



Recent developments in lithium ion batteries

Masataka Wakihara*

Department of Applied Chemistry, Tokyo Institute of Technology, Graduate School of Science and Engineering, Ookayama, Meguro-ku, Tokyo 152-8552, Japan

Accepted 23 February 2001

Abstract

Lithium ion rechargeable batteries are used as the power supply of cellular phones and several other portable electrical devices at present, and demand appears to increase exponentially. The concern about energy sources in the near future, either for electric vehicles (EV) or for large-scale batteries for electricity power storage, has made lithium ion rechargeable battery development into a growth area which has gained high momentum for its research activities. Here, while presenting the state of the art of lithium ion battery technology, the current research into materials, which constitute anode, electrolyte and cathode is described and the underlying problems associated with their development, advantages and drawbacks is analyzed. Both polymer electrolytes, which is a recent topic, as well as conventional organic liquids electrolyte, are also described. © 2001 Published by Elsevier Science B.V.

Keywords: Lithium ion battery; Anode; Electrolyte; Cathode; Polymer electrolyte

1. Introduction

Energy, environmental concerns and information technology (IT) have become thrust areas for the 21st century as they are closely linked to technological development. The search for energy sources to provide comfort and a smooth lifestyle have taken place since the beginning of civilization and the energy sources used so far include fossil fuel, nuclear energy, solar energy, etc. Beginning with industrialization, there arose a search for more efficient, convenient, pollution-free and safe energy sources. Currently, as the internal combustion engine is a major user of fossil fuel (oil), consuming about 1/3 of the annual total demand for energy, concern over global warming and air pollution has become evident. As an alternative energy source, battery has many advantages. Presently, the lithium ion battery, fuel cell technology and the nickel metal hydride battery have been acclaimed as advanced power sources, slowly replacing several versions of conventional systems such as the lead acid and nickel cadmium batteries. Of all the possible systems, the lithium ion battery stands as a forerunner and market leader with its high energy density in miniature batteries. It is a compact, rechargeable power source stable to over 500 cycles. It can be fabricated in size ranging from a few microns to a large-scale battery capable of providing power for computer memory chips, communication equipment, color motion pictures and electric vehicles (EV).

In Japan, the lithium ion rechargeable battery was first developed with high energy density and high discharge voltage (3.7 V) and introduced into the market place as early as 1991; Japan now supplies about 90 percent of the total battery market. Although a cylindrical battery was used in the

* Tel.: +81-3-5734-2145; fax: +81-3-5734-2146.

E-mail address: mwakihar@o.cc.titech.ac.jp (M. Wakihara).

early stages, at present prismatic-shaped cells with aluminum laminated version and square-shaped cells have flooded the market together with the rapid spread of cellular phones. The EV battery has reached the level of prototype test trials and should contain lithium ion batteries as the major part of the power source from in the years to come.

2. Features of the lithium ion rechargeable battery

The energy density per unit volume (Wh/l) and per unit weight (Wh/kg) of various rechargeable batteries are shown in Fig. 1 (not all batteries fall within the ranges shown). Details of the electrode, electrolyte, battery reaction and nominal voltage of various batteries are summarized in Table 1. Although the nickel hydride and lithium ion battery are both excellent in terms of their volume energy density, the lithium ion battery is superior in weight energy density as it provides 1.5 times as much energy as the nickel metal hydride battery. As shown in Table 1, the nominal voltage of a lithium ion battery is around 3.7 V, which is three times that of conventional nickel batteries (1.2 V) such as Ni–MH and Ni–Cd. The high voltage of the lithium ion battery arises as it uses the chemistry of intercalation reactions of the most electropositive ion, lithium with the cathode and anode. The principle underlying the operation of the lithium ion rechargeable battery is shown in Fig. 2 [1]. The lithium cobaltate, LiCoO_2 , which gives a high discharge voltage is, at present, the major cathode-active material of commercial lithium ion rechargeable batteries. Carbon (C) is used for the anode. This lithium battery couple could not function in an aqueous electrolyte, since its charge termination (cut-off) voltage (~ 4.5 V) is high enough to provide a strongly oxidizing environment resulting in electrolyte decomposition. However, organic liquids such as PC, EC, DEC, DMC with large potential window (stable potential domain) containing dissolved electrolyte salts (lithium salts such as LiClO_4 , LiPF_6 , LiBF_4) are stable to high voltage. The electrolyte is not consumed by the charge–discharge reaction in contrast to the case of the lead acid storage battery. Instead, the lithium ions are shuttled between anode and cathode. They have also contributed to the small size and light weight of the lithium ion battery. As shown in Table 1 and Fig. 2, during charging under an applied voltage, deintercalation of some of the lithium ions from the cathode (LiCoO_2) into electrolyte liquid occurs and simultaneously an equivalent amount of lithium ions from the electrolyte intercalate into the carbon anodes. During discharge, the reverse reaction proceeds spontaneously. On both charge and discharge, charge compensation occurs through the external circuit.

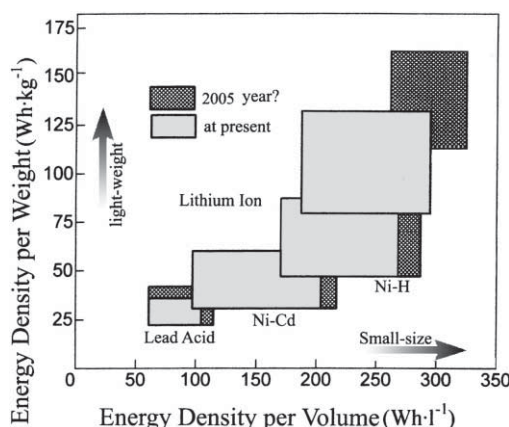


Fig. 1. Energy density of secondary batteries.

Table 1
Various secondary batteries and their characteristics

Battery system	Cathode	Electrolyte/reaction	Anode	Nominal voltage (V)
Lead acid	PbO ₂	$\text{H}_2\text{SO}_4 \text{ aqueous solution}$ $\text{Pb} + \text{SO}_4^{2-} \rightleftharpoons \text{PbSO}_4 + 2\text{e}^- \quad (\text{anode})$ $\text{PbO}_2 + 4\text{H}^+ + \text{SO}_4^{2-} + 2\text{e}^- \rightleftharpoons \text{PbSO}_4 + 2\text{H}_2\text{O} \quad (\text{cathode})$ $\text{PbO}_2 + 2\text{H}_2\text{SO}_4 + \text{Pb} \xrightleftharpoons[\text{charge}]{\text{discharge}} 2\text{PbSO}_4 + 2\text{H}_2\text{O} \quad (\text{total reaction})$	Pb	2
Ni–Cd	NiOOH	$\text{KOH aqueous solution}$ $\text{Cd} + 2\text{OH}^- \rightleftharpoons \text{Cd}(\text{OH})_2 + 2\text{e}^- \quad (\text{anode})$ $2\text{NiOOH} + 2\text{H}_2\text{O} + 2\text{e}^- \rightleftharpoons 2\text{Ni}(\text{OH})_2 + 2\text{OH}^- \quad (\text{cathode})$ $2\text{NiOOH} + \text{Cd} + 2\text{H}_2\text{O} \xrightleftharpoons[\text{charge}]{\text{discharge}} \text{Ni}(\text{OH})_2 + \text{Cd}(\text{OH})_2 \quad (\text{total reaction})$	Cd	1.2
Ni–MH	NiOOH	$\text{KOH aqueous solution}$ $\text{H}_2 + 2\text{OH}^- \rightleftharpoons 2\text{H}_2\text{O} + 2\text{e}^- \quad (\text{anode})$ $2\text{NiOOH} + 2\text{H}_2\text{O} + 2\text{e}^- \rightleftharpoons 2\text{Ni}(\text{OH})_2 + 2\text{OH}^- \quad (\text{cathode})$ $2\text{NiOOH} + \text{H}_2 \xrightleftharpoons[\text{charge}]{\text{discharge}} 2\text{Ni}(\text{OH})_2 \quad (\text{total reaction})$	Hydrogen adsorbed alloy	1.2
Lithium ion	CoO ₂	$\text{Organic electrolyte} + \text{Li salt}$ $\text{Li}(\text{C}) \rightleftharpoons \text{Li}^+ + \text{e}^- \quad (\text{anode})$ $\text{Li}^+ + \text{e}^- + \text{CoO}_2 \rightleftharpoons \text{LiCoO}_2 \quad (\text{cathode})$ $\text{Li}(\text{C}) + \text{CoO}_2 \xrightleftharpoons[\text{charge}]{\text{discharge}} \text{LiCoO}_2 \quad (\text{total reaction})$	C + Li	3.7

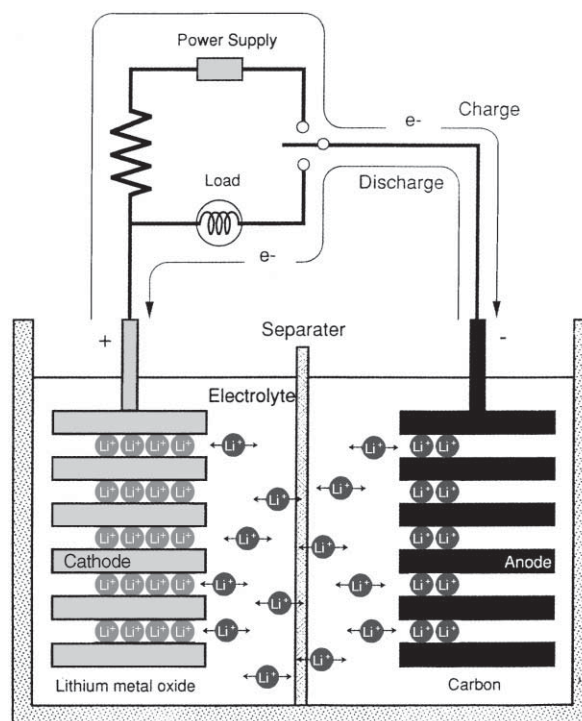


Fig. 2. Principle of lithium ion battery.

A lithium ion rechargeable battery is also known as a swing battery or rocking chair battery since two-way movement of lithium ions between anode and cathode through the electrolyte occurs during charge and discharge processes. Increasing high voltages are associated with increasing difficulty in removing a lithium ion from a particular site during charge or discharge; the site with the lowest potential energy will be occupied first by lithium ions. The redox potential of the lithium-intercalated graphite anode does not differ much from the lithium anode potential and falls by only ~ 0.2 V below that of lithium metal (i.e. the interaction between a lithium ion and the host carbon structure is small). Since lithium is intercalated into and not deposited over the surface of the graphite anode, the anode in a lithium ion battery differs from a pure lithium metal anode. Unlike the lithium metal anode, the graphite anode does not lend to dendrite formation during charging, and this eliminates any short circuits and thereby, provides safety to the cells.

A cylindrical-type battery is shown in Fig. 3 [2]. The aluminum foil, which is easy to process and is resistant to an oxidizing potential is used as the current collector for the cathode. Copper foil is used as the anode current collector since it does not react with lithium ion at low electrical potential. Fine, porous, thin films of polyethylene or polypropylene are used as separators, and they operate orthopedically on a sheet with binders (Teflon, PVdF, etc.) and conductive additives (acetylene black, ketjen black, etc.), which is rolled in the shape of a cylindrical pipe. The ionic conductivity of the organic liquid electrolyte containing lithium ions is 10^{-2} S/cm at room temperature, which is too small compared to the conductivity of aqueous electrolytes. In order to minimize the internal resistance of the cell so as to secure sufficient current and energy capacity, the separator films are processed into thin sheets with large surface area. The materials selected for use should have excellent thermal stability. When the temperature in the battery rises during unwarranted conditions such as an external short circuit, decomposition of the electrolyte occurs resulting in a build-up of

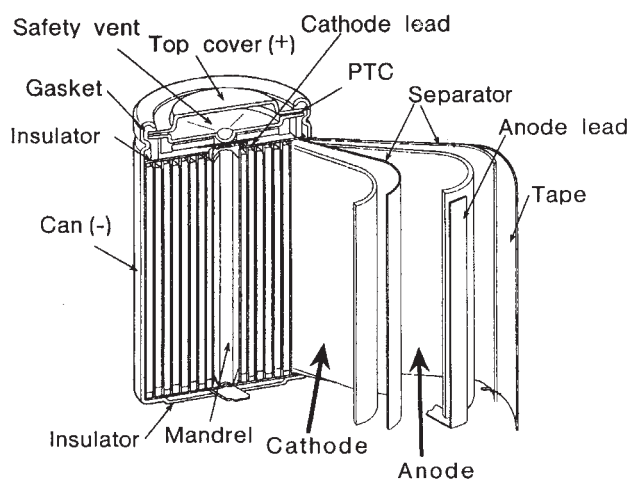


Fig. 3. A structure of cylindrical lithium ion battery.

gas pressure. To provide safety, a PTC element and a small gas discharge vent are placed inside. The lithium ion rechargeable battery marketed now by the Sony Company (SONY US18650; height 65 mm, diameter 18 mm and weight 45 g) is high-tech type with a cut-off voltage control circuit charger and is reported to have a nominal capacity of 1800 mAh with cycle life as high as 500.

3. Materials development for lithium ion rechargeable battery

3.1. Anode materials

In the lithium ion rechargeable battery marketed now, carbon is used as the anode-active material. Graphite is built of ABAB layers, which are held together by van der Waals forces; each layer contains conjugated sp^2 bond. If lithium ions intercalate into these layers, the layer arrangement changes to AAA^{2-} . Thus, graphite serves as the host structure for lithium intercalation and the structure is resilient enough to provide reversibility by allowing easy insertion and deinsertion of lithium. Graphite exists in various forms ranging from a crystalline state to an almost amorphous state, and the raw material used to produce anodes include natural graphite, oil pitch, coal tar, hydrocarbon gas, benzene, various resins, etc. These anodes are categorized into (1) graphite, (2) non-graphitized glass-like carbon (hard carbon) which does not graphitize even if it is heat treated at high temperature and (3) soft carbon, easily changeable with heat treatment. The schematic profile of these carbons is shown in Fig. 4 [1]. Generally, graphite and hard carbon are used as anodes. In practice, at room temperature, graphite accepts sufficient lithium to form LiC_6 which on delithiation can deliver 372 mAh/g. The intercalation of lithium into graphite and the electrochemical characteristics of graphite anodes have been reported by many researchers [3–5]. The relation between the electrochemical intercalation of lithium and the crystal structure of various carbons has been described in detail by Dahn et al. [6]. The charge–discharge curve of graphitized, micron-sized, mesocarbon micro beads (MCMB) is shown in Fig. 5 [7]; the graphite anode sintered at 3000°C has a capacity of 400 mAh/g during charging, while on discharge delivers a capacity as low as 290 mAh/g. This is based on the irreversible reaction (retention) when a thin, lithium ion conductive film (solid electrolyte interface, SEI) is formed on the surface of graphite during the first charge state. In

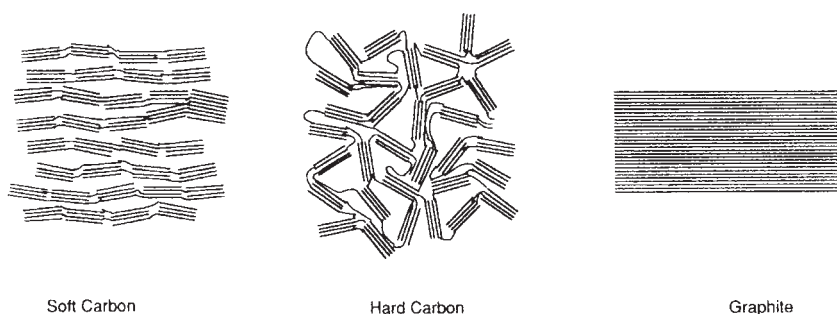


Fig. 4. Three types of carbon.

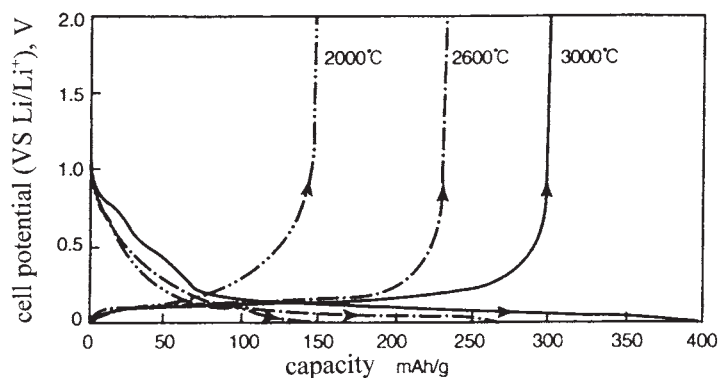


Fig. 5. Charge–discharge curve of MCMB heat treated at various temperatures.

graphite, since the charge–discharge voltage is flat, when it is combined with a cathode, the flat voltage discharge pattern is maintained. Such discharge characteristic is a prime requirement in most miniature electrical devices. On the other hand, in hard carbon prepared from polycondensation of oil pitch, lithium is taken in, not only between the carbon layers but also in the crevices between crystal particles (so-called doping place), and as a result, hard carbon accepts more lithium than given by the formula LiC_6 and becomes a high capacity anode. The charge–discharge curve of the first cycle of a typical hard carbon (pseudo-isotropic carbon, PIC) is shown in Fig. 6 [8]. Various

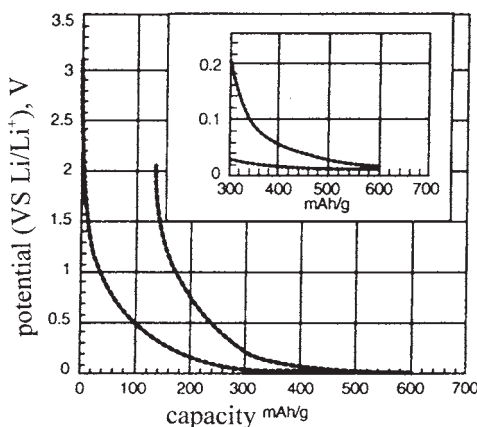


Fig. 6. Charge–discharge curve of a hard carbon (PIC).

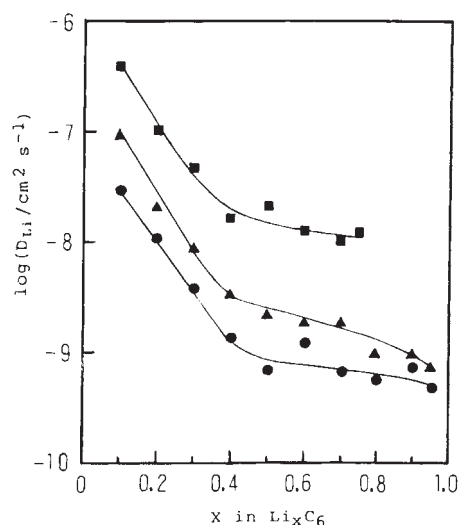


Fig. 7. Variation of chemical diffusion coefficient of lithium in carbons ((solid square) mesophase pitch-based carbon fiber heated at 3000°C; (solid triangle) artificial graphite; (solid circle) natural graphite) in 1 M LiPF₆-EC/DEC (1:1) electrolyte.

models of the microstructure of hard carbon have been proposed which to possess micro cavities such as pores and voids [9]. Some hard carbons are thought to intercalate or absorb lithium between graphene layers [10,11]. For hard carbons, the irreversibility (retention) of the first cycle as well the potential change that accompanies intercalation is considerable compared with graphite. When hard carbon is used as anode material, the discharge voltage gradually changes with time. Such a discharge pattern permits easy estimation of the remaining capacity of the cell. Also, when several cells with various initial discharge voltages (when unbalance arises in the capacities of cells in a battery) are connected in parallel for the cells with hard carbon as anode, the total battery system maintains a balanced voltage throughout its discharge.

Generally, carbon anodes do not have large energy capacity, and the diffusion of the Li⁺ ions between carbon layers is not fast. The chemical diffusion coefficient, $\tilde{D}$, of Li⁺ within carbon is closely related to the power density of battery. Some graphitized carbon fiber has $\tilde{D}$ which is one order of magnitude higher than that in natural graphite (Fig. 7) [12]. Takamura et al. [13] reported recently that covering the entire surface of a graphite fiber with an evaporated film of metallic Ag, Zn or Sn gives a promising technique for improving charge–discharge reaction rates. The most reasonable explanation of the effect is that a new SEI forms on the metal surface. It has been reported that B-doped mesophase pitch-based carbon fiber (MPCF) has an increase of about 10% in its charge capacity with improved cycle efficiency [14].

The search for newer and higher performance anode material leads to the development of alloy anodes based on Sn [15–17] and Si [18,19]. Though the lithium intercalated into Li₄M–Li_{4.4}M (M: metal) showed a high capacity of about 800–3000 mAh/g, a stable cycling performance was not obtained as the associated volume change was more than four times during lithium insertion. The use of oxide anode was also proposed and the tin oxides [20,21], InVO₄ [22], FeVO₄ [22] and Brannerite-type MnV₂O₆ [23] have been examined. Almost all these oxides change their form from crystalline to amorphous during lithium intercalation. The structure of Brannerite is shown in Fig. 8. It shows a very high capacity (~1000 mAh/g) during first intercalation, but thereafter, shows very high irreversible reaction (retention) and reduced lithiation capacity. The large capacity fade on cycling must be solved for their practice use [23]; stabilization of the structures of these oxide

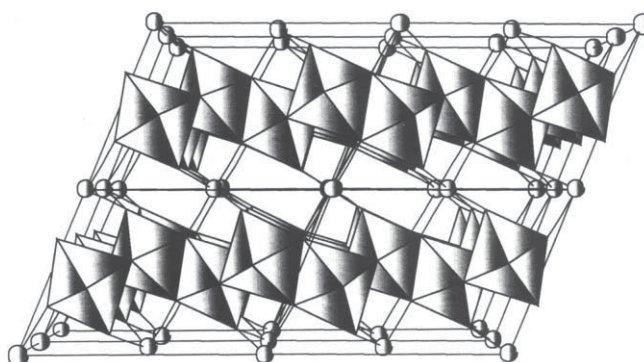


Fig. 8. Structure of Brannerite. Mn is represented by the circles and vanadium is located in the center of each octahedron.

materials may be possible by selective partial substitution of the transition metals with other elements.

3.2. Electrolyte materials

3.2.1. Organic electrolyte liquid

In lithium ion rechargeable batteries, since the mean charge or discharge voltage remains beyond 3 V ranges, an aqueous electrolyte cannot be used as it would decompose. Hence, inorganic salts (for example, LiClO_4) dissolved in organic liquids with a large stability window have been considered as possible electrolytes. To be a good electrolyte, such a non-protonic electrolyte must have good ionic conductivity, high chemical stability, assure safety and be cost-effective. The physical properties of some important organic solvents at room temperature are summarized in Table 2 [24] and their chemical formulae are shown in Fig. 9. Since a lithium ion rechargeable battery usually operates between -20 and $+60^\circ\text{C}$, solvents with low melting point, high boiling

Table 2
Physical properties of solvents at 25°C (unless otherwise noted)

Solvent	mp ($^\circ\text{C}$, 1 atm)	bp ($^\circ\text{C}$, 1 atm)	Relative permittivity	Viscosity (cP)	Dipole moment (D)	DN ^a	AN ^b
Acetonitrile (AN)	-45.72	81.77	38	0.345	3.94	14.1	18.9
γ -Butyrolactone (BL)	-42	206	39.1	1.751	4.12	—	—
Diethylether (DEE)	-116.2	34.60	4.27	0.224	1.18	19.2	3.9
1,2-Dimethoxyethane (DME)	-58	84.7	7.20	0.455	1.07	24	—
Dimethylsulfoxide (DMSO)	18.42	189	46.45	1.991	3.96	29.8	19.3
1,3-Dioxolane (DOL)	-95	78	6.79 ^c	0.58	—	—	—
Ethylene carbonate (EC)	39–40	248	89.6 ^d	1.86 ^c	4.80	16.4	—
Methylformate (MF)	-99	31.50	8.5 ^e	0.330	1.77	—	—
2-Methyltetrahydrofuran (MeTHF)	—	80	6.24	0.457	—	—	—
3-Methyloxazolidin-2-one (MO)	15.9	—	77.5	2.450	—	—	—
Propylene carbonate (PC)	-49.2	241.7	64.6	2.530	5.21	15.1	18.3
Sulfolane (S)	28.86	287.3	42.5 ^c	9.87 ^c	4.7	14.8	19.3
Tetrahydrofuran (THE)	-108.5	65.0	7.25 ^c	0.46 ^c	1.71	20.0	8.0

^a Donicity.

^b Acceptor number.

^c At 30°C .

^d At 40°C .

^e At 20°C .

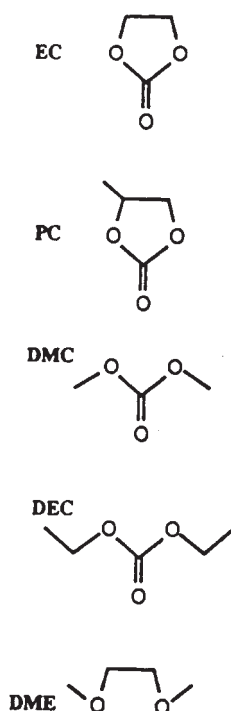


Fig. 9. Structural formulae of main organic solvents.

point and low vapor pressure are highly desirable. The ionic conductivity of Li^+ is proportional to its mobility and the number of mobile ions. Although cyclic carbonic acid esters (carbonate) like PC and EC have high dielectric constants, their viscosity values are high due to the interaction between molecules, which results in deviation of the electric charge of the molecule. Lower viscosity is more desirable for easier movement of the lithium ion. On the other hand, in chain-like esters such as dimethyl carbonate (DMC) and diethyl carbonate (DEC), even though their viscosity and dielectric constant values are quite low, they do not remain much restrictions for the movement of lithium ions between the molecules. Moreover, if the dielectric constant becomes large, the coulombic force between positive and negative sites in a molecule becomes high, imparting a fair degree of ionic dissociation in the neighboring molecule. It is common practice to mix two or more solvents so as to obtain a desired set of properties which is suitable for high performance batteries. The molar conductivity of PC + DMC using LiClO_4 or LiPF_6 is shown in Fig. 10 [25]. Since the electrolyte based on PC is reported to decompose in contact with graphitized carbon anode [26–28] a suitable solvent mixture (EC/DEC) has been recommended by Yamaki et al. [29]. It has also been proposed that lithium carbonate (Li_2CO_3) has an important role in providing a protective film on the surface of carbon [26]. The conductivity of mixtures of EC with other solvents is summarized in Table 3 [24]. The systems presented here show values around 10^{-2} S/cm. The conductivity of electrolytes based on mixed carbonate solvents is generally about one half that of electrolytes with DME as the co-solvent, although this depends on the type of lithium salt which is dissolved in it. The effect of electrolyte composition on the charge–discharge characteristics of carbon materials has been examined extensively [30–32]. In usual organic solvents, the water content must be less than 20 ppm, in order to prevent possible chemical side-reaction with lithium. From various investigations, including thermal stability and cyclic voltammetry, LiPF_6 -based organic electrolyte has become the electrolyte of choice for most commercial handy-type electronic products. The organic electrolyte

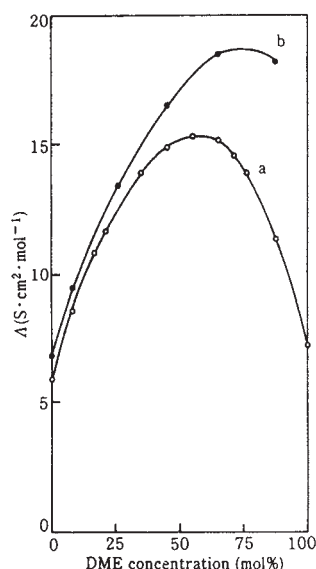


Fig. 10. Variation in the molar conductivity of (a) 1 M LiClO_4 and (b) LiPF_6 with solvent composition in mixed PC + DME at 30°C [22].

chosen must be non-inflammable with a wide potential window of more than 5 V on the upper side to satisfy safety requires events and be compatible with a wide range of cathode materials.

3.2.2. Polymer electrolyte

When aiming at developing a lithium ion rechargeable battery with full safety features, an all-solid electrolyte becomes very attractive. The development of polymer electrolytes has been in progress for some time, followed by which there has appeared in the market, a polymer-based rechargeable battery (plastic lithium ion battery, PLI) containing a polymer electrolyte membrane. The membrane acts both as the electrolyte and the separator. The concept is appealing to the battery industry since PLI batteries are expected to be of low cost and more easily sealed than their liquid electrolyte counterparts. The absence of free liquid implies that PLI batteries can be more easily

Table 3
Conductivity of EC-based electrolytes (EC: co-solvent, 1:1 by volume) at 25°C

Electrolytic salt (1 mol/dm^3)	Co-solvent	Specific conductivity (mS/cm)
$\text{Li}(\text{CF}_3\text{SO}_2)_2\text{N}$	DME	13.3
	DMC	9.2
	DEC	6.5
	MP	10.8
LiCF_3SO_3	DME	8.3
	DMC	3.1
	DEC	2.1
	MP	3.7
LiPF_6	DME	16.6
	DMC	11.2
	DEC	7.8
	MP	13.3

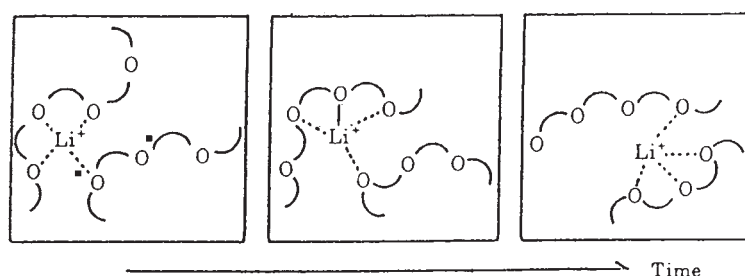
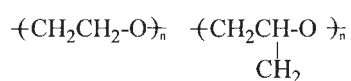


Fig. 11. Mechanism of Li^+ ion conduction in intrinsic (dry) SPE polymer.

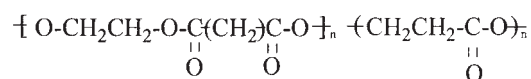
compacted in light-weight plastic containers, unlike conventional batteries which require metallic casing.

In 1973, Wright [33] made the first measurement of ionic conductivity in polyethylene oxide (PEO) complexed with sodium ions. Armand et al. [34] first examined lithium ion conductivity of mixed lithium salts in PEO and applied it to lithium secondary battery. The conduction mechanism of the lithium ion became clear gradually afterwards. Fig. 11 shows the segmental motion of the polymer chain in the amorphous state [35]. These electrolytes are intrinsic (dry) solid polymer electrolytes (SPE); cation mobility is regulated by lithium ion–polymer interaction involving cation ether oxygen coordination bonds. It has also been explained how local relaxation and segmental motion of the host polymer chains is essential to give high conductivity of the electrolyte. Many extensive reviews have been published [36–39]. Some examples for the dry SPE are shown in Fig. 12. Lower temperatures favor crystallization of the polymer in such dry SPE, and there is no practical use when the associated ionic conductivity falls below 10^{-8} S/cm at room temperature [34]. Therefore, to develop elastic and self-supporting polymer electrolytes, bridging of PEO chains [40], introduction of side chains [41,42] (comb-type polymer), blending of different kinds of polymers [43] and improvement of lithium salt (supporting salt) have all been tried and polymer electrolytes with conductivity of 10^{-3} – 10^{-4} S/cm at room temperature developed. Recently, Watanabe et al. [44] obtained a polymer electrolyte with high ionic conductivity using high molecular weight (10^{-5} – 10^{-6}) comb-shaped polymers, poly[ethylene oxide-co-2-(2-methoxyethoxy)ethyl glycidyl ether]

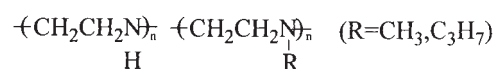
polyether



polyester



polyamine



polysulfide



Fig. 12. Examples of intrinsic (dry) SPE polymers.

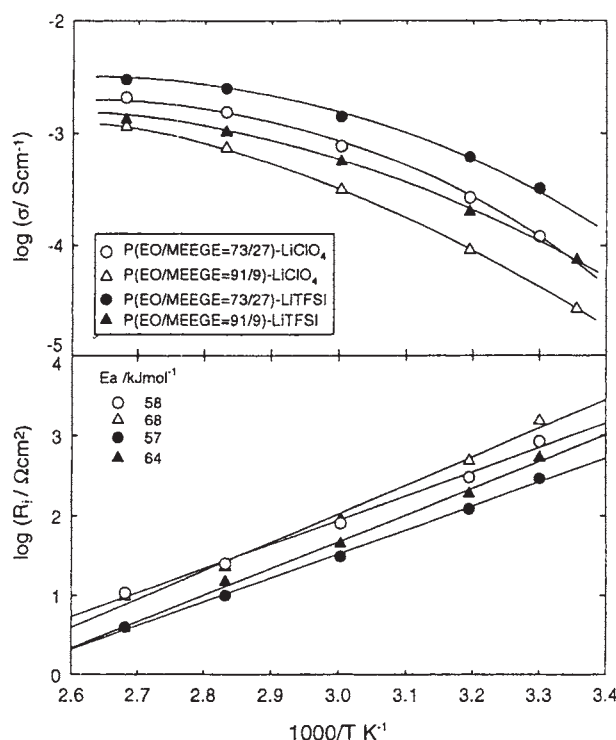


Fig. 13. Arrhenius plots of ionic conductivity (top), and interfacial resistance at the lithium electrode interface (bottom) for P(EO/MEEGE) electrolytes ($[Li]/[O] = 0.06$).

(P(EO/MEEGE)). The data are shown in Fig. 13 [44]. With increasing MEEGE content, the conductivity increased appreciably due to the fast ion transport assisted by highly flexible ether side chains. The imide salt LiTFSI ($LiN(CF_3SO_2)_2$) has the highest conductivity in intrinsic dry polymer at present. However, when organic plasticizer is added to the PEO host polymer, it is prone to attack the surface of the aluminum current collector in the cathode.

Another type of polymer electrolyte known as gel-type solid polymer electrolyte, was first proposed by Feuillard and Perche [45]. This gel-type SPE contains a small amount of suitable organic liquid known as a plasticizer. Plasticizer-containing PAN or PMMA polymer host has been reported to provide high ionic conductivity. The plasticizer effects the polymer in two ways: (1) it makes segmental motion easier and (2) it provides liquid-like character similar to that of a liquid electrolyte. Together, these provide enhanced ionic conductivity in the gel polymer. Plasticizer addition increases choice of host polymers enormously. The relevance of gel polymers to polymer batteries has been fully recognized by Abraham and Alamgir [46,47] and Nagasubramanian et al. [48]. An example of the host polymer for gel SPE is shown in Fig. 14. The ionically conducting polymer (three-dimensional bridge-type polyalkyleneoxide) presented by SANYO recently is shown in Fig. 15 [49]. For the weight ratio of polymer to electrolyte solution 1:10, the ionic conductivity values obtained were $\sim 5 \times 10^{-3}$ S/cm at 25°C and 2×10^{-3} S/cm at -10°C . Such high ionic conductivity values are almost same as those shown by organic liquid electrolyte solutions. There are reports that the ionic conductivity was slightly improved when inorganic fillers such as γ - $LiAlO_2$ and SiO_2 , etc. were added to the gel-type SPE [50–52]. The ionic conductivity of gel-type SPE is around 10^{-3} S/cm at room temperature which is far above that of dry SPE and gel-type SPE stands next only to dry solid polymer electrolyte in providing safety to the polymer. Usually, both Li^+ and the related

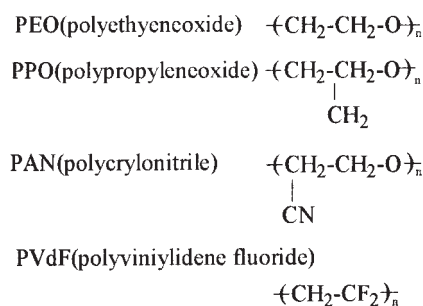


Fig. 14. Some host polymers of gel SPE.

anion are mobile in amorphous polymer electrolytes [53], and the transference number of Li^+ is less than 0.5. Methods to evaluate the transference number of lithium ions have been proposed by several researchers [54,55]. In general, polymer electrolytes have lower conductivity than liquid electrolytes and cannot deliver high power in room temperature and in particular, low temperature batteries. However, polymer electrolytes have many excellent points such as ease of battery fabrication in various shapes and better safety than conventional organic liquid electrolytes.

3.3. Cathode materials

Whittingham [56] first proposed the feasibility of using an inorganic compound, TiS_2 for non-aqueous secondary batteries of high specific and power density during the mid-1970s. This compound has good metallic character and undergoes lithium reversible intercalation. Despite its constant discharge voltage in excess of 2 V with current densities of 1–10 mA/cm^2 , the difficulties with practical non-aqueous batteries and reversible deposition over lithium negative electrode has restricted commercial $\text{Li}_x\text{TiS}_2/\text{Li}$ cells to button-size units. In 1980, Mizushima et al. [57] proposed using layered LiCoO_2 with $\alpha\text{-NaFeO}_2$ structure as an intercalation cathode. The measured open circuit voltage of the cell $\text{Li}_x\text{CoO}_2/\text{Li}$ was approximately twice that of Li_xTiS_2 giving a theoretical energy density of 1.1 kWh/kg . It took around 10 years to put LiCoO_2 to commercial use. This oxide is structurally more stable than TiS_2 .

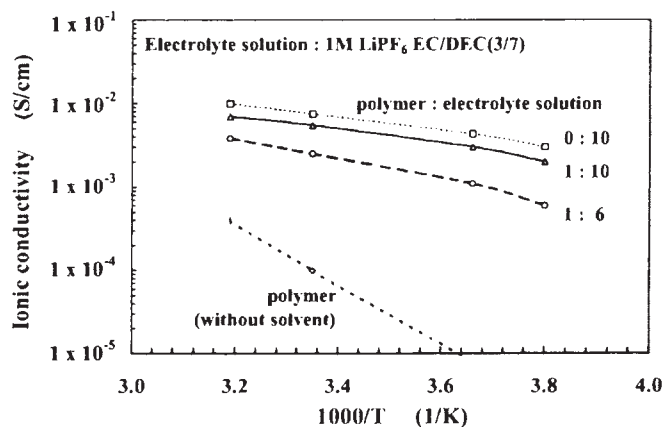


Fig. 15. Temperature dependence of ionic conductivity of gel polymer electrolytes at various weight ratios of polymer to electrolyte solution.

The principal characteristics required for cathode materials are as follows:

1. The discharge reaction should have large negative Gibbs free energy (high discharge voltage).
2. The host structure must have low molecular weight and the ability to intercalate large amount of lithium (high energy capacity).
3. The host structure must have high lithium chemical diffusion coefficient (high power density).
4. The structural modifications during intercalation and deintercalation should be as small as possible (long cycle life).
5. The materials should be chemically stable, non-toxic and inexpensive.
6. The handling of materials should be easy.

3.3.1. Materials with α -NaFeO₂ structure

As already stated, α -NaFeO₂-type LiCoO₂ is mainly used for the cathode in present lithium ion batteries. It is relatively easy to prepare. The structure is shown in Fig. 16 [58]; LiNiO₂, LiCrO₂ and LiVO₂, also take this structure. These materials contain first trivalent transition metal ions (Ni, Cr, V) having ionic radius smaller than Mn³⁺. They are rock salt-structured materials based on a close-packed network of oxygen atoms with Li⁺ and M³⁺ ions ordering on alternating (1 1 1) planes of the cubic rock salt structure. This (1 1 1) ordering introduces a slight distortion of the lattice to hexagonal symmetry. Hence, LiCoO₂ crystallizes in the space group ($R\bar{3}m$) with cell constants $a = 2.816$ Å and $c = 14.08$ Å. The lithium ion intercalates into or deintercalates from the van der Waals gap between CoO₂ layers (3a site) reversibly. The discharge curve (current density 0.25 mA/cm²) and the lattice parameter change in Li_{1-x}CoO₂ are shown in Fig. 17 [59]. In general, the a -axis changes little, but the c axis changes from 14.1 to 14.6 Å with lithium deintercalation. Since a new phase appears near $x = 0.5$, cycling is performed usually for x -values $0 < x < 0.5$.

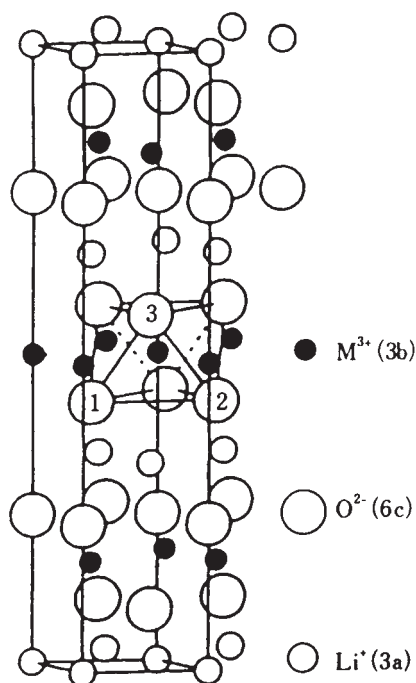


Fig. 16. Structure of α -NaFeO₂.

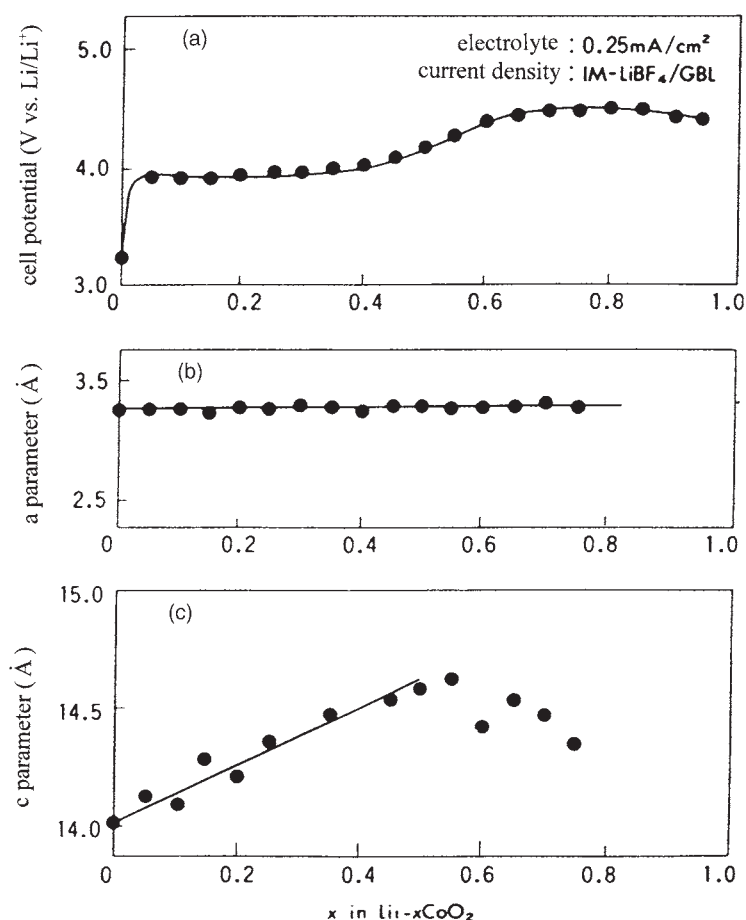


Fig. 17. (a) Cell voltage of $\text{Li}_{1-x}\text{CoO}_2$ ($0 < x < 1$); (b) hexagonal lattice parameter a ; (c) hexagonal lattice parameter c .

As regards mineral resources, only about 10 million t of cobalt deposits are available in the world. However, manganese is about 500 times more abundant (about 5 billion t) than cobalt and is therefore, much cheaper.

LiCoO_2 and LiNiO_2 form a complete solid solution, $\text{LiCo}_y\text{Ni}_{1-y}\text{O}_2$ ($0 < y < 1$) [60]. The charge–discharge behavior of the solid solution was studied first by Delmas and Saadoun [60]. A charge–discharge curve is shown in Fig. 18 [61]. From measurements of ^7Li NMR, it is clear that nickel is oxidized during first step, and cobalt in the second step [62,63]. Although the capacity of LiCoO_2 is about 130 mAh/g, the capacity of $\text{LiCo}_y\text{Ni}_{1-y}\text{O}_2$ with part of the cobalt substituted by nickel, increases to about 150 mAh/g but the discharge voltage falls slightly. This solid solution system, especially composition $\text{LiNi}_{0.8}\text{Co}_{0.2}\text{O}_2$, is expected to form a next-generation cathode, after LiCoO_2 .

Another layered compound of interest, LiNiO_2 , has been explored by several workers but suffers from poor thermal stability in its highly oxidized state ($\text{Ni}^{3+}/\text{Ni}^{4+}$). The Jahn–Teller distortion arising from Ni^{3+} (low spin state) may be a factor responsible for the instability. In fact, the removal of half the lithium from LiNiO_2 results in a metastable layered structure $\text{Li}_{0.5}\text{NiO}_2$ that transforms, on heating to 300°C , to the cubic spinel $\text{Li}[\text{Ni}_2]\text{O}_4$. However, constraints in the cubic structure make the spinel structure selective for insertion of Li^+ ions, reducing the Li^+ ion mobility and hence its conductivity. For these reasons, LiNiO_2 is of not practical importance at present.

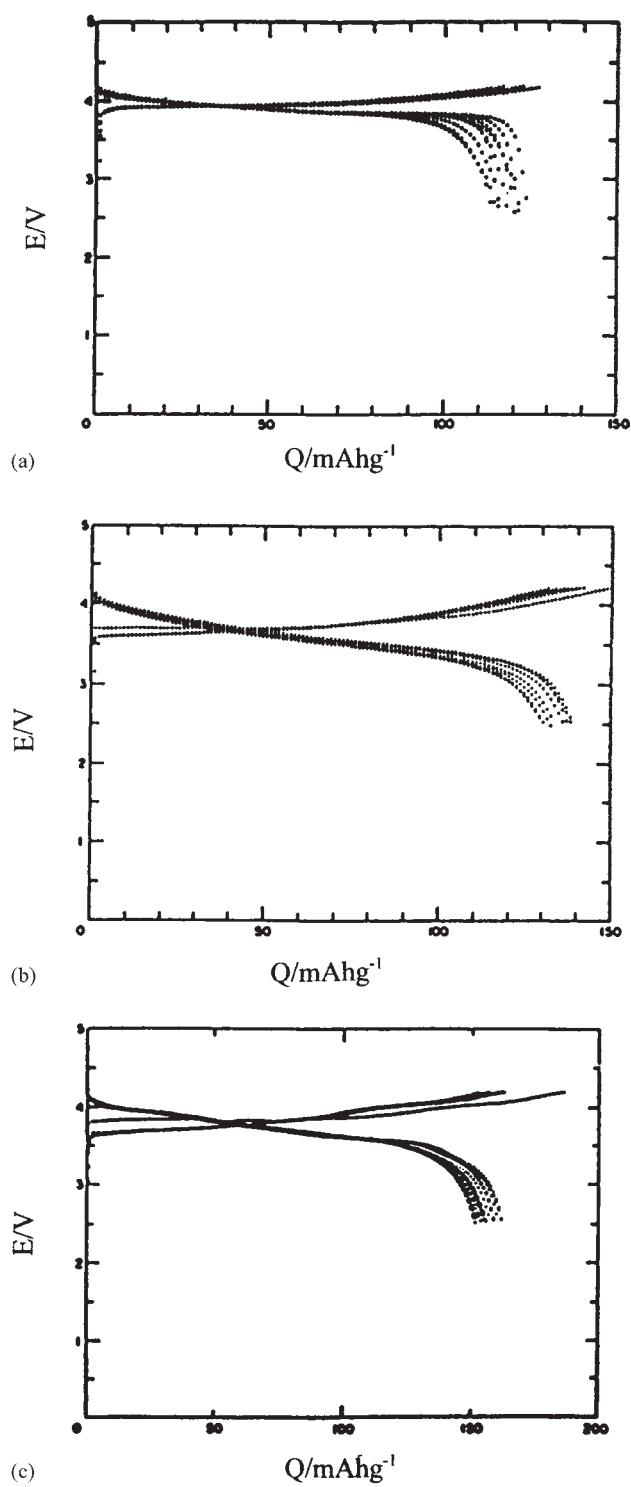


Fig. 18. Charge–discharge curve: (a) $LiCoO_2$; (b) $LiCo_{1/2}Ni_{1/2}O_2$; (c) $LiNiO_2$ (charge density = 0.17 mA/cm^2).

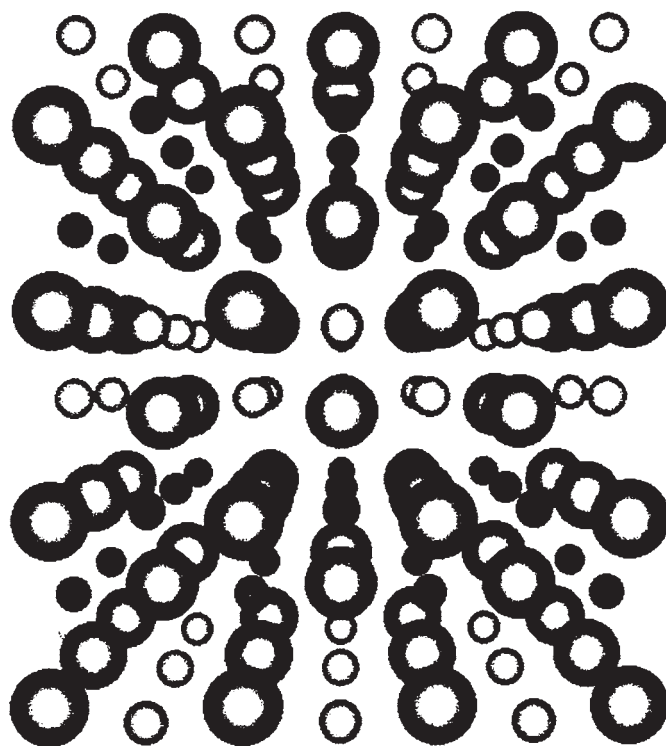


Fig. 19. Zigzag layered structure of LiMnO_2 . (Large circle) oxygen; (small open circle) manganese; (small solid circle) lithium.

3.3.2. $\text{Li}_x(\text{Mn}_{1-x}\text{Co}_x)\text{O}_2$ with zigzag layered structure

LiMnO_2 prepared by usual solid–solid reaction at high temperature slowly transforms into a spinel structure upon cycling. This results in capacity fade, whose extent varies with the cut-off voltage range. This problem has been improved by partial substitution of Mn by other metals. Recently, Armstrong et al. [64,65] prepared NaMnO_2 by solid reaction at high temperature and then synthesized Li_xMnO_2 and $\text{Li}_x(\text{Mn}_{1-y}\text{Co}_y)\text{O}_2$ with zigzag layered structure (Fig. 19) by ion exchange. When the cut-off voltage and current density were set at 2.5–4.8 V and 0.1 mA/cm^2 , respectively, for the composition $\text{Li}_x(\text{Mn}_{0.9}\text{Co}_{0.1})\text{O}_2$, the capacity exceeded 200 mAh/g (Fig. 20). Although it involves difficult a preparative procedure and shows poor cycle life, it has attracted interest among researchers due to its initial high capacity. A detailed review on cathode properties of manganese oxides including lithium manganese oxide spinels, is given by Thackeray [66].

3.3.3. LiMn_2O_4 spinel system

LiMn_2O_4 and related compounds with spinel structure are prepared from manganese salt, lithium salt and another metal salt when substitution is required, in the stoichiometric ratio, at temperatures around 750°C in air. LiMn_2O_4 has the cubic spinel structure ($Fd\bar{3}m$). Lithium occupies the 8a tetrahedral sites with manganese occupying octahedral (16d) site, and the other octahedral site (16c) is vacant. Oxygen forms a face centered cubic array. The ideal cubic unit cell is shown in Fig. 21(a). When Li^+ diffuses in the structure, first it moves from the 8a site to the neighboring empty octahedral 16c site, then to the next 8a site in such a way that the Li^+ ion takes the diffusion path (8a–16c–8a) (Fig. 21(b)). The angle of the diffusion path is about 108° . There have already been

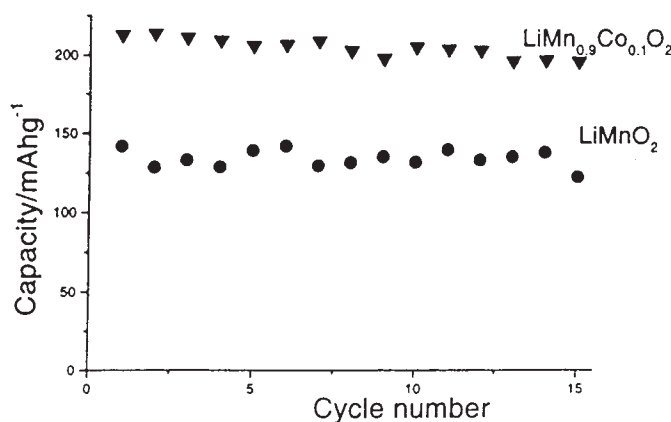


Fig. 20. Cycle performance of LiMnO_2 and $\text{LiMn}_{0.9}\text{Co}_{0.1}\text{O}_2$ [65].

many reports on the charge–discharge characteristics of the cathode $\text{Li}_x\text{Mn}_2\text{O}_4$ [67–69]. The open circuit voltage (OCV) curve of $\text{Li}_x\text{Mn}_2\text{O}_4$ ($0 < x < 2$) is shown in Fig. 22 [67]. Charge–discharge cycling in the region (I + II) is possible, while in the flat region (III), the reaction



proceeds accompanied by a phase transition from cubic spinel to an ordered, tetragonal, NaCl-type structure. Good cycling performance cannot be obtained in the 3 V region ($1 < x < 2$) because a volume expansion of about 6.4% is associated with the phase transition. The reason for the phase transition is an increase in concentration of Mn^{3+} ($3d^4$) ions that form during intercalation of lithium [68], causing a Jahn–Teller distortion. The flat part of the discharge curve in the range $x < 0.5$ is considered to be a two-phase region with a new cubic phase which exists at $x = 0.2$. The slight

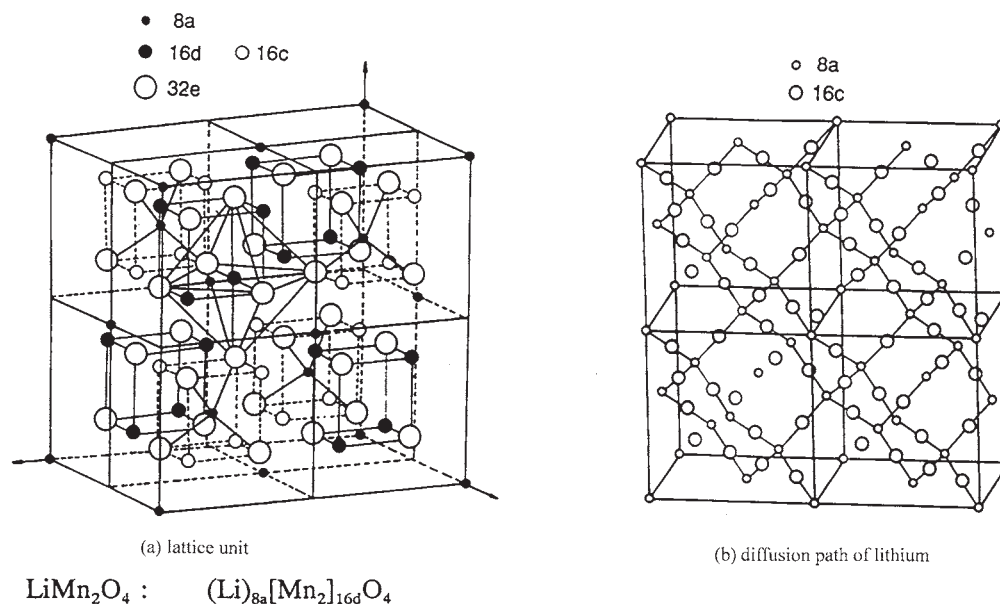


Fig. 21. Structure of spinel (a) unit cell and (b) diffusion path of lithium.

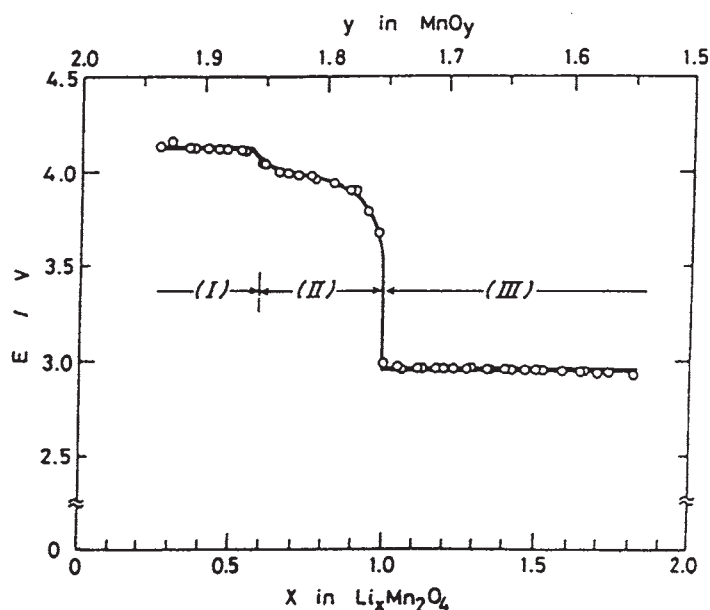


Fig. 22. Open circuit voltage (OCV) curve of $\text{Li}_x\text{Mn}_2\text{O}_4$ ($0 < x < 1$) at 30°C [67].

increase of voltage near $x = 0.5$ corresponds to an ordered configuration of lithium ions on one half of the tetrahedral 8a sites [70]. The charge–discharge curve in the 4 V region of LiMn_2O_4 prepared by the dry-type method by Wakihara et al. is shown in Fig. 23 [71]. Although the initial capacity is about 120 mAh/g, by the 100th cycle, it falls to about 60%. They attributed the capacity fade to weak bonding between Mn on 16d octahedral site and the six surrounding oxygen atoms, and calculated some octahedral bonding energies, including Mn–O, on the basis of thermodynamic data [72]. The result is shown in Table 4 [72]. These data were evaluated using Born–Haber cycle assuming a perfect ionic crystal model. The data show that the bonding of Mn–O is the weakest. So, it was thought that stabilization of the 16d octahedral site is essential for cycle life improvement. In order to stabilize the octahedral sub-lattice, attempts have been made by several workers to partially substitute Mn by other transition and non-transition metals.

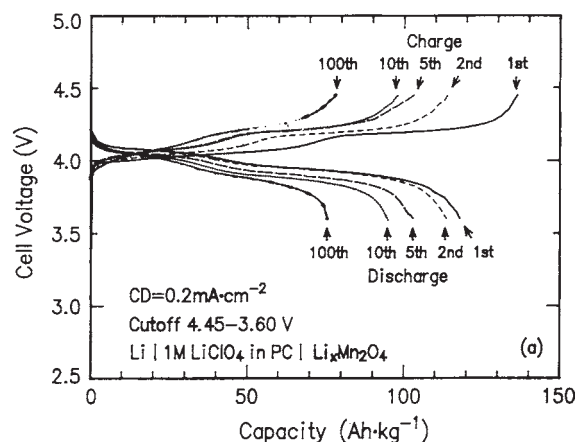


Fig. 23. Charge–discharge curves of $\text{Li}_x\text{Mn}_2\text{O}_4$ in 4 V range at room temperature.

Table 4
Bonding energy of octahedral $\text{MO}_{1.5}$, MO_2 , and $\text{MO}_{1.75}$

	E_{BE} (kJ/mol)		
	$\text{MO}_{1.5}$	MO_2	$\text{MO}_{1.75}$ ($0.5\text{M}_2\text{O}_{3.5}$)
Ti	1602	1912	1757
V	1497	1727	1612
Cr	1340	1492	1416
Mn	1133	1296	1215

The first charge–discharge characteristics of $\text{Li}_x\text{M}_{1/6}\text{Mn}_{11/6}\text{O}_4$ ($\text{M} = \text{Cr}, \text{Co}, \text{Al}$ and Ni) at room temperature are shown in Fig. 24 [71]. In this formula, $\text{M}_{1/6}$ implies that the metal M substitutes 1/12 of manganese at 16d sites. The capacity fade is minimized in all the substituted spinels. The initial discharge capacities ($>110 \text{ mAh/g}$) of substituted spinels $\text{Li}_x\text{M}_{1/6}\text{Mn}_{11/6}\text{O}_4$ ($\text{M} = \text{Cr}, \text{Co}, \text{Al}$) are higher than the initial capacity (95 mAh/g) of $\text{Li}_x\text{Ni}_{1/6}\text{Mn}_{11/6}\text{O}_4$. The nickel-substituted spinel differs from other spinels $\text{Li}_x\text{M}_{1/6}\text{Mn}_{11/6}\text{O}_4$ ($\text{M} = \text{Cr}, \text{Co}, \text{Al}$) due to its lower valence (Ni^{2+}). The substituents Cr^{3+} and Co^{3+} directly substitute for Mn^{3+} , whereas for Ni^{2+} substitution at the Mn^{3+} position, charge compensation increases the amount of Mn^{4+} . Reduction in the amount of Mn^{3+} causes reduced capacity in nickel-substituted spinel. However, there is little change in the discharge voltage with different substituent elements. The variation of energy density with cycle for $\text{LiMn}_{1/6}\text{Mn}_{11/6}\text{O}_4$ ($\text{M} = \text{Cr}, \text{Co}, \text{Ni}, \text{Al}$) is shown in Fig. 25. The cells with substituted LiMn_2O_4 show better cycle characteristics than the one with undoped LiMn_2O_4 . Actually, the electrochemical cycling properties on partial substitution of manganese by other metals has been reported by many researchers [68,71,73,74]. It has been reported that only about 10 mol% of substitution for Mn^{3+} in the 16d octahedral site is sufficient to effect improved cycle performance. It has been observed that Mn^{3+} ($3d^4$) is a Jahn–Teller ion and causes a phase transition from cubic to tetragonal (1.4 kJ/mol) in LiMn_2O_4 near 0°C [75], but the enthalpy of the phase transition in partially-substituted spinels gradually decreases with increasing amount of substituent, and the phase transition is completely suppressed with 10–20 mol% of substitution in octahedral Mn site [74]. A DSC curve of $\text{LiM}_y\text{Mn}_{2-y}\text{O}_4$ obtained by our group is presented in Fig. 26 [74]. For high cycle performance, it is desirable that a phase transition does not occur in the middle of an intercalation reaction.

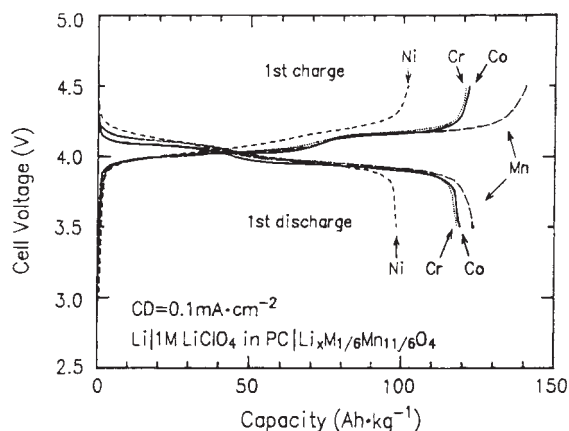


Fig. 24. The first charge–discharge curve of $\text{LiM}_{1/6}\text{Mn}_{11/6}\text{O}_4$ at room temperature.

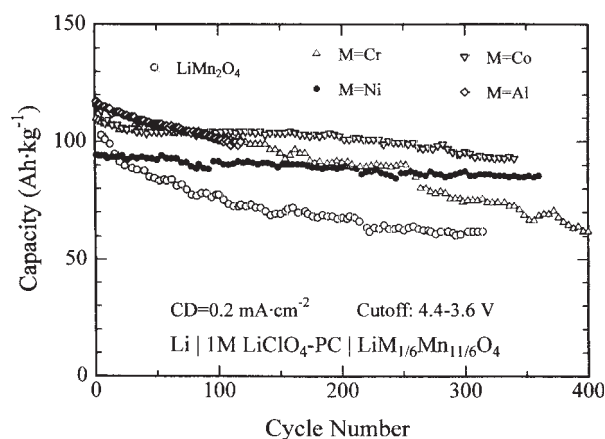


Fig. 25. The relationship between energy capacity and cycle number for $\text{Li}_x\text{Mn}_2\text{O}_4$ at room temperature.

As mentioned above, LiMn_2O_4 and $\text{LiM}_y\text{Mn}_{2-y}\text{O}_4$ can be prepared easily by carrying out high temperature calcination in air. These oxides are cost-effective and environmentally benign cathodes for applications from ranging miniature batteries to large-scale batteries for EV and energy storage applications. However, the capacity fade on cycling is much higher if cycling is performed at higher temperature, 50–70°C. Dissolution of manganese into the organic electrolyte liquid during cycling appears to be one of the causes [76,77]. In addition, the deposition of metallic Mn on the anode surface has also been mentioned as a possible reason for the large capacity fade. In our recent research [78,79], we found that dissolution of Mn is very low in doped LiMn_2O_4 , even at 50°C (Fig. 27) [78,79]. Among these dopants, Co seems to be effective and a good cycling performance has been obtained (Fig. 28) [78,79]. When Mn dissolves into the liquid electrolyte, it exists as Mn^{2+} as shown by ESR [80] and in situ XANES [81] measurements. It is also presumed that some Li^+ from the electrolyte may enter the 16d octahedral sites, causing some Mn^{3+} in the octahedral site to oxidize to Mn^{4+} . The problem of dissolution of Mn at high temperature must be solved for practical applications because the cell temperature in EV could rise as high as 70°C during summer. To overcome Mn dissolution, besides partial substitution, methods such as introduction of defects into

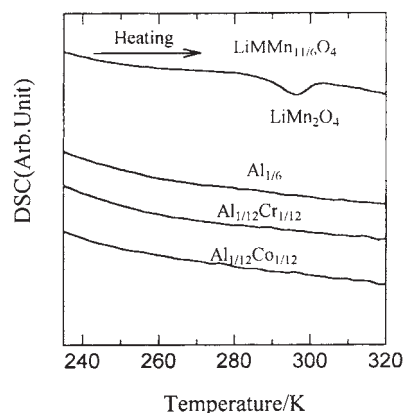


Fig. 26. DSC curves of $\text{LiM}_{1/6}\text{Mn}_{11/6}\text{O}_4$ ($\text{M} = \text{Al}_{1/6}, \text{Al}_{1/12}\text{Co}_{1/12}, \text{Al}_{1/12}\text{Cr}_{1/12}$) and LiMn_2O_4 at temperatures between 235 and 320 K on heating.

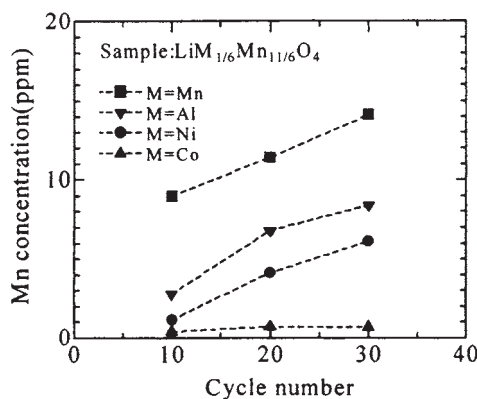


Fig. 27. Dissolved Mn concentration in the electrolyte for $\text{LiM}_{1/6}\text{Mn}_{11/6}\text{O}_4$ ($M = \text{Al}, \text{Ni}, \text{Co}$) at 50°C .

the structure, use of a polymer electrolyte membrane and reexamination of the quality of the electrolyte liquid have all been considered.

In situ XANES and EXAFS spectra sometimes give effective information on the change in valence state of metals during electrochemical cycling. Fig. 29 shows Mn K-edge in situ XANES spectra of $\text{Li}_x\text{Mn}_2\text{O}_4$ during deintercalation of lithium [82]. The absorption spectrum shifts to higher energy with deintercalation of lithium, indicating that Mn^{3+} in the spinel oxidizes to Mn^{4+} .

Considering the possible use of spinel-based cathodes, one may conclude that materials from the $\text{LiM}_y\text{Mn}_{2-y}\text{O}_4$ ($M = \text{Co}, \text{Cr}, \text{Al}, \text{Ni}, \text{Li}$) family will be the most likely candidates for cathodes in the next generation of power sources.

3.3.4. Other oxides

Crystalline V_2O_5 with a shear structure [83,84], amorphous $\text{a-V}_2\text{O}_5$ [85], $\text{a-V}_2\text{O}_5\text{-B}_2\text{O}_3$, and $\text{a-V}_2\text{MoO}_8$ [86] have all been considered. The average discharge voltage is around 2.5 V and is not as high as that of LiCoO_2 and $\text{LiM}_y\text{Mn}_{2-y}\text{O}_4$. Since there is also capacity fade with cycling, these materials have not been exploited for large-scale development. Recently, it has been reported that $\text{Li}_x\text{Fe}_y\text{O}_z$ with ($\text{Li}^+/\text{Fe}^{3+} = 0.69$) prepared at 200°C had a capacity of about 140 mAh/g at an average discharge voltage of ~ 2 V during cycling [87]. Since the cost of Fe is very cheap, it may become an attractive candidate in the future. An olivine (M_2SiO_4)-based cathode using the crevice

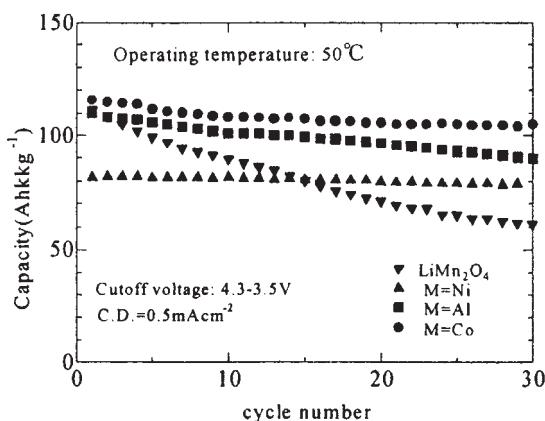


Fig. 28. Cycle performance for $\text{Li} | \text{LiM}_{1/6}\text{O}_4$ ($M = \text{Al}, \text{Ni}, \text{Co}$) and $\text{Li} | \text{LiMn}_2\text{O}_4$ cells at 50°C .

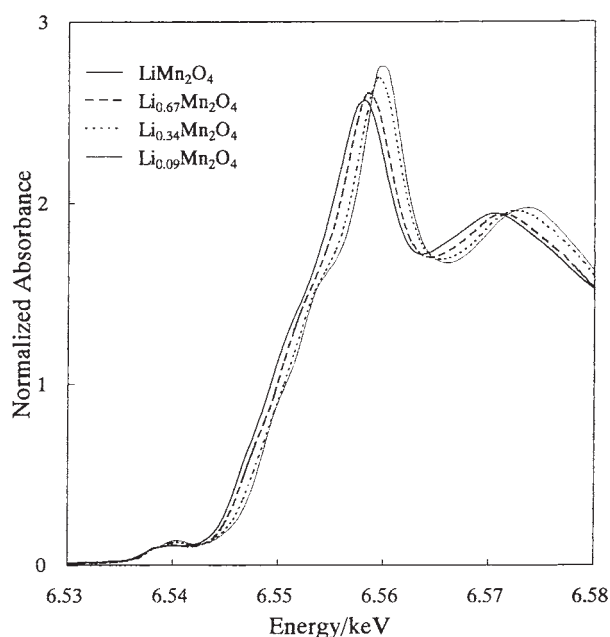


Fig. 29. Mn K-edge in situ XANES spectra of $\text{Li}_x\text{Mn}_2\text{O}_4$ ($0 < x < 1$).

between MO_4 tetrahedra has been reported recently by Padhi et al. [88]. They considered four iron phosphates, $\text{Li}_3\text{Fe}_2(\text{PO}_4)_3$, LiFeP_2O_7 , $\text{Fe}_4(\text{P}_2\text{O}_7)_3$ and LiFePO_4 and found that Li_xFePO_4 delivered 130 mAh/g at an average cell voltage of 3.3 V. In order to increase the discharge voltage, LiCoPO_4 instead of LiFePO_4 has been prepared, and its cycling behaviors examined [89]. Although the average discharge voltage increased to 4.5 V, satisfactory cycleability could not be observed because of gradual decomposition of the organic electrolyte. There are no stable organic electrolyte liquids that work well at discharge–charge voltages above 4.5 V at present, and further work to obtain improved electrical characteristics of organic electrolytes is needed.

4. Manufacture process

So far, the diverse research activities that lead to the development of cathode and anode active materials, separator, electrolyte, current collector (metal foil; cathode is aluminum foil and anode Cu foil), material optimization and possible materials for use in a lithium ion battery have been described.

The manufacturing processes consist of (1) mixing the cathode or anode materials with binder and conductive additive, (2) painting on the current collector (metal foil), (3) drying and (4) pressing (Fig. 30). The next step involves (1) assembly of cathode, anode and the simultaneous rolling-up with separator, (2) electrode insertion, (3) electrolyte injection into the battery case and (4) sealing.

In the electrode manufacturing process, a mixture of active materials with conductive additive such as acetylene black or ketjen black, and a binder such as Teflon or polyvinylidenefluoride (PVdF) dissolved in *n*-methyl-2-pyrrolidinone (NMP) are made in the form of a paste. The paste is painted over both sides of metal foil, dried and roll-pressed. Then it is cut to the desired width. In the case of polymer lithium batteries [38], after carrying out direct polymerization of the gel electrolyte sheet, roll-press is carried out over the cathode and anode sheets which are then cut a suitable size,

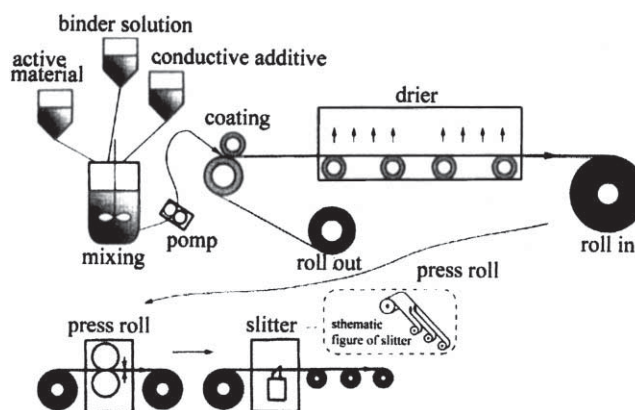


Fig. 30. Schematic processing of cathode film for lithium ion battery.

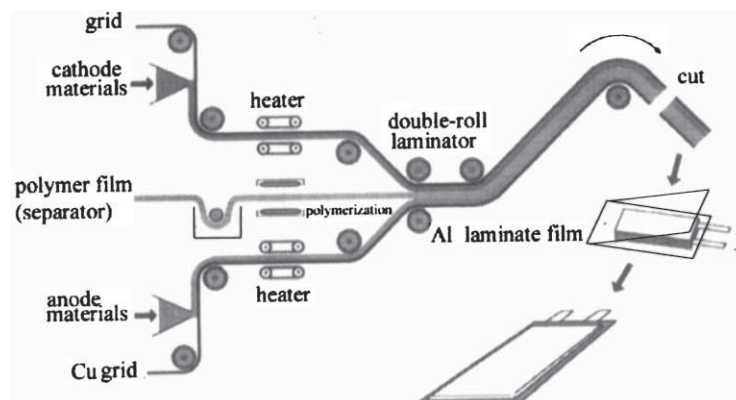


Fig. 31. Schematic manufacture processing of lithium polymer battery.

wrapped in aluminum lamination film and heat welded at the edges (Fig. 31). Finally, the battery is checked for short-circuit over 2–4 weeks. A protective thin film (SEI) will form at the anode–carbon interface during this period. Shipment inspection has to be conducted and the products shipped. Many battery manufacturing companies worldwide have announced their involvement in large-scale production of lithium secondary batteries. However, the level of information released is limited and thus, it is impossible to evaluate the status of the different batteries at this stage.

5. Conclusion

A lithium ion rechargeable battery appears to occupy a prime position in the market place and it took almost a decade to reach this strong position. Attempts have been made to eliminate the use of detrimental heavy metal, to avoid environmental hazards, and to make material improvements to give cost-effectiveness. An immense amount of research has been carried out on the cathode, anode and electrolyte and simplification of the manufacturing process. New materials developments and new technical developments are expected to help realize the goal of large-size batteries to power electric vehicle as well producing a range of small batteries for the next millennium.

Acknowledgements

The author wishes to thank Dr. A. Veluchamy for his valuable discussion and Dr. Y. Uchimoto, Dr. H. Ikuta and Dr. S. Dong for their experimental work and helpful discussion. Financial support from following source: Grant-in-Aid for Scientific Research on Priority Areas (B) (No. 11229201) “Fundamental Studies for Fabrication of All Solid State Ionic Devices” from Ministry of Education, Science, Sports and Culture in Japan.

References

- [1] Y. Nishi, Performance of the first lithium ion battery and its process technology, in: M. Wakihara, O. Yamamoto (Eds.), *Lithium Ion Batteries*, Kodansha, Tokyo; Wiley/VCH, Weinheim, 1998, p. 181.
- [2] K. Nakajima, Y. Nishi, Advanced Li-ion batteries, in: T. Osaka, M. Datta (Eds.), *Energy Storage Systems for Electronics*, Gordon and Breach, Amsterdam, 2000, p. 109.
- [3] Z.X. Shu, R.S. McMillan, J.J. Murry, *J. Electrochem. Soc.* 140 (1993) 922.
- [4] J.M. Tarascon, D. Guyomard, *Electrochim. Acta* 38 (1993) 1221.
- [5] T. Ohzuku, Y. Iwakoshi, K. Swai, *J. Electrochem. Soc.* 140 (1993) 2490.
- [6] J.R. Dahn, A.K. Sleight, H. Shi, J.N. Reimers, Q. Zhong, B.M. Way, *Electrochim. Acta* 38 (1993) 1179.
- [7] N. Takami, in: T. Takamura (Ed.), *Battery Handbook*, Asakura Shoten, Tokyo, 1996, p. 787.
- [8] N. Sonobe, M. Ishikawa, T. Iwasaki, in: *Proceedings of the Abstracts of 35th Battery Symposium*, Nagoya, Japan, 1994, p. 47.
- [9] A. Mabuchi, K. Tokumitsu, H. Fujimoto, T. Kasuh, *J. Electrochem. Soc.* 142 (1995) 1041.
- [10] K. Sato, M. Noguchi, A. Demachi, N. Oki, M. Endo, *Science* 264 (1994) 556.
- [11] T. Zheng, J.S. Xue, J.R. Dahn, *Chem. Mater.* 8 (1996) 389.
- [12] N. Takami, A. Satoh, M. Hara, T. Ohasaki, *J. Electrochem. Soc.* 142 (1995) 1090.
- [13] T. Takamura, K. Sumiya, J. Suzuki, C. Yamada, K. Sekine, *J. Power Sources* 81/82 (1999) 368.
- [14] M. Endo, C. Kim, T. Karaki, Y. Nishimura, M.J. Matthews, S.D.M. Brown, M.S. Dresselhaus, *Carbon* 37 (1999) 561.
- [15] J.O. Besenhard, J. Yang, M. Winter, *J. Power Sources* 68 (1997) 87.
- [16] J. Yang, Y. Takeda, N. Imanishi, T. Ichikawa, O. Yamamoto, *Extended Abstracts, SSI-12, A-31, Halkidiki, Greece*, 1999, p. 88.
- [17] M. Nagayama, T. Morita, H. Ikuta, M. Wakihara, M. Takano, S. Kawasaki, *Solid State Ionics* 106 (1998) 33.
- [18] M. Wakihara, T. Morita, A. Modeki, H. Ikuta, *Extended Abstracts, SSI-12, A-34, Halkidiki, Greece*, 1999, p. 92.
- [19] H. Kim, Y.-J. Kim, D.-G. Kim, H.-J. Sohn, T. Kang, B. Park, *Extended Abstracts, IMLB10, Como, Italy*, 2000, p. 78.
- [20] Y. Idota, T. Kubota, A. Matsuji, Y. Maekawa, T. Miyasaka, *Science* 276 (1997) 1397.
- [21] P. A. Connor, F. Belliard, M. Behn, J.T.S. Irvan, *Extended Abstracts, SSI-12, A-29, Halkidiki, Greece*, 1999, p. 85.
- [22] S. Denis, E. Baudrin, F. Orsini, G. Ouvrard, M. Toboul, J.-M. Tarascon, *J. Power Sources* 81/82 (1999) 79.
- [23] S.-S. Kim, H. Ikuta, M. Wakihara, *Solid State Ionics* 139 (2001) 57.
- [24] M. Morita, M. Ishikawa, Y. Matsuda, *Organic electrolytes for rechargeable lithium ion batteries*, in: M. Wakihara, O. Yamamoto (Eds.), *Lithium Ion Batteries*, Kodansha, Tokyo; Wiley/VCH, Weinheim, 1998, p. 156.
- [25] M. Matsuda, M. Morita, F. Tachihara, *Bull. Chem. Soc. Jpn.* 59 (1986) 1967.
- [26] Y. Ein-Eli, B. Markovsky, D. Aurbach, Y. Carmeli, H. Yamin, S. Luski, *Electrochim. Acta* 39 (1994) 2559.
- [27] D.E. Irish, Z. Deng, M. Odziemkowski, *J. Power Sources* 54 (1995) 28.
- [28] P. Liu, H. Wu, *J. Power Sources* 56 (1995) 81.
- [29] M. Arakawa, J. Yamaki, *J. Electroanal. Chem.* 219 (1987) 273.
- [30] D. Aurbach, Y. Ein-Eli, B. Markovski, A. Zaban, S. Luski, Y. Carmeli, H. Yamine, *J. Electrochem. Soc.* 142 (1995) 2882.
- [31] T. Iijima, K. Suzuki, Y. Matsuda, *Synth. Met.* 73 (1995) 9.
- [32] A. Ohta, H. Koshina, H. Okuno, H. Murai, *J. Power Sources* 54 (1995) 6.
- [33] P.V. Wright, *Br. Polym. J.* 7 (1975) 319.
- [34] M.B. Armand, J.M. Chabano, M.J. Duclot, in: P. Vashista, J.N. Mundy, G.K. Shenoy (Eds.), *Fast Ion Transport in Solids*, North-Holland, New York, 1979, p. 131.
- [35] D.F. Shriver, G.C. Farrington, *Chem. Eng. News* 20 (1985) 42.
- [36] B. Scrosati, R. Neat, in: B. Scrosati (Ed.), *Publication of Electroactive Polymers*, Chapman & Hall, London, 1993, p. 182.
- [37] M. Armand, J.Y. Sanchez, M. Gauthier, Y. Coquette, in: J. Lopkowski, P.N. Ross (Eds.), *Electrochemistry of Novel Materials*, VCH, Weinheim, 1994, p. 65.

- [38] B. Scrosati, Lithium ion plastic batteries, in: M. Wakihara, O. Yamamoto (Eds.), *Lithium Ion Batteries*, Kodansha, Tokyo; Wiley/VCH, Weinheim, 1998, p. 218.
- [39] F.B. Dias, L. Plomp, J.B. Veldhuis, *J. Power Sources* 88 (2000) 169.
- [40] J.F. Le Nest, S. Callens, A. Gandini, M.B. Armand, *Electrochim. Acta* 37 (1992) 1585.
- [41] P.M. Blonsky, D.F. Schriver, P. Austin, H.R. Allcock, *Solid State Ionics* 18/19 (1986) 258.
- [42] A. Nishimoto, M. Watanabe, Y. Ikeda, S. Kohjiya, *Electrochim. Acta* 43 (1998) 1177.
- [43] S. Yokoyama, T. Kobayashi, Y. Kato, H. Ikuta, M. Wakihara, *Extended Abstracts, IMLB10, Como, Italy, 2000*, p. 308.
- [44] M. Watanabe, T. Endo, A. Nishimoto, K. Miura, M. Yanagida, *J. Power Sources* 81/82 (1999) 786.
- [45] G. Feullard, P. Perche, *J. Appl. Electrochem.* 5 (1975) 63.
- [46] K.M. Abraham, M. Alamgir, *J. Electrochem. Soc.* 136 (1990) 1657.
- [47] K.M. Abraham, M. Alamgir, *J. Power Sources* 44 (1993) 195.
- [48] G. Nagasubramanian, A.I. Attia, G. Halpert, *J. Appl. Electrochem.* 24 (1994) 298.
- [49] S. Narukawa, I. Nakane, *Extended Abstracts, IMLB10, Como, Italy, 2000*, p. 38.
- [50] J.E. Weston, B.C. Steele, *Solid State Ionics* 7 (1982) 75.
- [51] F. Croce, B. Scrosati, *J. Power Sources* 43 (1993) 9.
- [52] M.C. Borghini, M. Mastragostino, S. Passerni, B. Scrosati, *J. Electrochem. Soc.* 142 (1995) 2118.
- [53] P.G. Bruce, C.A. Vincent, *Solid State Ionics* 40/41 (1990) 607.
- [54] P.R. Sorensen, T. Jacobsen, *Electrochim. Acta* 27 (1982) 1671.
- [55] P.M. Blonsky, D. Shriver, P. Austin, H.R. Allcock, 18/19 (1986) 258.
- [56] M.S. Whittingham, *Prog. Solid State Chem.* 12 (1978) 41.
- [57] K. Mizushima, P.C. Jones, P.J. Wiseman, J.B. Goodenough, *Mater. Res. Bull.* 15 (1980) 783.
- [58] T.A. Hewston, B.L. Chamberland, *J. Phys. Chem. Solids* 48 (1987) 97.
- [59] K. Hoshino, T. Murakami, A. Atsuka, Y. Ozaki, S. Watanabe, Y. Takahashi, *Nat. Tech. Rep.* 40 (1994) 31.
- [60] C. Saadoun, I. Delmas, *Solid State Ionics* 53–56 (1992) 370.
- [61] T. Ohzuku, A. Ueda, M. Nagayama, Y. Iwakoshi, H. Komori, *Electrochim. Acta* 38 (1993) 1159.
- [62] M. Menetrier, A. Rougier, C. Delmas, *Solid State Commun.* 90 (1994) 439.
- [63] C. Marichal, J. Hirschinger, P. Granger, M. Menetrier, A. Rougier, C. Delmas, *Inorg. Chem.* 34 (1995) 1773.
- [64] A.R. Armstrong, P.G. Bruce, *Nature* 381 (1996) 499.
- [65] A.R. Armstrong, H. Huang, R.A. Jennings, P.G. Bruce, *J. Mater. Chem.* 8 (1998) 255.
- [66] M.M. Thackeray, *Prog. Solid State Chem.* 25 (1997) 1.
- [67] T. Ohzuku, M. Kitagawa, T. Hirai, *J. Electrochem. Soc.* 137 (1990) 769.
- [68] J.M. Tarascon, E. Wang, F.K. Shokoohi, W.R. Mckinnon, S. Colson, *J. Electrochem. Soc.* 138 (1991) 2859.
- [69] J.M. Tarascon, D. Guyomard, *J. Electrochem. Soc.* 138 (1991) 2864.
- [70] J.B. Goodenough, M.M. Thackeray, W.I.F. David, P.G. Bruce, *Rev. de Chim. Miner.* 21 (1984) 435.
- [71] G. Li, H. Ikuta, T. Uchida, M. Wakihara, *J. Electrochem. Soc.* 143 (1996) 178.
- [72] M. Wakihara, G. Li, H. Ikuta, Cathode active materials with a three-dimensional spinel framework, in: M. Wakihara, O. Yamamoto (Eds.), *Lithium Ion Batteries*, Kodansha, Tokyo; Wiley/VCH, Weinheim, 1998, p. 26.
- [73] G. Pistoia, G. Wang, *Solid State Ionics* 66 (1993) 135.
- [74] D. Song, H. Ikuta, T. Uchida, M. Wakihara, *Solid State Ionics* 117 (1999) 151.
- [75] A. Yamada, M. Tanaka, *Mater. Res. Bull.* 30 (1995) 715.
- [76] Y. Xia, M. Yoshio, *J. Electrochem. Soc.* 143 (1996) 825.
- [77] D.H. Jang, Y.J. Shin, S.M. Oh, *J. Electrochem. Soc.* 143 (1996) 825.
- [78] D. Song, H. Ikuta, M. Wakihara, *Electrochemistry* 68 (2000) 460.
- [79] M. Wakihara, *Extended Abstracts, IMLB10, Como, Italy, 2000*, p. 16.
- [80] S. Kanamura, H. Naito, T. Yao, Z. Takehara, *J. Mater. Chem.* 6 (1996) 33.
- [81] I. Nakai, Private Communication.
- [82] I. Nakai, Y. Shiraishi, F. Nishikawa, *Spectrochim. Acta B54* (1999) 143.
- [83] J.M. Cocciantelli, J.P. Doumerc, M. Pouchard, M. Broussely, J. Labat, *J. Power Sources* 34 (1991) 103.
- [84] J.M. Cocciantelli, M. Menetrier, C. Delmas, J.P. Doumerc, M. Pouchard, P. Hagenmuller, *Solid State Ionics* 50 (1992) 99.
- [85] C. Delmas, S. Brethes, M. Menetrier, *J. Power Sources* 34 (1991) 113.
- [86] M. Wakihara, Manganese spinel oxides and vanadium oxides for cathode active materials, in: Z. Ogumi (Ed.), *The Latest Technology of the New Secondary Battery*, CMC, Tokyo, 1997, p. 31.
- [87] J. Kim, A. Manthiram, *J. Electrochem. Soc.* 146 (1999) 4371.
- [88] A.K. Padhi, K.S. Nanjundaswamy, C. Masquelier, S. Okada, J.B. Goodenough, *J. Electrochem. Soc.* 144 (1997) 1609.
- [89] S. Okada, H. Arai, J. Yamaki, *Denki Kagaku* 65 (1997) 802.