

## DEVELOPMENT OF LITHIUM RECHARGEABLE BATTERIES IN JAPAN

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### Summary

Lithium primary batteries have been developed in Japan since 1973 as power sources for small consumer devices. There has also been progress, following research and development of lithium rechargeable batteries, towards the replacement of sealed-type nickel-cadmium batteries. Recent work in Japan on the development of lithium rechargeable batteries is reviewed briefly.

### Introduction

The several types of battery produced in Japan during 1986 are shown in Table 1. Lithium batteries were developed for use as power sources for small consumer devices that, since 1973, reflect domestic electronics technologies. Thus, lithium-organic electrolyte-solid cathode-type primary

TABLE 1

Production ratio of batteries in Japan in 1987 by value

Primary batteries		Secondary batteries	
Manganese dry cells	18.3%	Lead-acid batteries	50.0%
Alkaline manganese cells	8.6%	Auto-batteries	33.6%
Silver oxide cells	3.4%	Others	16.4%
Lithium cells	3.2%	Ni-Cd alkaline batteries	16.0%
Li/MnO <sub>2</sub>	2.0%	Sealed type	13.9%
Li/(CF) <sub>n</sub>	1.1%	Sintered type	1.2%
Li/SOCl <sub>2</sub>	0.1%	Pocket type	0.9%
Others	0.5%	Others	0.0%
Total	34.0%	Total	66.0%

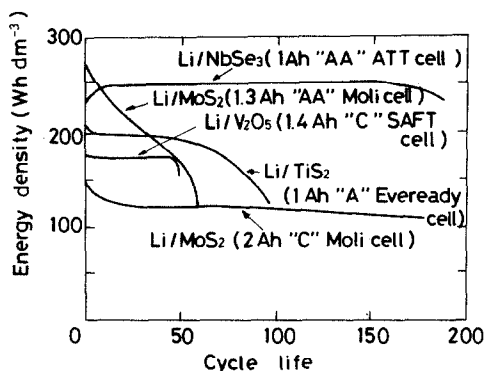


Fig. 1. Cycle life *vs.* energy density of some secondary lithium battery systems.

batteries, *e.g.*,  $\text{Li}/(\text{CF})_n$ ,  $\text{Li}/\text{MnO}_2$  batteries, with their high safety, reliability, and long shelf life, have been developed as power sources for watches (26%), cameras (35%), calculators (10%), and others (29%). Around 1983, lithium batteries began to be used as memory back-up power sources for micro-computerized equipment. The production value of lithium batteries was 3500 million yen in 1980, 8000 million yen in 1982, and 13 000 million yen in 1986. If lithium rechargeable batteries are developed, they may be used to replace sealed-type nickel-cadmium alkaline batteries which, in Japan, have a market of about 56 000 million yen. Rechargeable lithium batteries of various types have now been developed throughout the world, as shown in Fig. 1 [1].  $\text{Li}/\text{MoS}_2$ -type batteries, especially, have been commercialized by Moli Energy in Canada and used in Japan as the power source for pocket-telephones. A great deal of research in Japan has been devoted to the development of lithium rechargeable batteries with high energy density.

### Cathode materials with good rechargeability

Rechargeable cathode materials for use in lithium batteries have recently received world-wide attention. The most promising materials were considered to be  $\text{TiS}_2$ ,  $\text{MoS}_2$ ,  $\text{NbSe}_3$ ,  $\text{V}_2\text{O}_5$  and  $\text{SO}_2$ . In Japan, studies to produce cathodes of high energy density and good rechargeability have progressed as outlined below.

#### (i) Carbon cathodes

The  $\text{Li}/\text{C}$  coin-type rechargeable battery was commercialized for the first time in Japan by Matsushita Electric Ind. in 1985 [2]. In this battery, an active carbon with a surface area of about  $1000 \text{ m}^2 \text{ g}^{-1}$ , serves as cathode, a fusible alloy consisting of Pb, Cd, and In, serves as a substrate material for lithium, and propylene carbonate solution with 1 M  $\text{LiClO}_4$  provides the

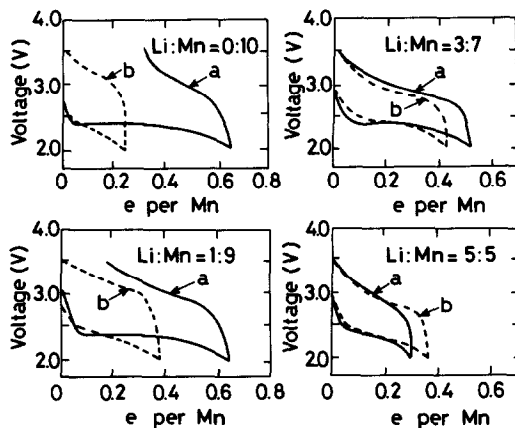
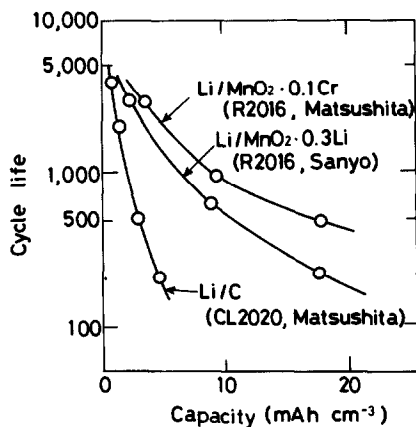


Fig. 2. Capacity vs. cycle life of some secondary lithium battery systems.

Fig. 3. Effect on discharge and charge cycleability of the mole ratio of  $\text{MnO}_2$  to  $\text{LiOH}$ . (a) 1st cycle; (b) 10 cycles.

electrolyte. The CL2020 coin-type battery (20 mm dia. and 2.0 mm high) has a capacity of 1.0 mA h for a discharge from 3.5 to 1.5 V at constant load. Charging and discharging are possible over a temperature range of 60 °C to -20 °C, and it has long term cycleability, as shown in Fig. 2. This battery is likely to be used as a power source for memory back-up and for small consumer equipment using a solar cell hybrid.

#### (ii) Manganese dioxide cathodes

Since  $\text{MnO}_2$  is a most useful cathode and has a high and flat discharge voltage, it has been studied by many companies in Japan.

$\text{MnO}_2$  modified with  $\text{LiOH}$ , and prepared by heating a mixture of  $\gamma\text{-MnO}_2$  and  $\text{LiOH}$  at 375 °C, was used as a cathode by Sanyo Electric [3]. Though the crystal structure of this compound has not yet been clarified, it may be considered, from X-ray diffraction patterns, to be a mixture of  $\text{Li}_2\text{MnO}_3$  and  $\gamma\text{-}\beta\text{MnO}_2$ .

Cycle tests were carried out using a coin-type battery with a cathode mixture of modified  $\text{MnO}_2$  with 10 wt.% carbon black and 10 wt.% Teflon<sup>®</sup>, an anode of lithium-aluminum alloy, and an electrolyte of a mixed solution of propylene carbonate and 1,2-dimethoxyethane with 1 M  $\text{LiClO}_4$ . Figure 3 shows the effect of the  $\text{MnO}_2$  to  $\text{LiOH}$  ratio on cycleability. Though  $\gamma\text{-}\beta\text{MnO}_2$  without  $\text{LiOH}$  has the largest capacity on first discharge, its charge and discharge cycleability is poorer. Therefore, to obtain higher cycleability, at least 30 mol%  $\text{LiOH}$  must be mixed with the  $\text{MnO}_2$ .

Spinel  $\text{LiMn}_2\text{O}_4$  is prepared by heating a mixture of  $\text{Li}_2\text{CO}_3$  and  $\text{Mn}_2\text{O}_3$  at 850 °C. Figure 4 shows the cycling properties of modified  $\text{MnO}_2$  with 30 mol%  $\text{LiOH}$ ,  $\gamma\text{-}\beta\text{MnO}_2$ , and spinel  $\text{LiMn}_2\text{O}_4$  as the cathodes. The cathodes of  $\text{MnO}_2$  modified with  $\text{LiOH}$  and spinel  $\text{LiMn}_2\text{O}_4$  have better cycleability than  $\gamma\text{-}\beta\text{MnO}_2$  at a discharge depth of 0.14 e per Mn. At the deeper discharge

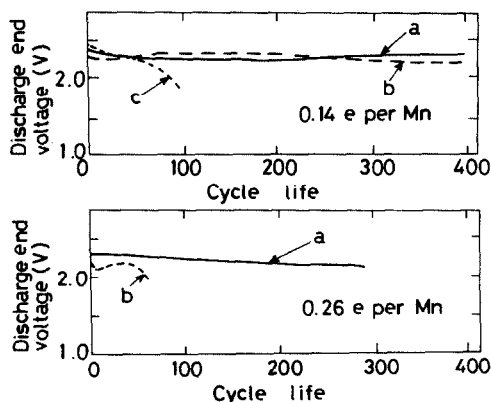


Fig. 4. Cycling properties of Li(Al)/PC-DME-LiClO<sub>4</sub>/MnO<sub>2</sub> coin-type batteries. (a) MnO<sub>2</sub> with 30 mol% LiOH; (b) spinel LiMn<sub>2</sub>O<sub>4</sub>; (c)  $\gamma$ - $\beta$ MnO<sub>2</sub>.

of 0.26 e per Mn, the cathode of LiOH-modified MnO<sub>2</sub> has better cycleability than spinel LiMn<sub>2</sub>O<sub>4</sub>. The excellent cycleability of MnO<sub>2</sub> modified with LiOH may be attributed to the easy reversibility of its crystal structure for the insertion and removal of lithium ions.

Another modified MnO<sub>2</sub> cathode was prepared by Matsushita Electric Ind. on heating  $\gamma$ -MnO<sub>2</sub> with 5 mol% Cr<sub>2</sub>O<sub>3</sub> [4]. This preparation gave the same performance as an MnO<sub>2</sub> cathode modified with LiOH, as shown in Fig. 2.

Sony Energytec recently announced a new Li/MnO<sub>2</sub> AA-size cylindrical battery delivering 700 mA h at an operating voltage of 2.8 V and able to achieve 200 cycles [5]. Since this battery, with almost the same construction as the Li/MoS<sub>2</sub> battery of Moli Energy, has an operating voltage of 2.8 V compared with 1.8 V for the latter, it has higher energy densities of 220 W h dm<sup>-3</sup> and 110 W h kg<sup>-1</sup> than those of the Li/MoS<sub>2</sub> battery (140 W h dm<sup>-3</sup> and 50 W h kg<sup>-1</sup>). However, details regarding the nature of the cathode material and electrolyte have not yet been disclosed.

### (iii) Chromic oxide cathodes

Chromic oxides, Cr<sub>2</sub>O<sub>5</sub> and Cr<sub>3</sub>O<sub>8</sub>, are expected to behave as cathode materials with a higher energy density than MnO<sub>2</sub>. Cr<sub>2</sub>O<sub>5</sub>, prepared by heating a water solution of CrO<sub>3</sub> at 340 °C in air, was used as a cathode by Matsushita Electric Ind. [6]. Though LiOH-modified MnO<sub>2</sub> has an operating voltage of 2.5 V at a capacity of 650 mA h cm<sup>-3</sup>, Cr<sub>2</sub>O<sub>5</sub> has a higher operating voltage of 3.1 V at a capacity of 900 mA h cm<sup>-3</sup>.

The coin-type battery (23 mm in diameter and 2.0 mm in height) was prepared from a cathode mixture of Cr<sub>2</sub>O<sub>5</sub> with 4.5 wt.% carbon black and 4.5 wt.% Teflon<sup>®</sup>, an anode disk of Pb, Cd, and In alloy attached to the cap and a lithium disk, and an electrolyte consisting of a mixed solution of propylene carbonate and 1,2-dimethoxyethane with 1 M LiClO<sub>4</sub>. The anode

and cathode were separated by poly(propylene) film. Though the discharge voltage gradually decreased from 3.6 to 2.6 V at 2 mA discharge, a high volumetric energy density of  $170 \text{ W h dm}^{-3}$  was obtained. The loss in capacity after 1 month of storage at  $60^\circ \text{C}$  was only about 2%. However, the discharge capacity gradually decreased as cycling progressed and life was only 120 cycles. The cycleability could be improved beyond 400 by increasing the amount of carbon in the cathode. This may be attributed to better electronic contact between particles and better ionic contact between the particles and the electrolyte.

$\text{Cr}_3\text{O}_8$ , in which the average oxidation state of chromium is 5.3, is also an attractive cathode material. An amorphous  $\text{Cr}_3\text{O}_8$  with a high specific area was prepared by Yamamoto *et al.* [7] on heating a mixture of  $\text{Cr}_3\text{O}_8$ ,  $\text{H}_2\text{O}$ , and  $(\text{NH}_4)_2\text{SO}_4$  at  $250^\circ \text{C}$ . This amorphous  $\text{Cr}_3\text{O}_8$  exhibited good cycleability over the range 0.2 - 1.2 e/Cr.

#### (iv) Vanadium oxide cathodes

Though  $\text{V}_2\text{O}_5$  is a well-known cathode material, its cycleability is poor. An amorphous  $\text{V}_2\text{O}_5$  with  $\text{P}_2\text{O}_5$  was prepared by Electrical Communications Lab. of NTT [8] on heating a mixture of  $\text{V}_2\text{O}_5$  and  $\text{P}_2\text{O}_5$  for 1 h at  $750^\circ \text{C}$ .

The cycle tests were carried out using a coin-type battery and an Li/mixed solution of ethylene carbonate and 2-methyltetrahydrofuran with  $\text{LiAsF}_6$ /amorphous  $\text{V}_2\text{O}_5$ - $\text{P}_2\text{O}_5$ . The capacities of a crystalline and an amorphous  $\text{V}_2\text{O}_5$  were larger on the first discharge, but gradually degraded with cycling. On the other hand, the capacity of an amorphous  $\text{V}_2\text{O}_5$  with  $\text{P}_2\text{O}_5$  remained virtually constant over extended cycling, as shown in Fig. 5. Thus, the preferred composition was a material containing 95 mol%  $\text{V}_2\text{O}_5$  and 5 mol%  $\text{P}_2\text{O}_5$ . With such a cathode, the battery could be cycled for about 600 times at a high rate and high energy density. The discharge voltage gradually decreased from 3.5 to 2 V at  $1 \text{ mA cm}^{-2}$ , and 0.7 e/V was obtained. The increased cycleability of amorphous  $\text{V}_2\text{O}_5$  with  $\text{P}_2\text{O}_5$  may be attributed to the modification in the V-O bond length. This modification probably acts as a structure stabilizer.

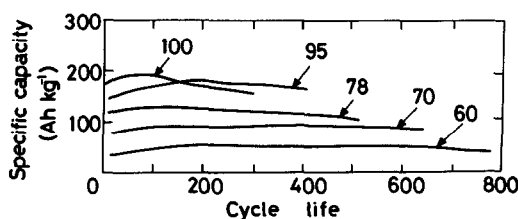


Fig. 5. Cycling properties *vs.* specific capacity, in relation to composition of  $\text{V}_2\text{O}_5$  and  $\text{P}_2\text{O}_5$ , during discharge from 3.5 to 2.0 V *vs.*  $\text{Li}/\text{Li}^+$  at  $0.5 \text{ mA cm}^{-2}$ . ( $\text{V}_2\text{O}_5$  mol% in amorphous mixture of  $\text{V}_2\text{O}_5$  and  $\text{P}_2\text{O}_5$  is shown.)

A  $V_2O_5$  modified with  $MoO_3$ ,  $Mo_{0.1}V_{1.8}O_{4.8}$ , was prepared by Kishi *et al.* [9] on heating a mixture of  $V_2O_5$  and  $MoO_3$  at 700 °C. This, also, is expected to show better cycleability and larger capacity.

(v) *Other inorganic materials as cathodes*

Chevrel phase materials as cathodes have been examined by Wakihara *et al.* [10]. Copper in Chevrel phase materials such as  $Cu_2Mo_6S_{7.8}$  was replaced by lithium during discharge and the replaced material was used as a rechargeable cathode, but its lattice expansion after intercalation of lithium was very large. The iron chevrel phase compound,  $Fe_{1.25}Mo_6S_{7.8}$ , has a better cycleability and its lattice expansion during discharge was small.

$FeOCl$ , which is a layered compound, has been applied in the cathode material of a lithium primary battery. Since  $FeOCl$  decomposes into  $\alpha$ - $Fe$ ,  $LiCl$ , and  $Li_2O$ , during discharge, it was able to provide  $3e/Fe$ ; it could not be used as a rechargeable cathode, however.

We found that the stability of  $FeOCl$  intercalated by lithium was improved by the intercalation of basic organic compounds such as 4-aminopyridine, 2-vinylpyridine and aniline. A cathode mixture of  $FeOCl$  intercalated by aniline, with 15 wt.% acetylene black and 5 wt.% Teflon<sup>®</sup>, could be cycled for more than 100 times at  $1 \text{ mA cm}^{-2}$  in an electrolyte consisting of propylene carbonate with 1 M  $LiBF_4$ ; it had a capacity of 250 mA h and an energy density of 400 mW h per g of cathode.

(vi) *Conductive polymers as cathodes*

Conductive polymers as rechargeable cathodes have attracted considerable attention since the demonstration by MacDiarmid *et al.* in 1979 [12] of electrochemical doping and undoping of polyacetylene. Since polypyrrole, polythiophene, and polyaniline, which have conjugated double bonds similar to polyacetylene, can be synthesized by the anodic oxidation of a solution containing each monomer, they are expected to be stable in an electrochemical oxidizing environment. Thus, the application of the polymers to a rechargeable cathode has been attempted by many researchers.

The suitability for the lithium rechargeable battery of various conductive polymers in propylene carbonate solution with 1 M  $LiClO_4$  has been examined by Yoshida *et al.* [13]. The polyaniline film prepared by electropolymerization onto a platinum plate from a 2 M  $HClO_4$  aqueous solution containing 1 M aniline, had the best cathode cycleability of the various conductive polymers, as shown in Fig. 6 and Table 2. The redox reaction of polyaniline in propylene carbonate solution with 1 M  $LiClO_4$  was accompanied by the doping and undoping of  $ClO_4^-$  anions solvated with 3 - 4 propylene carbonate molecules. Polyaniline yielded 100% coulombic efficiency at a charge and discharge of  $1 \text{ mA cm}^{-2}$  until the charging capacity reached about  $120 \text{ A h kg}^{-1}$ . Its retained capacity after 30 days, for a charge of  $120 \text{ A h kg}^{-1}$ , was 93% of the original value, and it showed low self-

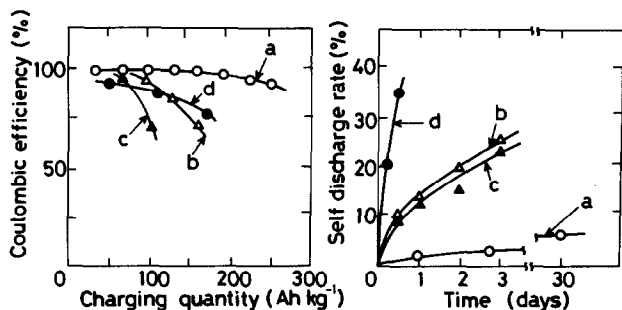


Fig. 6. Coulombic efficiencies and self-discharge rates of various conductive polymers. (a) Polyaniline; (b) polypyrrole; (c) polythiophene; (d) polyacetylene.

TABLE 2

Cycleabilities of various conductive polymers

Polymer	Cycleability (cycles)
Polyaniline	1000 (120 A h kg <sup>-1</sup> )
Polypyrrole	300 (60 A h kg <sup>-1</sup> )
Polythiophene	100 (30 A h kg <sup>-1</sup> )
Polyacetylene	45 (100 A h kg <sup>-1</sup> )

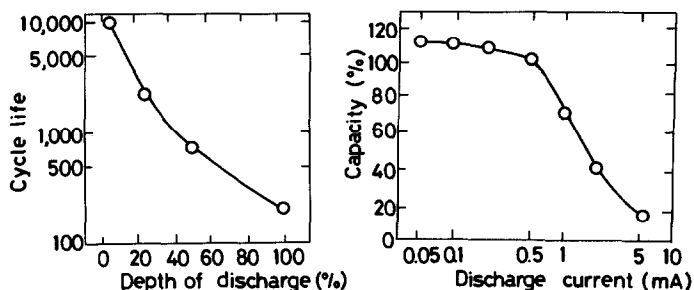


Fig. 7. Cycling property and capacity of Li/polyaniline coin-type battery of AL 2016.

discharge. Also, it could be cycled for approx. 1000 times with a capacity of 120 A h kg<sup>-1</sup> at 1 mA cm<sup>-2</sup>.

The AL 2016 coin-type battery (20 mm in diameter and 1.6 mm in height) had a capacity of 4.0 mA h at 3.3 V charge voltage and at 3.0 V operating voltage for a 0.5 mA discharge, and was commercialized by Bridgestone Corporation in 1986 [14]. It was constructed using a polyaniline film as cathode, a lithium-aluminium alloy as anode, and a mixed solution of propylene carbonate and 1,2-dimethoxyethane with LiBF<sub>4</sub> as electrolyte. Figure 7 shows the cycleability and the capacity of such a

battery. Though its cycleability was only 200 times with a capacity of 4 mA h, it could be cycled up to 2000 times with a capacity of 1 mA h.

### Anode materials with good rechargeability

Studies to improve the reversibility of the lithium anode during charge and discharge have taken place in Japan. The lithium-aluminium alloy anode may be the best available to date.

The use of fusible alloys made from Pb, Sn, Bi, and Cd (represented by Wood's metal) as an anode substrate to replace the Li-Al anode was examined by Toyoguchi *et al.* [6]. Lead, Sn, and Bi adsorb metallic lithium, but the addition of more than 20 wt.% Cd was necessary to maintain their morphological stability. Though Pb-Cd alloy had the lowest capacity for the adsorption of lithium in propylene carbonate solution with 1 M LiClO<sub>4</sub>, it showed good cycleability, as shown in Fig. 8(a). In order to decrease the self-discharge, indium must be added to Pb-Cd alloy, as shown in Fig. 8(b). Thus, an alloy of 68 wt.% Pb, 27 wt.% Cd and 5 wt.% In was found to be the best anode substrate. When using this alloy, a potential plateau appears around 0.5 V *versus* Li/Li<sup>+</sup> corresponding to a capacity of *ca.* 150 mA h g<sup>-1</sup> in the solution of propylene carbonate and 1,2-dimethoxyethane with 1 M LiClO<sub>4</sub>.

A disk of the above alloy was attached to the cap of a coin-type battery and a disk of metallic lithium was pressed onto it. After introducing a cathode separator, an electrolyte, and sealing, the battery was stored at 60 °C for one day. During this period, the metallic lithium was absorbed by the alloy.

A linear-graphite hybrid was used as an anode substrate by Toshiba Battery [15]. It was a crystalline and amorphous hybrid structure produced by the carbonization of organic, high molecular compounds. It had a capacity of 120 mA h g<sup>-1</sup> and 120 mA h cm<sup>-3</sup> at an operating potential between 0 and 0.75 V *versus* Li/Li<sup>+</sup>. It could be cycled for more than 100 times.

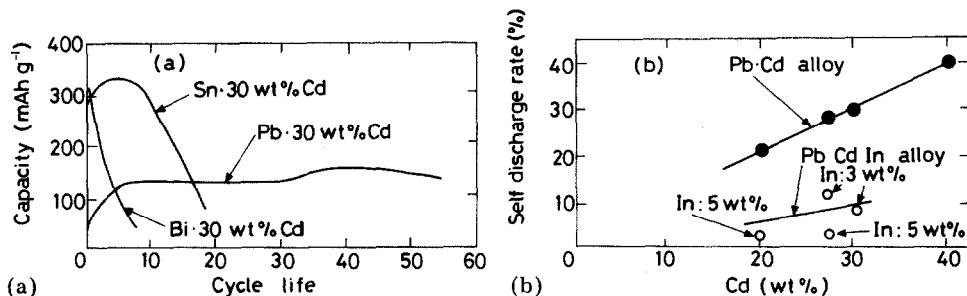


Fig. 8. (a) Cycling properties of various alloys at 1 mA and (b) self-discharge rates of various alloys after 1 month's storage at 60 °C in PC-1 M LiClO<sub>4</sub> of a coin-type R 2320 battery.



The carbon material, prepared by thermal decomposition of polymers such as poly(2-chlorophenylacetylene) at about 800 °C, was also used as an anode substrate by Yamamoto *et al.* [16].

### Electrolytes for rechargeable batteries

It is necessary to select a stable liquid or solid electrolyte having a high ionic conductivity throughout the charge and discharge. A mixed solution of 2-methyltetrahydrofuran and an organic ester compound with  $\text{LiAsF}_6$  is probably the best electrolyte known to date, but its conductivity is low. Therefore, the use of various mixed solvents is now under examination [17].

Lithium ion-conductive solid electrolytes are also used in rechargeable lithium batteries. Though  $\text{Li}_3\text{N}$  is the most conductive lithium ion conductor known to date, it decomposes easily under oxidizing conditions. The ternary system  $\text{Li}_3\text{N-LiI-LiOH}$ , with a conductivity of  $0.95 \text{ S m}^{-1}$  at 25 °C, was developed as an electrolyte stable under these conditions by Obayashi *et al.* [18]. It is expected to be used as the electrolyte of an  $\text{Li/TiS}_2$  rechargeable battery. Polymer electrolytes such as poly(ethylene oxide) or poly(propylene oxide) with lithium salt have been developed as electrolytes for lithium rechargeable batteries [19]. We have prepared an ultra-thin, solid polymer electrolyte film by hybridizing plasma polymerized octamethylcyclotetra-siloxane with poly(propylene oxide) and  $\text{LiClO}_4$  [20]. It could be used as an electrolyte for an  $\text{Li/TiS}_2$  rechargeable battery.

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