

# An overview of positive-electrode materials for advanced lithium-ion batteries

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Available online 28 June 2007

## Abstract

Positive-electrode materials for lithium and lithium-ion batteries are briefly reviewed in chronological order. Emphasis is given to lithium insertion materials and their background relating to the “birth” of lithium-ion battery. Current lithium-ion batteries consisting of  $\text{LiCoO}_2$  and graphite are approaching a critical limit in energy densities, and new innovating materials are needed in order to continue the advance of lithium-ion batteries. In particular, the recent trends on material researches for advanced lithium-ion batteries, such as layered lithium manganese oxides, lithium transition metal phosphates, and lithium nickel manganese oxides with or without cobalt, are described. Trials on new applications of lithium insertion materials for high-power lithium-ion batteries as well as hybrid capacitors leading for 12 V lead-free accumulators are also highlighted.

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**Keywords:** Lithium insertion materials; Lithium-ion battery; Olivine; Lithium nickel manganese oxides with or without cobalt

## 1. Introduction

The lithium-ion battery was “born” in 1991 and grew rapidly as the power source of choice for portable electronic devices, especially wireless telephones and laptop computers, during the past 16 years. Today, the modern world cannot be described without considering lithium-ion batteries. Current lithium-ion battery technology consists of  $\text{LiCoO}_2$  and graphite, which is the first generation of lithium-ion batteries. The lithium-ion batteries currently available in market range in capacity from 550 mAh to 2.5 Ah for portable applications and up to 45 Ah for motive power and stationary applications. In order to advance lithium-ion batteries, several concepts have been developed, leading to innovative new positive and negative electrode materials.

In this paper, we briefly review positive-electrode materials from the historical aspect and discuss the developments leading to the introduction of lithium-ion batteries, why lithium insertion materials are important in considering lithium-ion batteries, and what will constitute the second generation of lithium-ion batteries. We also highlight new applications of lithium insertion materials.

## 2. Brief history of primary lithium batteries

Lithium is the third element in the periodic table. It has the most negative electrode potential and is stable only in non-aqueous electrolytes. It was not popular electrode material in battery community before 1970. Purification of organic solvents and lithium salts to remove water was especially hard work in each laboratory. Pure, water-free organic solvents and electrolytes were not readily available. Lithium metal was used as a negative electrode in  $\text{LiClO}_4$ ,  $\text{LiBF}_4$ ,  $\text{LiBr}$ ,  $\text{LiI}$ , or  $\text{LiAlCl}_4$  dissolved in organic solvents. Positive-electrode materials were found by trial-and-error investigations of organic and inorganic materials in the 1960s. Prototype cells reported before 1973 included  $\text{Li/CuF}_2$ ,  $\text{Li/CuCl}_2$ ,  $\text{Li/NiF}_2$ ,  $\text{Li/CdF}_2$ ,  $\text{Li/Ni}_3\text{S}_2$ ,  $\text{Li/CuS}$ ,  $\text{Li/Ag}_2\text{CrO}_4$ ,  $\text{Li/MoO}_3$ ,  $\text{Li/SO}_2$ , and  $\text{Li}/(\text{CF})_n$  [1]. Such electrode systems may be represented as the combination of an electrode of the first kind ( $\text{Li/Li}^+$ ) and electrodes of the second kind, e.g.,  $\text{Cu/CuF}_2/\text{F}^-$  except  $\text{MoO}_3$ ,  $\text{SO}_2$ , and  $(\text{CF})_n$ . A basic concept underlying such trials was the extension of the electrochemistry of aqueous batteries by using electrodes of the second kind [2], such as  $\text{Cd/Cd}(\text{OH})_2/\text{OH}^-$ ,  $\text{Pb/PbSO}_4/\text{SO}_4^{2-}$ ,  $\text{Hg/HgO}/\text{OH}^-$ ,  $\text{Ag/Ag}_2\text{O}/\text{OH}^-$ , etc. Electrodes of the second kind, however, could not be used in practical lithium batteries because soluble metal ions reacted with lithium, depositing an inactive surface film on lithium electrode.

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Among materials examined before 1973, the primary battery of  $\text{Li}/(\text{CF})_n$  was first developed and fabricated by Panasonic (Matsushita Electric Ind. Corp.) in the early 1970s [1]. It was used as power sources for fishing floats, digital watches and Kodak disk cameras in the late 1970s. This was dawn of the lithium battery era. Carbon mono-fluoride  $(\text{CF})_n$  is white in color, insulator, hydrophobic, and chemically stable.  $(\text{CF})_n$  is easy to handle even in moist air due to hydrophobic nature of the material. Consequently, no electrochemical activity is observed for  $(\text{CF})_n$  in aqueous electrolytes. During discharge in non-aqueous electrolyte  $(\text{CF})_n$  is reduced to conducting carbon and crystalline  $\text{LiF}$ , so that expansion of positive electrode is quite large. It should be noted here that conducting carbon is not essential to study the white  $(\text{CF})_n$  powders in non-aqueous lithium cells because conducting carbon is formed to collect electrons from an electrode matrix in the initial moments, once discharge reaction occurs. Operating voltage of ca. 2.5 V is approximately two times higher than that of aqueous primary batteries.

In 1975 Ikeda et al. [3] reported heat-treated electrolytic manganese dioxides (HEMD) as cathode for primary lithium batteries. At that time,  $\text{MnO}_2$  is believed to be inactive in non-aqueous electrolytes because the electrochemistry of  $\text{MnO}_2$  is established in terms of an electrode of the second kind in neutral and acidic media by Cahoon [4] or proton–electron mechanism in an alkaline solution by Kozawa and Powers [5]. Proton and water were believed to be necessary for the depolarizability of  $\text{MnO}_2$ . Ikeda's finding at Sanyo [6] would find impact on rechargeable lithium manganese dioxide batteries later. The heat-treated EMD was applied to primary lithium batteries, challenged the  $\text{Li}/(\text{CF})_n$  system and developed quickly as the power source for automatic cameras with 35 mm films since the mid-1980s. Today, primary lithium batteries of manganese dioxide are quite popular over the world. Implementation and practical reality of primary batteries based on  $\text{MnO}_2$  is the milestone of the primary lithium batteries. The great success of primary lithium batteries consisting of manganese dioxide gave confidence to further pursue the development of the science and technology of rechargeable lithium batteries which eventually led to the development of lithium-ion batteries through rechargeable conducting polymer and metallic lithium systems.

### 3. Milestone of rechargeable lithium batteries

Because electrodes of the first kind are reversible electrodes, rechargeable lithium batteries had been examined since the early 1970s. Electrodes of the first kind, however, have not been used in practical rechargeable batteries when one looks back the history of rechargeable batteries. Rechargeable nickel oxyhydroxide–zinc alkaline batteries, for example, had been examined many times without success. Dissolution of zinc ions into solution is no problem on discharge. However, recharging or electroplating of zinc from zincate ions in a solution bulk is typical of problems in applying electrodes of the first kind to battery electrodes. Dimensional instability due to change in morphology, mossy, and dendrite formation, has not been solved yet. Similar problems arise for rechargeable batteries with metallic lithium electrodes.

Meanwhile, Moli Energy (now E-One Moly Energy Ltd.) announced rechargeable molybdenum disulfide lithium batteries in 1985, called MoliceL. They showed AA- and C-size rechargeable lithium batteries. Rechargeable capacity for AA size was 600 mAh and operating voltage was 1.3–2.4 V. Cycle life was more than 250 cycles when charged at 60 mA with a voltage end point of 2.4 V [7]. This demonstrated the practical reality of rechargeable lithium batteries to battery community. At that time, the prototype AA-size cells consisting of lithiated manganese dioxides and metallic lithium were also fabricated and demonstrated the basic functions, i.e., 750 mAh capacity with operating voltage of 2.5–3.4 V. The MoliceL was used as power sources for NTT-mobile phones in 1987–1989. The rechargeable lithium MoliceL was withdrawn from the market after a safety incident in Japan. Although rechargeable lithium batteries of  $\text{MoS}_2$  or  $\text{MnO}_2$  are not available at present, rechargeable lithium batteries of molybdenum disulfide were a milestone in the 1980s. Going forward, the safety issues raised as a result of this incident have made safety equal to battery performance toward high-energy density systems.

### 4. The germ of lithium-ion (shuttlecock) battery

Lithium-ion batteries consist of two lithium insertion materials, one for the negative electrode and a different one for the positive electrode in an electrochemical cell. Fig. 1 depicts the concept of cell operation in a simple manner [8]. This combination of two lithium insertion materials gives the basic function of lithium-ion batteries. More specifically, lithium ions are inserted into/extracted from a solid matrix without the destruction of core structures, so called topotactic reactions, in positive and negative electrodes during charge and the reverse process on discharge. Electrons are simultaneously extracted from one electrode and injected into another electrode, storing and delivering electrical energy, during which materials are oxidized or reduced in positive and negative electrodes. Lithium ions shuttle between positive and negative electrodes, named lithium-ion (shuttlecock, swing, etc.) batteries. An advantage of lithium-ion battery concept is that the operating voltage of the batteries can be designed by the choice of insertion reac-

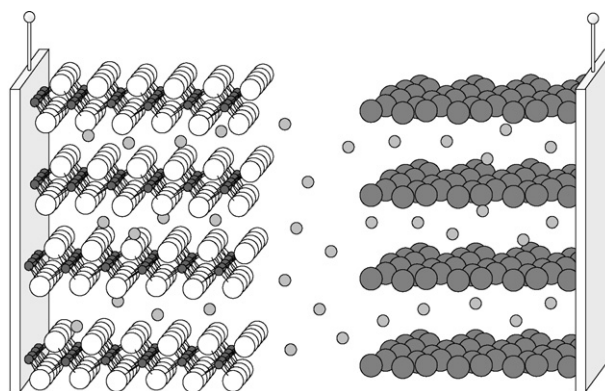


Fig. 1. A schematic illustration on a lithium-ion battery consisting of two lithium insertion electrodes. During charge and discharge, lithium ions shuttle between positive and negative electrodes, so that amount of electrolyte can be minimized.

tion in terms of operating voltage and its charge–discharge profile.

The lithium-ion battery concept was completely new and differs significantly from other batteries consisting of electrodes of the first and/or the second kind [9]. Reactions in lithium-ion batteries are usually described in terms of topotactic reactions. A basic concept of applying ternary phases to battery materials based on topochemical reaction was proposed by Whittingham [10,11] in the 1970s. Combining the basic concept of topotactic reaction with insertion or intercalation, allows one to achieve the lithium-ion battery concept. Topotactic reactions in the 1970s were summarized in 1978 by Whittingham [12] and in 1979 by Murphy and Christian [13]. Here, mainly transition metal calcogenides materials were for positive electrodes in non-aqueous lithium cells. In 1980,  $\text{LiCoO}_2$  having cubic close-packed oxygen array, called O3 stacking, was contrasted to  $\text{LiTiS}_2$  having hexagonally close-packed sulfur array, called H2 stacking, by Mizushima et al. [14]. A few years later, Mendiboure et al. [15] reported a new  $\text{LiCoO}_2$  having ABCBA oxygen stacking, called O2 stacking, prepared by ion-exchange reaction from  $\text{Na}_{0.7}\text{CoO}_2$ . They demonstrated the difference in operating voltages between  $\text{LiCoO}_2(\text{O}2)$  and  $\text{LiCoO}_2(\text{O}3)$  structures.

In the early 1980s, this work on  $\text{LiCoO}_2$  coupled with the work of Hunter [16] who reported on a new manganese dioxide called  $\lambda\text{-MnO}_2$  having a spinel-framework structure prepared from  $\text{LiMn}_2\text{O}_4$  and Thackeray et al. [17] who reported the electrochemical behavior of manganese oxides having a spinel-framework structure in 1983, provided the germ of current lithium insertion materials for lithium-ion batteries. Although these papers were directly related to the development of lithium-ion batteries, the battery community paid little attention because their 4 V operating voltage was thought to be too high for a stable system.

Lazzari and Scrosati [18] in 1980 described a rechargeable  $\text{Li}_x\text{WO}_2/\text{TiS}_2$  cell consisting of two insertion electrodes. Auburn and Barberio [19] proposed rechargeable cells without metallic lithium, based on  $\text{MoO}_2/\text{LiCoO}_2$  and  $\text{WO}_2/\text{LiCoO}_2$  combination. They combined the positive electrodes in  $\text{Li}/\text{MoO}_2$  and  $\text{Li}/\text{WO}_2$  cells as negative electrodes in their lithium-ion cells consisting of  $\text{LiCoO}_2$  and  $\text{MoO}_2$  (or  $\text{WO}_2$ ) although they did not call it lithium-ion battery. Their idea made good sense. The low voltage of the  $\text{WO}_2$  and  $\text{MoO}_2$  made them relatively useless as positive electrodes in lithium metal non-aqueous cells. However, they can function as negative electrodes in lithium-ion batteries. Yazami and Touzain [20] proposed lithium–graphite compounds as a negative electrode for secondary batteries in 1983. Carbon materials show the lowest operating voltage among the materials reported so far. Mohri et al. [21] first demonstrated excellent cycle life of more than 500 cycles in 1988 for a cell consisting of pyrolytic carbon and pre-lithiated chromium oxide.

As described above, there was substantial grounding for the birth of lithium-ion batteries, had matured in the late 1980s. The real question was when, who, where, and how would the first secondary lithium batteries, without metallic lithium, would be designed, fabricated, and introduced to consumer market.

## 5. Lithium-ion batteries consisting of $\text{LiCoO}_2$ and graphite

In 1991, Sony [22] announced new batteries, called lithium-ion batteries, which strongly impacted the battery community all over the world because of their high operating voltage. According to Nagaura [23,24], they had been examining four rechargeable systems for several years, i.e.,  $\text{Li}_x\text{MnO}_2$  (lithiated manganese dioxide),  $\text{LiMn}_2\text{O}_4$ ,  $\text{LiNiO}_2$ , and  $\text{LiCoO}_2$ , in which  $\text{LiNiO}_2$  was prepared from  $\text{NaNiO}_2$  by ion exchange. They actually demonstrated AA-size rechargeable batteries consisting of lithiated manganese dioxide and metallic lithium. The operating voltage was 2.5–3.3 V depending on current drain. They did not succeed in making the metallic lithium battery safe, especially at the end of cycle life or on quick charge as evidenced by the total recall of rechargeable batteries with metallic lithium [25]. The first lithium-ion batteries reported in literature consisted of  $\text{LiCoO}_2$  and petroleum coke [23]. These had the sloping charge and discharge curves so characteristic of the first lithium-ion batteries. Maximum limit of charge-end voltage was 4.1 V, which helped to make the energy density of lithium-ion batteries smaller than that of lithium-ion batteries currently available in market.

Current lithium-ion batteries mainly consist of  $\text{LiCoO}_2$  and graphite with engineering improvements to produce an energy density of over  $500 \text{ Wh dm}^{-3}$ . Fig. 2 shows charge and discharge curves of  $\text{LiCoO}_2$  and graphite operated in non-aqueous lithium cells. At the end of charge for a  $\text{Li}/\text{LiCoO}_2$  cell in Fig. 2, a voltage plateau is clearly seen at 130–140  $\text{mAh g}^{-1}$  due to the phase change in  $\text{LiCoO}_2$  from rhombohedral to monoclinic structure [26,27]. Graphite also shows voltage plateaus, especially at the end of charge for  $\text{Li}/\text{LiC}_6$  cells, related to the phase change from fourth to eighth stages of lithium graphite intercalation compounds [28]. Such voltage plateaus can be used as a signal for the end of charge and discharge for current lithium-ion batteries consisting of  $\text{LiCoO}_2$  and graphite.

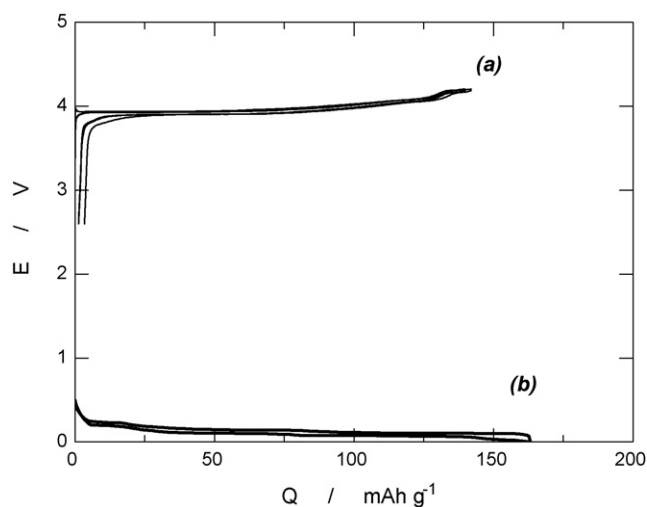


Fig. 2. Charge and discharge curves of (a)  $\text{Li}/\text{LiCoO}_2$  and (b)  $\text{Li}/\text{graphite}$  cells. Combination of  $\text{LiCoO}_2$  and graphite gives a lithium-ion battery. Specific capacity of graphite (b) is given in 1/2 reduction.

Current lithium-ion batteries are normally charged to 4.2 V which is 0.1 V higher than that adopted in the initial stage, so that energy density has been increased correspondingly during the past 6 years. For example, energy density of lithium-ion batteries was approximately  $350 \text{ Wh dm}^{-3}$  in 2000 [29,30]. Coupled with improved cell designs, the energy density now exceeds  $500 \text{ Wh dm}^{-3}$  [31], approaching a critical limit as far as the energy density of lithium-ion batteries consisting of  $\text{LiCoO}_2$  and graphite is concerned.

## 6. Positive-electrode materials for advanced lithium-ion batteries

As described above, researchers have been pursuing high-energy density batteries in developing both lithium and lithium-ion batteries over the past 25 years. In Fig. 2,  $\text{LiCoO}_2$  shows flat operating voltage of 3.9 V versus lithium and graphite shows the lowest operating voltage of 0.1 V versus lithium among the lithium insertion materials reported so far. Both materials show high volumetric and gravimetric specific capacities [28,32,33]. Therefore, finding of positive-electrode materials with superior energy density to  $\text{LiCoO}_2$  for lithium-ion batteries may be difficult. Intensive studies have been directed at finding materials with higher voltage and/or larger rechargeable capacity than  $\text{LiCoO}_2$  [34–39].

Fig. 3 shows the selected lithium insertion materials examined for advanced lithium-ion batteries.  $\text{LiMn}_2\text{O}_4$  having a spinel-framework structure has been extensively examined because it shows a flat operating voltage of 3.95–4.1 V with theoretical capacity of  $148 \text{ mAh g}^{-1}$ . It has been developed as a possible alternative to  $\text{LiCoO}_2$  [38,40]. The performance of  $\text{LiMn}_2\text{O}_4$ -based materials have been improved to quite high level and reviewed by Amatucci and Tarascon [38]. However, rechargeable capacity is lower than that of  $\text{LiCoO}_2$ .

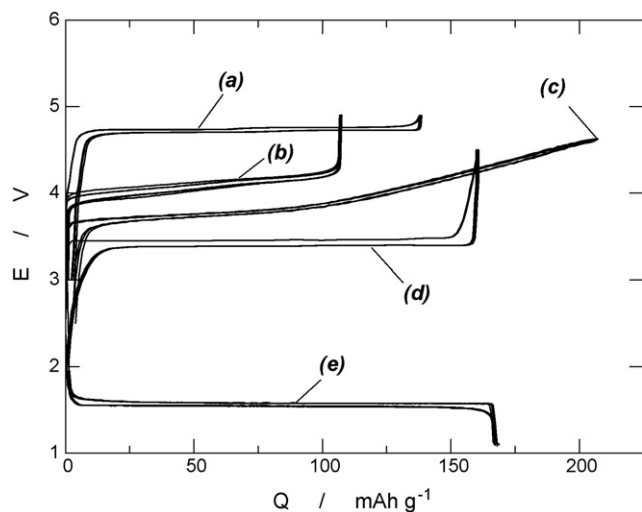


Fig. 3. Charge and discharge curves of (a)  $\text{Li}[\text{Ni}_{1/2}\text{Mn}_{3/2}]\text{O}_4$ , (b)  $\text{LiMn}_2\text{O}_4$ -based material of lithium aluminum manganese oxide (LAMO), (c)  $\text{LiCo}_{1/3}\text{Ni}_{1/3}\text{Mn}_{1/3}\text{O}_2$ , (d)  $\text{LiFePO}_4$ , and (e)  $\text{Li}[\text{Li}_{1/3}\text{Ti}_{5/3}]\text{O}_4$  examined in non-aqueous lithium cells.

A series of 5 V lithium insertion materials based on manganese spinel-framework structure [41] seems to be one option. Other possible 5 V materials include  $\text{Li}[\text{Ni}_{1/2}^{2+}\text{Mn}_{3/2}^{4+}]\text{O}_4$  with a superlattice structure of  $P4_332$  [42] and an extremely flat operating voltage of 4.75 V against lithium. This is ca. 0.8 V higher than that of  $\text{LiCoO}_2$ , with rechargeable capacity of  $135 \text{ mAh g}^{-1}$ , yielding a higher energy density can be expected if  $\text{Li}[\text{Ni}_{1/2}\text{Mn}_{3/2}]\text{O}_4$  is combined with graphite-negative electrode.

$\text{LiNiO}_2$  is isostructural with  $\text{LiCoO}_2$  and shows larger rechargeable capacity than that of  $\text{LiCoO}_2$ , but lower operating voltage with sloping charge and discharge curves. Because  $\text{LiNiO}_2$  and  $\text{LiCoO}_2$  (or  $\alpha\text{-LiAlO}_2$ ) form a solid solution [43,44],  $\text{LiCo}_x\text{Ni}_{1-x}\text{O}_2$  and  $\text{LiAl}_x\text{Ni}_{1-x}\text{O}_2$  including  $\text{LiAl}_x\text{Co}_y\text{Ni}_{1-x-y}\text{O}_2$  ( $x+y < 0.25$ ), were extensively examined. These positive-electrode materials usually show larger rechargeable capacities than that of  $\text{LiCoO}_2$ . However, their lower operating voltage than that of  $\text{LiCoO}_2$  effectively cancels out their larger capacity when the energy density is calculated.

Layered  $\text{LiMnO}_2$  is isostructural with  $\text{LiCoO}_2$  [45] and seems to retain the structural instability due to mobile manganese ions forming disordered spinel structures [46]. In order to stabilize layered  $\text{LiMnO}_2$ , several trials have been done. Amundsen and Paulsen [37] in a review of their works on positive-electrode materials based on layered manganese oxides suggested that tetravalent manganese ions in oxides enhanced the cycling stability of the layered structures, e.g.,  $\text{Li}[\text{Li}_{0.2}\text{Cr}_{0.4}\text{Mn}_{0.4}]\text{O}_2$  or more generally  $\text{LiM}_x\text{Mn}_{1-x}\text{O}_2$  ( $0.03 < x < 0.1$  with  $M = \text{Cr}$  or  $\text{Al}$ ) [47]. Dahn et al. systematically investigated the layered manganese oxides of T2, O6, O2, P2-type  $\text{A}_{2/3}[\text{M}'_{1/3}\text{M}^{4+}_{2/3}]\text{O}_2$ , where  $A = \text{Li}$ ,  $M' = \text{Ni}$  or  $\text{Mg}$ , and  $M = \text{Ti}$  or  $\text{Mn}$ , in which titanium and manganese ions are in the tetravalent states [48]. They succeeded to stabilize a layered lithium manganese oxide, which does not convert to spinel in contrast to layered and orthorhombic forms of  $\text{LiMnO}_2$  [49]. The material shows the rechargeable capacity of  $150\text{--}160 \text{ mAh g}^{-1}$  with sloping charge and discharge curves in voltage ranging from 2.5 to 3.8 V. It may be possible to improve rechargeable capacity and operating voltage for layered lithium manganese oxides.

In 2001, lithium nickel manganese oxides with or without cobalt were proposed as possible alternatives to  $\text{LiCoO}_2$  [50,51].  $\text{LiCo}_{1/3}\text{Ni}_{1/3}\text{Mn}_{1/3}\text{O}_2$  consists of  $\text{Co}^{3+}$ ,  $\text{Ni}^{2+}$ , and  $\text{Mn}^{4+}$  [52] while  $\text{LiNi}_{1/2}\text{Mn}_{1/2}\text{O}_2$  consists of  $\text{Ni}^{2+}$  and  $\text{Mn}^{4+}$  [53]. Although operating voltage of  $\text{Li}/\text{LiCo}_{1/3}\text{Ni}_{1/3}\text{Mn}_{1/3}\text{O}_2$  is slightly lower than that of  $\text{LiCoO}_2$ , rechargeable capacity is larger, so that lithium-ion battery consisting of  $\text{LiCo}_{1/3}\text{Ni}_{1/3}\text{Mn}_{1/3}\text{O}_2$  and graphite is equivalent or superior to current lithium-ion batteries of  $\text{LiCoO}_2$  and graphite with respect to energy density [54].  $\text{LiNi}_{1/2}\text{Mn}_{1/2}\text{O}_2$  shows almost the same operating voltage and rechargeable capacity as those of  $\text{LiCo}_{1/3}\text{Ni}_{1/3}\text{Mn}_{1/3}\text{O}_2$ . However, battery-active  $\text{LiNi}_{1/2}\text{Mn}_{1/2}\text{O}_2$  is difficult to prepare and the specific crystal structure is still unknown. One of the difficulties in understanding the crystal structure of  $\text{LiNi}_{1/2}\text{Mn}_{1/2}\text{O}_2$  is that observed integrated intensity of (1 0 4) line is stronger than that of (0 0 3) in XRD. According to our knowledge learnt from  $\text{LiNiO}_2$  ( $R\bar{3}m$ ), even a small amount of nickel ions in lithium sites plays a crucial role on irreversible and rechargeable capac-

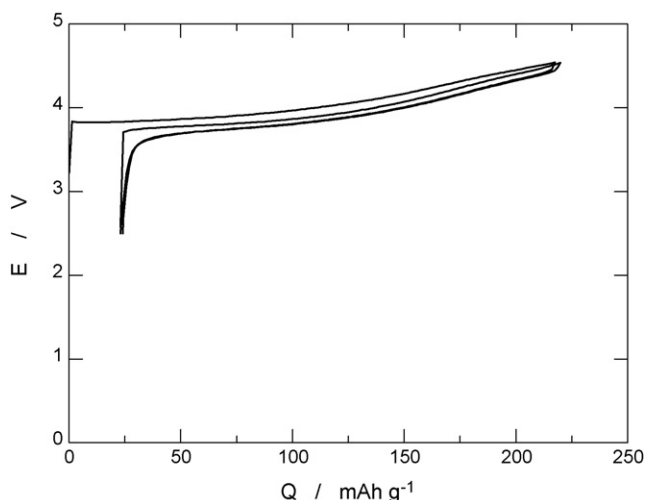


Fig. 4. Charge and discharge curves of a Li/LiNi<sub>1/2</sub>Mn<sub>1/2</sub>O<sub>2</sub> cell operated at a rate of 0.17 mA cm<sup>-2</sup> at 30 °C. Electrolyte used was 1 M LiPF<sub>6</sub> dissolved in EC/DMC (3/7 by volume). Electrode consisted of 88 wt.% LiNi<sub>1/2</sub>Mn<sub>1/2</sub>O<sub>2</sub>, 6 wt.% acetylene black, and 6 wt.% PVdF.

ity in addition to polarization [55,56]. There seems to be a general agreement that amount of nickel ions in the lithium sites in LiNiO<sub>2</sub> must be as low as possible for battery-active LiNiO<sub>2</sub> [57]. Delmas's research group has developed an excellent understanding of the relation between the crystal structure and electrochemical reactivity of LiNiO<sub>2</sub> [57,58]. In contrast to such our knowledge, LiNi<sub>1/2</sub>Mn<sub>1/2</sub>O<sub>2</sub> shows 200 mAh g<sup>-1</sup> of rechargeable capacity [59] with relatively small irreversible capacity and low polarization as seen in Fig. 4, although analytical XRD results show an 8–9% displacement between 3(a) and 3(b) sites when a structural model based on  $R\bar{3}m$  is assumed. LiNi<sub>1/2</sub>Mn<sub>1/2</sub>O<sub>2</sub> shows clear extra spots in electron diffraction patterns in addition to fundamental spots based on  $R\bar{3}m$  [60]. However, the XRD pattern does not show any diffraction line corresponding to extra spots, i.e., d-values, even when strong X-ray beam is used for measurements. In order to understand such anomalous behavior, several other works provide additional information on the preparation, structure, and electrochemistry of LiNi<sub>1/2</sub>Mn<sub>1/2</sub>O<sub>2</sub> [61–63]. Although LiNi<sub>1/2</sub>Mn<sub>1/2</sub>O<sub>2</sub> is not fully understood, it has superior properties to LiCoO<sub>2</sub> and has similar characteristic to LiCo<sub>1/3</sub>Ni<sub>1/3</sub>Mn<sub>1/3</sub>O<sub>2</sub>, and may replace LiCoO<sub>2</sub> as the positive electrode of choice, in future.

Lithium nickel manganese oxides with or without cobalt may be the first good example, where co-operative research between theoretical and experimental approaches have been carried out in such a way that first-principles calculations predict new materials, which are then prepared, examined, and developed [64].

Basic concepts underlying the structure and characteristics of lithium insertion materials discussed above are the same as those described in ref. [32]. All good insertion materials have a framework illustrated in Fig. 5(a and b), respectively, for layered and spinel-framework structures, where the transition metal and lithium ions are located at octahedral sites in a close-packed oxygen array and have an optimum chemical composition of LiMO<sub>2</sub> or MO<sub>2</sub> (M: transition metal).

In 1997, Padhi et al. [65] reported a new class of lithium insertion materials based on the LiFePO<sub>4</sub> olivine structure shown in Fig. 5(c). When properly prepared, LiFePO<sub>4</sub> shows rechargeable capacity of ca. 160 mAh g<sup>-1</sup> with extremely flat operating voltage of ca. 3.5 V against lithium [66,67]. However, energy density of a lithium-ion battery consisting of LiFePO<sub>4</sub> and graphite is less than that of current lithium-ion batteries mainly due to its lower operating voltage and smaller density than LiCoO<sub>2</sub>. Replacing the iron in LiFePO<sub>4</sub> by other trivalent transition metal ions, leads to new materials with operating voltages over 4 V and a rechargeable capacity of 160 mAh g<sup>-1</sup> or more materials design based on polyanion in olivine or its relatives may open up new material strategies leading to high-energy density lithium-ion batteries [68,69]. The phosphate positive-electrode materials are less susceptible to thermal runaway and demonstrate greater safety characteristics than the LiCoO<sub>2</sub>-based systems.

## 7. New applications of lithium insertion materials

As described in Section 6, current lithium-ion batteries consisting of LiCoO<sub>2</sub> and graphite have excellence in their performance. So as was discussed by Broussely and Archdale [70] in 2004, many lithium insertion materials explored, especially during the past 15 years may not find application for high-energy density lithium-ion batteries. Tarascon and Armond [30] in 2001 have reviewed several scientific and technological issues to be considered in further developing rechargeable batteries. Battery history has told us that unless new applications of lithium insertion materials are proposed, designed, fabricated and introduced for consumer use, the interest in basic and applied research will fade year by year [9].

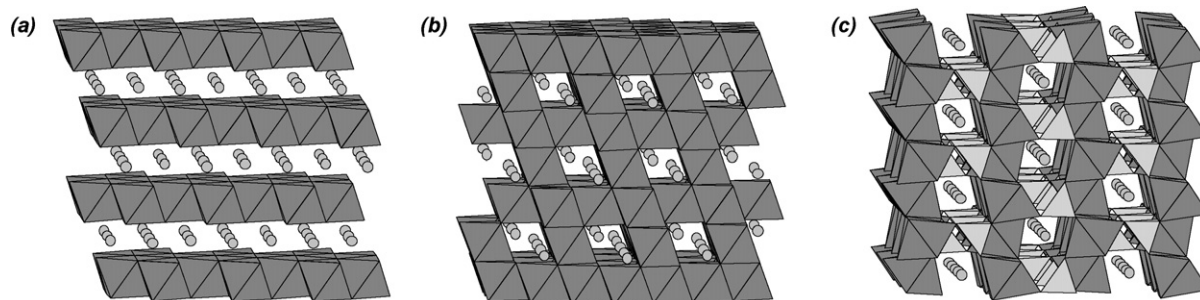


Fig. 5. Schematic Illustrations on the crystal structures of (a) LiCoO<sub>2</sub> (layered structure), (b) LiMn<sub>2</sub>O<sub>4</sub> (spinel structure), and (c) LiFePO<sub>4</sub> (olivine structure). Structures are illustrated by a Wadsley's method with MO<sub>6</sub>-octahedra (M: transition metal) and PO<sub>4</sub>-tetrahedra.

Taking a second look at the unique or intrinsic characteristics of lithium insertion materials, we can realize that each lithium insertion material has its own characteristic value. Lithium titanium oxide (LTO) is an example of a zero-strain insertion material,  $\text{Li}[\text{Li}_{1/3}\text{Ti}_{5/3}]\text{O}_4$  [71,72] in Fig. 3(e). It is an ideal insertion material for long-life lithium-ion batteries, with about  $175 \text{ mAh g}^{-1}$  of rechargeable capacity and extremely flat operating voltage of 1.55 V versus lithium.  $\text{LiFePO}_4$  in Fig. 3(d) is thermally quite stable even when all of lithium ions are extracted from it [73]. It has an operating voltage of ca. 3.5 V with rechargeable capacity of ca.  $160 \text{ mAh g}^{-1}$ , as previously noted. It is not clear how one can provide the opportunity for new unique lithium insertion materials to work as positive or negative electrode in rechargeable batteries.

Amatucci et al. [74] proposed an asymmetric non-aqueous energy storage cell consisting of active carbon and  $\text{Li}[\text{Li}_{1/3}\text{Ti}_{5/3}]\text{O}_4$ . They replaced one of active carbon electrodes with  $\text{Li}[\text{Li}_{1/3}\text{Ti}_{5/3}]\text{O}_4$  in electrochemical double-layer capacitors in order to avoid a risk of lithium plating and to improve capacitance. The positive electrode is activated carbon and the negative electrode is  $\text{Li}[\text{Li}_{1/3}\text{Ti}_{5/3}]\text{O}_4$ . The idea has merit although the advantage of lithium-ion battery concept is limited because the concentration of lithium salt in electrolyte varies during charge and discharge. They demonstrated a prototype 500 F asymmetric hybrid advanced supercapacitor for hybrid electric vehicle (HEV) applications [75].

Recently, A123Systems Inc. [76] announced a high-power lithium-ion batteries consisting of a  $\text{LiFePO}_4$ -positive electrode and graphitic carbon-negative electrode as power sources for power tools. They have shown power density of  $3 \text{ kW kg}^{-1}$  or  $5.8 \text{ kW dm}^{-3}$  for a R26650 cell (26 mm of diameter and 65.0 mm of height) and 10 times longer cycle life than that of Ni–Cd batteries currently used in power tools. Nominal capacity of R26650 is 2.3 Ah with operating voltage of ca. 3.3 V, so that energy density is calculated to be ca.  $100 \text{ Wh kg}^{-1}$  or  $200 \text{ Wh dm}^{-3}$  by using 70 g of battery weight and dimension of R26650. This is an excellent example of the improvements brought through the use of lithium iron phosphate-positive-electrode materials.

More recently, 12 V “lead-free” accumulators have been proposed for automobile and stationary applications by using basic research results on lithium insertion materials [77,78]. According to their conceptual designs, 12 V lead-free accumulators can be made by connecting five cells consisting of  $\text{Li}[\text{Li}_{1/3}\text{Ti}_{5/3}]\text{O}_4$  and  $\text{LiMn}_2\text{O}_4$ -based material [79] in series or alternatively of four cells consisting of  $\text{Li}[\text{Li}_{1/3}\text{Ti}_{5/3}]\text{O}_4$  and  $\text{Li}[\text{Ni}_{1/2}\text{Mn}_{3/2}]\text{O}_4$  [80] in series. While the energy density of such a 12 V “lead-free” accumulator is estimated to be far less than that of current lithium-ion batteries consisting of  $\text{LiCoO}_2$  and graphite, the new battery has two to five times higher energy densities than the current 12 V lead-acid batteries (normally  $30 \text{ Wh kg}^{-1}$ ). For example, the energy density of lead-free accumulator consisting of lithium aluminum manganese oxide (LAMO:  $105 \text{ mAh g}^{-1}$  of rechargeable capacity) and lithium titanium oxide (LTO,  $175 \text{ mAh g}^{-1}$ ) is calculated to be  $170 \text{ Wh kg}^{-1}$  [78,79]. Assuming weight distribution of cell stack components reported by Broussely and Archdale [70], the energy density is estimated to be about  $100 \text{ Wh kg}^{-1}$ . Although power density is difficult

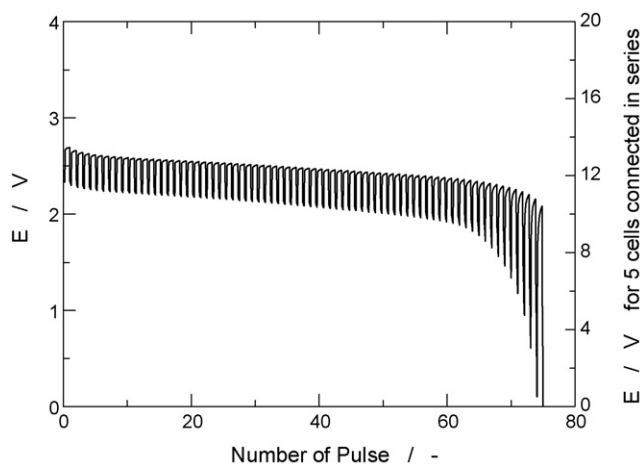


Fig. 6. A pulse discharge curve of a cell consisting of LAMO and  $\text{Li}[\text{Li}_{1/3}\text{Ti}_{5/3}]\text{O}_4$ . Applied current was 38.5 mA ( $3 \text{ cm}^2$ ) corresponding to  $1 \text{ A g}^{-1}$  based on LAMO (47.3 mg,  $97 \mu\text{m}$  thick.) and LTO weight (47.6 mg  $132 \mu\text{m}$  thick.). The current was switched on for 5 s and off for 15 s. Electrolyte used was 1 M  $\text{LiPF}_6$  in EC/DMC (3/7 by volume).

to estimate, the basic research result in Fig. 6 suggests that a 20 Ah 12 V lead-free accumulator consisting of LAMO (1 kg) and LTO (600 g) could deliver a 5 s burst of energy of more than 6 kW (600 A, 10 V). Although implementation and practical reality of such 12 V lead-free accumulators are not known at present, strong requirements toward cleaner environment combined with renewable and sustainable energy technologies, such as solar and wind power generation systems, especially for off-grid areas, could drive the development of the 12 V lead-free accumulators. Recently, valence technology introduced phosphate based Li-ion accumulators for stationary energy storage and motive power applications [81].

## 8. Concluding remarks

In this paper, a brief history of lithium batteries including lithium-ion batteries together with lithium insertion materials for positive electrodes has been described. Lithium batteries have been developed as high-energy density batteries, and they have grown side by side with advanced electronic devices, such as digital watches in the 1970s, automatic cameras in the 1980s, mobile phones in the 1990s, and laptop computers, especially during the past 5 years, 2000–2005. New demands usually stimulate the development of new batteries and consequently accelerate the researches on new lithium insertion materials. Recent market demands for advanced lithium-ion batteries emphasize not only high-energy density but also very high-power density for both charge and discharge, especially for power tools, electric vehicle (EV) and hybrid electric vehicle (HEV) applications. Development of advanced lithium-ion batteries for these applications will require basic and applied research and development on lithium insertion materials for both positive and negative electrodes. New concepts and approaches from quite different angles become more important than has been previously recognized.

Material economy and safety are not described in this paper, and the authors have not stated what the second generation of

lithium-ion battery is, which will be given in future by artificial or society selection of novel lithium-ion batteries. Current lithium-ion batteries could be considered by analogy with teenagers, still growing with unfulfilled promise. We have to watch lithium-ion batteries as to which way to go, i.e., large steps toward the next generation or status quo temporarily.

There is a challenge for material chemists to develop innovative concepts to extend specific Ah-capacity with characteristic high or low operating voltage. They must accept this challenge to break through the present limit on energy density of current  $\text{LiCoO}_2$  and graphite lithium-ion batteries. Success for the next generation lithium-ion batteries will require integrated, cooperative research among many disciplines including electrochemists, solid state and theoretical chemists, and physicists as well as ceramists. It must be recognized that insertion reactions are not limited to lithium ions. Other ions, such as sodium, magnesium, among others can shuttle between positive and negative electrodes of a system. These new insertion reactions could be found application in a 12 V lead-free accumulator in future by exploring such insertion materials for both positive and negative electrodes. All disciplines can contribute to the next technology breakthrough in order to open a new window on the next generation of lithium-ion batteries. A bright future in science and technology relating to lithium-ion batteries can be expected through continuing basic and applied research on lithium insertion materials.

## Acknowledgements

The authors wish to thank Dr. Kingo Ariyoshi and Dr. Yoshinari Makimura for their help in preparing the manuscript. The present work was partially supported by a grant-in-aid from the Osaka City University (OCU) Science Foundation.

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