrolytes was proposed, many types of cathodes have

been tested such as transition metal disulfides^[120] and Chevrel type cathodes in the DCC electrolytes.^[118] Among them, Chevrel type cathodes, Mo_6T_8 (T = S, Se or their combinations) exhibited promising properties for a practical use while the transition metal disulfides such as TiS_2 , NiS_2 and FeS_2 cathodes did not show promising results. Figure 19.6 shows the electrochemical behavior of the first working Mg rechargeable cell prototype that is composed of a Mg anode, a Chevrel type Mo_6S_8 cathode and DCC electrolyte. From a cathode materials point of view, reversible Mg insertion into Mo_6S_8 could be achieved due to the fast insertion kinetics of Mg^{2+} ions provided by its structure that has many vacant sites for Mg, a short diffusion distance between accommodation sites and easy charge compensation of the metallic Mo cluster during Mg diffusion.^[121] However, the temperature-dependent irreversible capacity on the first cycle and rate capability should be improved although this cell shows good cycling stability.

Aurbach et al. categorized Mg-cell electrolytes into four types in their recent review paper:^[119] (1) Grignard-based electrolytes, (2) advanced Grignard-based electrolytes with high anodic stability, (3) non-Grignard based electrolytes, and (4) MgTFSI_2 -based electrolytes. The first electrolyte for Mg rechargeable cells was reported in the 1920s, which was composed of Grignard reagents (R-MgX , R = C_6H_5 X = Br, Cl).^[122] The Mg metal anode was stable and passivation-free in the Grignard reagent electrolytes, however, their ionic conductivity was too low and their voltage window was too narrow for practical use. As mentioned above, these problems of Grignard reagent electrolytes could be overcome with the DCC electrolyte. However, the voltage window of DCC electrolytes was still narrow (~ 2.4 V) so it is necessary to extend it. In 2011, Aurbach et al. and Kim et al. proposed notable advanced Grignard-based electrolytes such as the all phenyl complex (APC) electrolyte solution^[123] and the AlCl_3 -containing HMDSMgCl

electrolyte,^[124] respectively. These electrolytes exhibited voltage windows of ~ 3.2 V and 100 % Coulombic efficiency that indicates good reversibility for the Mg redox reaction. The development of non-Grignard based electrolytes is driven by the high cost, high hazard level, and high susceptibility toward oxidation of Grignard reagents. Recently, inorganic salts containing a magnesium aluminum chloro complex (MACC) have been proposed, which exhibit a high operating voltage of 3.1 V, low overpotential for Mg deposition and high Coulombic efficiency of up to 99 %.^[125] However, before using a MACC electrolyte, an electrochemical “pre-conditioning” process is required in order to obtain good electrochemical performance.

The last strategy of electrolyte modification is the use of simple salts in organic solvents or ionic liquids. The simple addition of Mg trifluoromethanesulfonimide ($\text{Mg}(\text{TFSI})_2$) salt into various organic solvents or ionic liquids significantly improved the properties such as ionic conductivity, chemical stability with the cathode (due to lack of corrosive elements such as chlorides) and a wide voltage window, however, the compatibility of $\text{Mg}(\text{TFSI})_2$ with Mg anodes is still issue.^[126]

3.4 Future challenges

Because the fundamental chemistry of Na ion cells is same as that of Li ion cells, Na ion cells are consequently compared to Li ion cells. Even though the materials cost of Na ion cells is lower than that of Li ion cells, the Na-ion cell will not be used if the performance of cell is not high enough. Because current Na-ion cells commonly show low energy density and a relatively short cycle life due to some disadvantages such as the large ionic size of Na and the relatively lower operating voltage, it is clear that both anode and cathode materials as well as the electrolyte system need to be improved. However, it

hasn't been very long since Na ion cells have received attention again in the rechargeable cell field, so modern nano-technologies and the experience of developing Li-ion cells might allow improvement of the materials that were already reported in the 1970s and 1980s. Many Na based compounds have been reported in the inorganic crystallographic structure database (ICSD), which can potentially be employed but have not been investigated as electrode materials for Na ion cells. Commercially available high temperature Na/S cells are currently manufactured by the NGK company in Japan for a large scale energy storage systems, however, safety concerns are still an issue for this system.

Current issues that must be overcome are still the need for appropriate electrolytes and electrode materials. Although some Mg rechargeable prototype cells showed excellent cycling performance, but their energy densities are relatively low. Therefore, an electrolyte that provides a wider voltage window, reversible Mg redox reactions with no passivating layer and a cathode that exhibits fast diffusion of the Mg^{2+} ion, high specific capacity, high operating voltage and good reversibility must be developed. Of course, compatibility between the new high voltage cathodes and the electrolyte must be achieved. Mg alloy based anodes such as Sn, Bi, Sb and $Bi_{1-x}Sb_x$ are also considered to provide an opportunity to avoid the problems of the Mg metal anode.^[127, 128] This Mg ion cell concept might be able to lead to other approaches to overcome current issues, as in the case of Li ion cells.

4 Metal/air batteries

A unique feature of metal/air batteries compared to other batteries is the gas phase O_2 cathode which does not require oxygen to be stored in the cell, but can be supplied by air. Because of

the absence of a solid state cathode material in the cell and the high theoretical energy density of light metal anodes, in principle, metal/air batteries can have a very high specific energy (although their practical specific energy is limited due to low utilization efficiency of the metal anode and sluggish kinetics of the O₂ cathode). Metal/air batteries can be considered as a hybrid system of a battery and a fuel cell because they have both the features of fuel cell operation during discharge (consuming O₂) and are electrochemically rechargeable (evolving O₂). In comparison with a fuel cell, metal/air batteries can simply employ the light metal anodes (Zn is also very popular anode material for metal/air batteries although it is not a light metal), which have several advantages such as a comparable theoretical specific energy (shown in Table 19.4), a relatively low prices, abundance and a low environmental impact while the fuel cell suffers from low stability of the electrodes, high cost and complicated design due to the H₂ gas delivery system.^[129]

Metal Oxygen	Cell Voltage (V)	Specific Energy	Energy Density
		(Wh kg ⁻¹)	(Wh L ⁻¹)
CaO	3.11	2972	9960
MgO	3.03	4032	14400
Li ₂ O ₂	2.98	3487	8050
Li ₂ O	2.93	5252	10600
Al ₂ O ₃	2.75	4332	17300
Na ₂ O	1.97	1109	3870

Table 19.4 Metal oxygen specific energies and energy densities^[130]

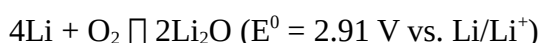
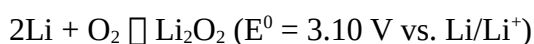
Metal/air rechargeable cells can be classified as rechargeable and refuellable cells depending on the method of charging the cell. The refuellable cell is not a fully electrochemically rechargeable system; instead, it can be recharged by simple mechanical replacement of the discharged anode and used electrolyte with a fresh electrode and electrolyte, respectively, which indicates that the electrochemical operation only involves the discharge process.^[1] The most common type, known as a metal/air cell is a rechargeable type

of cell. The overall electrochemical reaction depends on the anode material and the type of electrolyte such as aqueous, non-aqueous, or solid-state type and their combinations.^{[1, 13, 131-}

^{133]} Because metal anodes react excessively with H₂O, protective layers such as ionically conductive ceramics or glass, e.g. LiSICON or NaSICON type ionic conductors must cover the surface of the metal anode in an aqueous electrolyte.^[134] In aqueous systems, alkaline solutions are commonly used as the electrolyte rather than acidic solutions owing to their better oxygen reduction kinetics, lower overpotentials and a better stability of catalysts. Complicated oxygen reduction reactions (ORRs) which can be classified as four-electron pathway reactions (e.g. O₂ + 2H₂O + 4e⁻ → 4OH⁻, in alkaline solution, E⁰ = 0.401 V vs. SHE) and two-electron pathway reactions (peroxide pathway, e.g. O₂ + H₂O + 2e⁻ → HO²⁻ + OH⁻, in alkaline solution, E⁰ = □ 0.065 V vs. SHE) may occur during the discharge process depending on the catalytic materials and their structure.^[133, 135]

Despite the advantages of aqueous electrolytes such as low cost and high ionic conductivity, the working voltage of the aqueous cells is limited to the voltage window of H₂O corresponding to evolution of H₂ or O₂ gas, and light metal cathodes require special protection to prevent violent reaction of the light metal anodes with H₂O which suggests the potential safety problem caused by mechanical fracture of the protection layer. Some modifications of cell structure proposed to solve these problems, which are composed of a two component electrolyte such as a combination of aqueous and non-aqueous or aqueous and solid state electrolytes.^[136] In addition, organic liquid electrolytes have attracted much attention for light metal anodes due to the stability of metals in organic solvents and the wide voltage window of some organic solvents. The Li/air cell which is one of the popular metal/air rechargeable cells due to its large theoretical specific energy of nearly 11,700 W□h kg⁻¹ (5200 W□h kg⁻¹ when the mass of O₂ is included) commonly employs organic solvents

and Li salts as electrolyte. Basically, the same organic electrolytes used for Li ion cells such as carbonates, ethers and esters with Li salts (LiPF₆, LiAsF₆, LiN(SO₂CF₃)₂ and LiSO₃CF₃) are considered for Li/air cells. There are two major reactions between Li and O₂ simply expressed as:



However, the actual ORRs are not as simple as expressed above, instead, stepwise ORRs occur which are strongly dependent on the electrolytes and catalysts.^[137] Recently, it was also demonstrated that the decomposition of the organic carbonates actively occurs in the carbonate electrolyte system during the discharge process and forms other species such as Li₂CO₃, HCO₂Li, C₃H₆(OCO₂Li)₂ and HCO₂Li on the carbon (positive) electrode when carbonate based solutions are used as the electrolyte. The electrolyte decomposition leads to the accumulation of insoluble solid species in the pores of the air electrode and consumption of the electrolyte, which causes the performance degradation of the cell.^[138] For this reason, the stability of organic electrolytes is considered to be an important issue, therefore, other organic solvents such as esters, ethers and ionic liquids or solid-state electrolytes have been explored to obtain a more stable electrolyte system. Another remarkable approach that can improve the reversibility of the cell reaction is the catalytic materials. Catalysts act very important role to determine the reversible O₂ cathode reaction, which can modify the chemical reaction without being consumed itself, have been extensively studied in the fuel cell field for many years, so detailed mechanisms for oxygen reduction are available in the literature.^[1, 133, 135, 139] Noble metals and their alloys (e.g. Pt or Pt based catalyst) have high stability and excellent electrocatalytic activity, however, their scarcity and high cost are critical problems. Carbonaceous materials, transition metal oxides and inorganic-organic

composites have been studied to replace the noble metal catalyst,^[132] but their effectiveness are not as good as that of the noble metal catalysts.

Among other light metal/air batteries, Mg/air cells have comparable theoretical operating voltage of 3.09 V) and a specific energy of 3910 W h kg⁻¹ based on the overall reaction in aqueous alkaline electrolyte ($2\text{Mg} + \text{O}_2 + 2\text{H}_2\text{O} \rightarrow 2\text{Mg}(\text{OH})_2$).^[140, 141] The abundance, low environmental impact and low price of Mg are significant advantages. However, Mg/air cells in aqueous electrolyte suffer from the low Coulombic efficiency, irreversible polarization characteristics during discharge, fast coagulation of Mg(OH)₂ in the electrolyte and self-discharge of the Mg anode that generates heat. Organic electrolytes might be a solution, but as mentioned above, formation of a passivation layer on the Mg anode limits the usage of organic electrolytes in Mg/air batteries. Another light metal, Al can also be used as an electrode material for metal/air cells due to its high specific energy of 4302 W h kg⁻¹. The overall reaction of the Al/air cell in alkaline electrolyte can be expressed as $4\text{Al} + 3\text{O}_2 + 6\text{H}_2\text{O} \rightarrow 4\text{Al}(\text{OH})_3$ (2.71V), however, this system cannot be electrochemically recharged because the anodic reaction (forming gel-like Al(OH)₃) is not reversible. Instead, the cell can be refueled by a mechanical change of the Al anode. The price of Al is very low as long as the Al(OH)₃ can be recycled as pure Al.^[142] However, Al/air cells in aqueous electrolyte also suffer from rapid self-discharge causing heat-generation as is the case for Mg/air cells.

As discussed here, the metal/air cells, especially Li/air cells, potentially have very promising properties as high specific energy rechargeable cells. It is also necessary to explore the unrevealed scientific and the unsolved technical issues to develop practical metal/air cells. For instance, the reaction mechanism of the O₂ electrode and the electrocatalytic effects are still not very clear, so it will be important to the design and development of the cells if those

reaction chemistries are clearly demonstrated. As is known from fuel cell and metal/air cell research, catalytic materials are essential to achieve a reversible electrochemical reaction of the O₂ electrode, so developing inexpensive catalysts is required to have a competitive price for the cell. In particular, most of the lab scale experiments have been conducted with pure O₂ gas as cathode reactant instead of air due to the negative effect of CO₂ or H₂O which exist in air. This is counter to the basic concept of metal/air batteries, in principle, because if metal/air batteries are only operated with a pure O₂ cathode, an O₂ gas storage cylinder must be included in the battery system, which causes a great reduction of specific energy and safety of the battery. Although current metal/air cells suffer from low practical specific energy and poor cycleability due to the problems discussed above, their potential to be an advanced rechargeable battery is significant, however, scientific breakthroughs are required to realize a commercial rechargeable metal/air battery.

5 Summary and outlook

In recent years, because of the rapid growth of electronic technologies, the market demands for high energy or high power rechargeable batteries have greatly increased. Unfortunately, current Li ion cells cannot satisfy the requirements, e.g. one of main reasons that battery-powered electric vehicles have not been realized is the lack of an appropriate energy storage system. Therefore, it is necessary to develop the advanced anodes, cathodes and electrolytes for Li ion cells or some other alternative energy storage system. As discussed above, light metals such as Li, Na, Mg, Al, etc. can be mainly considered as high specific energy anode materials (or as elements for metal ion batteries) due to their high theoretical specific energy.

Various light metal based rechargeable batteries have been discussed here briefly. In principle, if light metals are directly employed as anode materials as in the Li/S cell, Mg

rechargeable cells and the metal/air cells, a high specific energy can be achieved, but the poor cycle life of metallic anodes and safety concerns still limit their practical use. Metal ion batteries can provide better safety and cycleability, however, their theoretical specific energies are much lower than those of metallic anode systems. Li based systems, such as Li-ion, Li/S and Li/air cells have been the most intensively studied among all light metal cells due to lithium's highly negative potential and large specific capacity. However, other light metals such as Na and Mg also have comparable properties and their own advantages, especially their low price and abundance. Furthermore, those light metals have been much less explored than Li based systems, which means that their ability to compete with Li based cells might be developed through intensive scientific effort. In conclusion, it is clear that all these cells are facing difficult challenges but many promising accomplishments have been reported, therefore, we believe that the next generation rechargeable batteries (containing light metals) will be realized and will contribute to a better world.

6 References

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