

## DEVELOPMENT OF RECHARGEABLE LITHIUM BATTERIES

### II. LITHIUM ION RECHARGEABLE BATTERIES

By T. Nagaura\*

#### Introduction

The need for the development of rechargeable lithium batteries has grown because of the great desire for alternatives to Ni-Cd and lead-acid batteries which have been receiving increased attention from environmentalists.

Cathode materials basically characterize the energy density of the lithium rechargeable batteries. Therefore, there has been a large amount of research and proposals developed on cathodes for lithium rechargeable batteries (1). However, what has hindered the development of lithium rechargeable batteries is the unusual characteristics of the lithium electrode during cycling (2). When cells with a metallic lithium anode are used at the lower discharge currents, cycle life of the cells is decreased. We regret that there has only been a few good developments for improving these unusual characteristics of metallic lithium anodes. To avoid the weaknesses of the metallic lithium anode, the  $\text{Li}_x\text{Al}$ -alloy and Li-Carbon Intercalation Compounds have been proposed (3,4). In terms of energy density, both have a slight disadvantage as compared to metallic lithium as an anode because aluminum and carbon occupy some volume inside the cells and do not participate as an active material. There is no doubt that the rechargeable lithium batteries we are developing should be replacements for existing Ni-Cd and sealed lead-acid batteries with some advantage in energy density as well as other performance characteristics. The  $\text{Li}_x\text{MO}_2$  ( $\text{M}=\text{Co}, \text{Ni}, \text{Mn}$ ) cathode provides a 4 V system with the  $\text{Li}_x\text{Al}$  and Li-CIC anode. This system would be able to recover some of the lost energy density due to their higher operating voltage. Especially, the Li-CIC/ $\text{Li}_x\text{MO}_2$  system will be expected to be a promising rechargeable battery featuring remarkably improved safety and cycle life, because no metallic lithium appears in the cell and only lithium ions are reversibly intercalated into the cathode or anode with little or no structural change during cycling. We called this system the "Lithium Ion Rechargeable Battery" (5-7).



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### Lithium Cobalt Oxide (LiCoO<sub>2</sub>) (8-10)

LiCoO<sub>2</sub> was prepared by heating the mixture of Li<sub>2</sub>CO<sub>3</sub> and CoCO<sub>3</sub> (Li:Co=1:1 in mole ratio) at 900° C in air for five hours.

### Lithium Nickel Oxide (LiNiO<sub>2</sub>) (11)

Well-mixed powders of Na<sub>2</sub>O<sub>2</sub> and NiO (Na:Ni=1.05:1 in mole ratio) were heated at 900° C in O<sub>2</sub> for four hours. The prepared material (NaNiO<sub>2</sub>) was then ground into powder and mixed with excess LiNO<sub>3</sub> followed by heating at 300° C in air for three hours. After that, the remaining LiNO<sub>3</sub> was removed by washing with water. The newly prepared LiNiO<sub>2</sub> was better than the one prepared by the heating of Li<sub>2</sub>CO<sub>3</sub> and NiCO<sub>3</sub>.

### Lithium Manganese Oxide (LiMn<sub>2</sub>O<sub>4</sub>) (12)

LiMn<sub>2</sub>O<sub>4</sub> was prepared by heating a mixture of Li<sub>2</sub>CO<sub>3</sub> and EMD (Li:Mn=1:2 in mole ratio) at 850° C in air for five hours. The EMD had been heat-treated at 400° C prior to use.

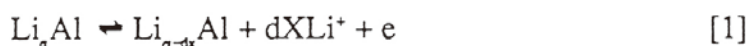
### Charge and Discharge Characteristics of Li<sub>4</sub>MO<sub>2</sub>

Fig. 1 shows low rate charge and discharge curves for the already mentioned synthesized materials (Li<sub>4</sub>MO<sub>2</sub>) using the same cathode test cells as described in a previous paper (13). The cathode mix consisted of 88.9 weight percent (w/o) Li<sub>4</sub>MO<sub>2</sub>, 9.3 w/o graphite and 1.8 w/o Teflon binder. A disk made of the cathode mix was placed in the test cell against a metallic lithium anode disk. As shown in Fig. 1, LiCoO<sub>2</sub> was better than the others based on delivered capacity and polarization.

From the battery manufacturing standpoint, Li-containing compounds would be suited for cathode materials mating to an aluminum or carbon anode, because the Li<sub>4</sub>Al or Li-CIC can be prepared as an anode inside cells by the first charging. Of course, it is necessary for lithium ions to be extracted from the compounds by electrochemical oxidation. As a matter of fact, only the Li<sub>4</sub>MO<sub>2</sub> (M=Co, Ni, Mn) has been found to be the right materials.

### Cycle Life of Li<sub>4</sub>Al

The composition of the lithium aluminum alloy reversibly changes during charging and discharging as indicated in equation [1].



The cycle life of Li<sub>4</sub>Al was affected by the degree of composition change (dx) during cycling. Fig. 2 shows the relations between cycle life and dx. The cycle number decreased for all Li<sub>x</sub>Al (x=0.33~0.73) as dx increased. There is also a tendency in which the smaller lithium ratio, α, in the composition of the alloy, Li<sub>4</sub>Al, gives the shorter cycle life. Estimated cycle life at dx=0.18 is less than 50 cycles, but at dx=0.05, it is more than 300 cycles, which may be acceptable for the general life of a rechargeable battery. However, dx=0.05 gives too low an energy density in a practical cell configuration as a replacement for Ni-Cds as a rechargeable battery.



## Cycle Life of $\text{Li}_x\text{C}$

Certain carbons become a Li-Carbon Intercalation Compound, a so-called Li-CIC, by electrochemical reduction in an organic electrolyte containing lithium ions. Li-CIC is able to operate as an anode for nonaqueous rechargeable batteries according to equation [2].

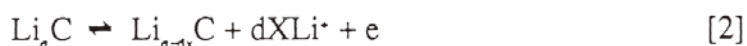


Figure 3 shows cycle number during battery life versus discharge capacity,  $dx$ , in equation [2] for various carbon materials. In any carbon material, cycle numbers were decreased when  $dx$  was increased. A  $dx$  of 0.13 was equivalent to 290 mAh per gram of carbon. So, as far as using No. 5 carbon with 290 mA/g, we can expect 2000 cycles of life for a lithium ion rechargeable battery if the cycle life was determined by the anode life.

## $\text{Li}_x\text{Al}/\text{Li}_{1-x}\text{CoO}_2$ System

The  $\text{Li}_x\text{Al}/\text{Li}_{1-x}\text{CoO}_2$  battery was produced by the first charging of the  $\text{Al}/\text{LiCoO}_2$  system which was present when first assembled. The cell structure of the  $\text{Li}_x\text{Al}/\text{Li}_{1-x}\text{CoO}_2$  battery was made with the cell structure similar to that of lithium manganese oxide batteries which is described in a companion paper. Electrodes were processed in the same way as those of the lithium manganese oxide battery using  $\text{LiCoO}_2$  for a cathode material and aluminum foil for the anode instead of  $\text{Li}_{0.5}\text{MnO}_2$  and lithium sheet, respectively.

### Attractive Performance

Fig. 4 illustrates the typical discharge curve of an AA-size  $\text{Li}_x\text{Al}/\text{Li}_{1-x}\text{CoO}_2$  battery. Discharge capacity and energy density were 440 mAh and 205 Wh/l, respectively, obtained from an 18 ohm discharge of a AA-size cell which gave 2.4 hours of discharge time with a 3.5 V operating voltage. In terms of energy density, the high operating voltage of this system yielded a superior advantage, although discharge capacity itself is lower than that of metallic lithium anode systems such as Li/manganese oxide rechargeable batteries (600-700 mAh for AA-size).

As compared with the unusual characteristics of metallic lithium anode systems, the  $\text{Li}_x\text{Al}/\text{Li}_{1-x}\text{CoO}_2$  battery is insensitive to overdischarging. As shown in Fig. 5, after normal cycling to a 2.75 V cutoff, discharge of the 10th to 15th cycles were carried out without the normal cutoff voltage limitation and until the cell voltage reached almost zero (0.01V). There was no indications of degraded performance in subsequent charge and discharge curves.

### Cycle Life

As a matter of course, characteristics of the Li-aluminum anode during cycling agreed with the cycle life of the  $\text{Li}_x\text{Al}/\text{Li}_{1-x}\text{CoO}_2$  battery. In short, cycle life of the  $\text{Li}_x\text{Al}/\text{Li}_{1-x}\text{CoO}_2$  battery was determined by the depth of discharge (DOD). As shown in Fig. 6, cycle number during cell testing was only 40 cycles at 100% DOD which was too small a number of cycles for this system for substitution of the Ni-Cd system. Although more than 250 cycles were achieved at 25% DOD, energy density at 25% DOD was only 47 Wh/l which is not even half that of the Ni-Cd system.

## Li<sub>4</sub>C/Li<sub>1-x</sub>CoO<sub>2</sub> System (Lithium Ion Rechargeable Battery)

The Li<sub>4</sub>C/Li<sub>1-x</sub>CoO<sub>2</sub> battery was produced by the first charging of Carbon/LiCoO<sub>2</sub> cells which is their state after assembly.

The cell structure of the Li<sub>4</sub>C/Li<sub>1-x</sub>CoO<sub>2</sub> battery was also similar to that of the lithium manganese oxide battery. The carbon electrode was processed in the same way as the cathode of the lithium manganese oxide battery using carbon for the active material and copper foil for the current collector instead of Li<sub>0.5</sub>MnO<sub>2</sub> and aluminum foil, respectively. Fig. 7 is a photograph of the anode and cathode sheet electrodes and separators used in the assembly of practical cells. Fig. 8 is a cell element wound into a jellyroll.

### Attractive Performance

A typical charge and discharge voltage profile of the lithium ion rechargeable battery is illustrated in Fig. 9 for an AA-size cell. When charging a lithium ion rechargeable battery, a maximum limit should be set for the charging voltage. A normal charging voltage is approximately 4.1 V per cell. At a charging current of 600 mA for the AA cells, the voltage reached the setting in about 25 minutes then current virtually ceased to flow and finally the charging is complete within one hour. Of course, charging can be carried out at lower charging currents if a long period of time could be tolerated.

Fig. 10 shows capacity versus cycle number at various discharge currents. 200 mA is equivalent to 0.5C, 40 mA is C/10 and 20 mA is C/20. There is no tendency toward short life in cycling at low current discharges as observed with metallic lithium anode systems. Although there is a slight capacity decrease as a function of cycle number, quite stable discharge characteristics were obtained during every cycle up to 1200 cycles, which is an extraordinary number of cycles compared to the lithium manganese oxide and Li<sub>4</sub>Al/Li<sub>1-x</sub>CoO<sub>2</sub> systems.

The basic performance of the three different sizes of lithium ion rechargeable batteries are summarized in Table I. Energy density, cycle life, drain capability and low temperature characteristics all met our performance target requirements for the lithium rechargeable battery which should be able to replace existing Ni-Cd and sealed lead-acid batteries. A published report (7) concerning the lithium ion battery further describes the performance of this system.

### Safety Device

Fig. 12 is a schematic of an anti-overcharging safety device. This schematic shows how charging is safely stopped when control of the charging conditions is lost. Whenever the cell voltage exceeds more than 4.5 V, internal pressure rapidly increases perhaps due to decomposition of the electrolyte. Consequently, the aluminum burst disk (1) bulges and then the lead (2) from the cell element is broken. There is no need to worry about the current shut-down mechanism during normal charging conditions at high temperature. Fig. 13 shows floating characteristics at 60° C. Cells were still good even after 1000 hours of floating charge at 60° C as long as the charging was within the limit of the charging voltage.

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Table I. Performance Summary

Type of Cell	US-61 14500 (AA size)	US-61 16530 ( $\phi 16 \times 53$ mm)	US-61 20500 ( $\phi 20 \times 50$ mm)
Volume	7.5 cm <sup>3</sup>	11.3 cm <sup>3</sup>	16.5 cm <sup>3</sup>
Weight	18 g	28 g	39 g
Operating Voltage	3.6 V	3.6 V	3.6 V
Capacity at 0.2C	400 mAh	640 mAh	1080 mAh
Energy-Density	192 wh/l 78 wh/kg	204 wh/l 83 wh/kg	236 wh/l 99 wh/kg
Cycle Life in 100% DOD	1200 cycle	1200 cycle	1200 cycle
Drain Capability Capacity at 1C 2C	370 mAh 330 mAh	600 mAh 530 mAh	1000 mAh 880 mAh
Low Temp. 0.5C Discharge Capacity at 0°C -20°C	335 mAh 250 mAh	550 mAh 430 mAh	920 mAh 720 mAh



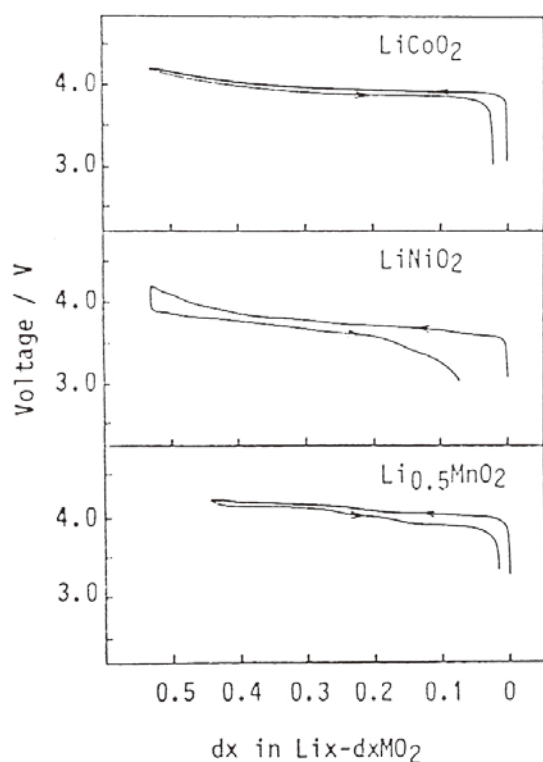


Fig. 1 Charge and discharge curves of  $\text{Li}/\text{Li}_x\text{MO}_2$  ( $\text{M}=\text{Co}, \text{Ni}, \text{Mn}$ )  
Charge:  $0.5 \text{ mA}/\text{cm}^2$  with max. limit of  $4.2 \text{ V}$ .  
Discharge:  $0.5 \text{ mA}/\text{cm}^2$  with  $3.3 \text{ V}$  cutoff.

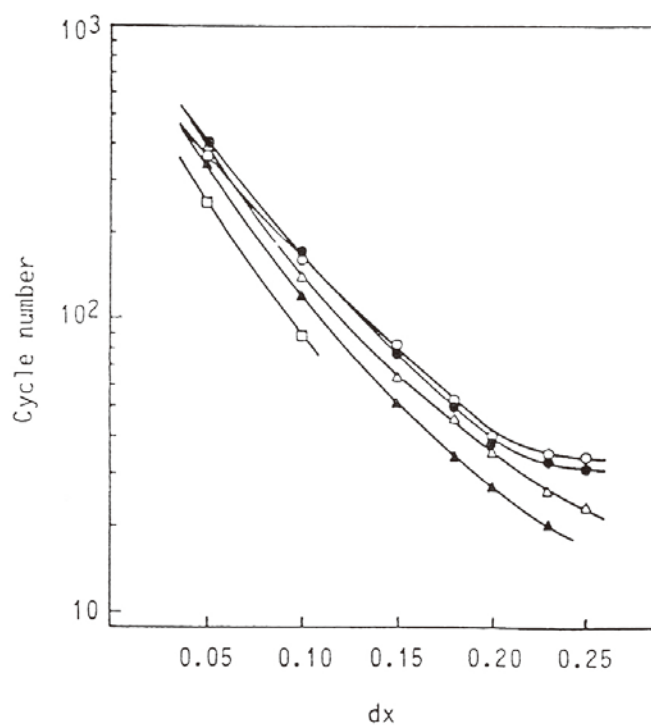


Fig. 2 Cycle number vs. depth of discharge ( $\text{dX}$ ) in  $\text{Li}_x\text{Al}$  for aluminum alloy electrode.  
 $\circ$ :  $x=0.73$   $\bullet$ :  $x=0.63$   $\Delta$ :  $x=0.53$   
 $\blacktriangle$ :  $x=0.43$   $\square$ :  $x=0.33$

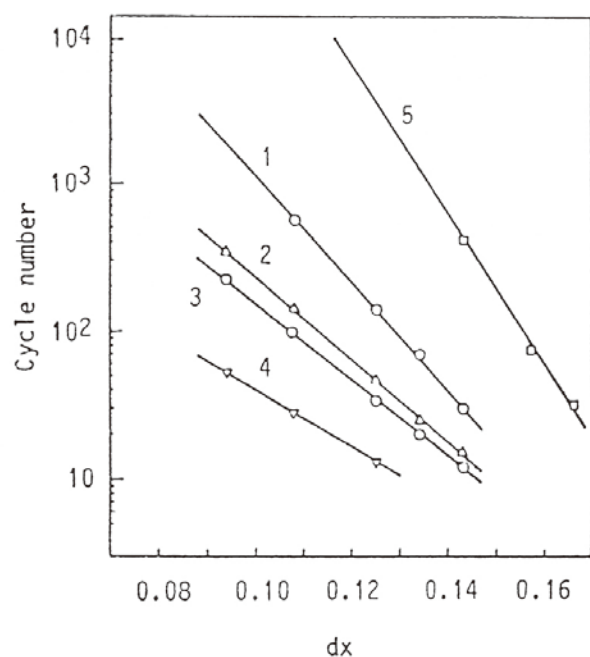


Fig. 3 Cycle number vs. charge and discharge capacity ( $\text{dX}$  in  $\text{Li}_x\text{dXC}$ ) for various carbon materials. Sample carbon materials were carbonized of:  
1. polyvinyl alcohol  
2. polyacrylonitrile  
3. acrylonitrile-butadiene-styrene resin  
4. vinylidene chloride resin  
Carbon (5) applied for Sony Li ion rechargeable batteries.

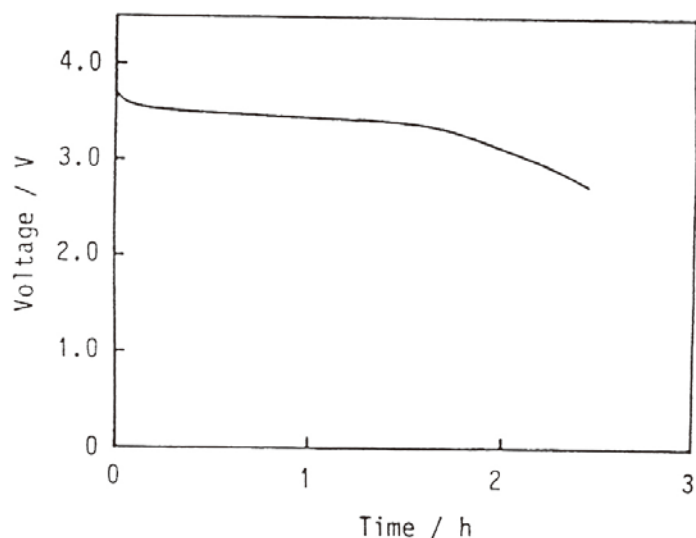


Fig. 4 Typical discharge curves of  $\text{Li}_x\text{Al}/\text{Li}_{1-x}\text{CoO}_2$  AA-size cells.  
Discharge: 18 ohm

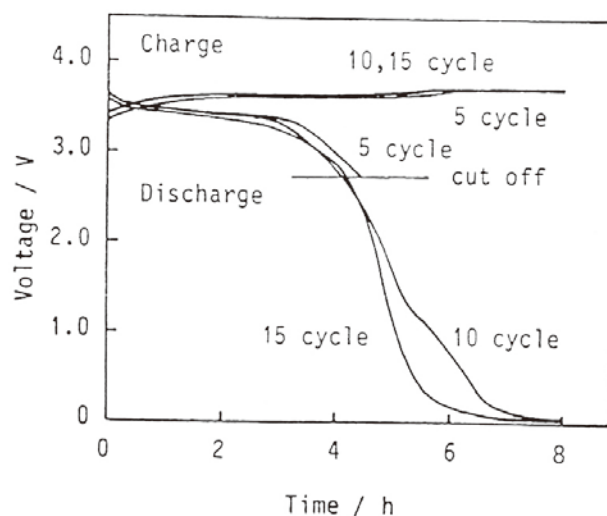


Fig. 5 Typical charge and discharge curves of  $\text{Li}_x\text{Al}/\text{Li}_{1-x}\text{CoO}_2$  AA-size cells.  
Charge: 65 mA x 8 hrs. with max. limit of 3.7 V.  
Discharge: 36 ohm with and without cutoff voltage (2.75 V).

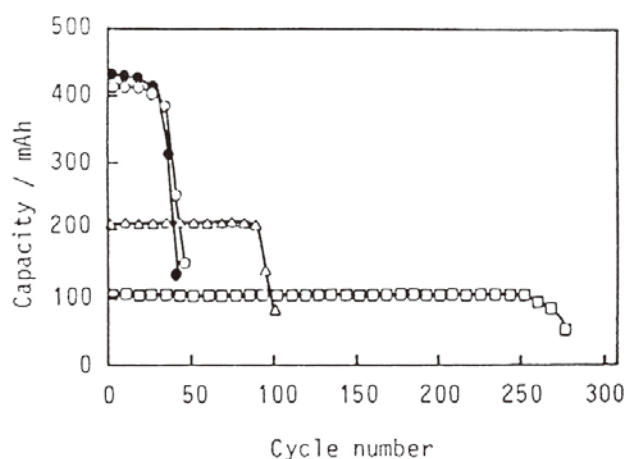


Fig. 6 Capacity vs. cycle number for  $\text{Li}_x\text{Al}/\text{Li}_y\text{CoO}_2$  AA-size cells at various DOD.  
Charge: 65 mA x 8 hrs. with max. limit of 3.7 V.  
Discharge: ○: 100% DOD with 2.75 V cutoff at 0.5C.  
●: 100% DOD with 2.75 V cutoff at 0.05C.  
△: 50% DOD at 0.5C.  
□: 25% DOD at 0.5C.

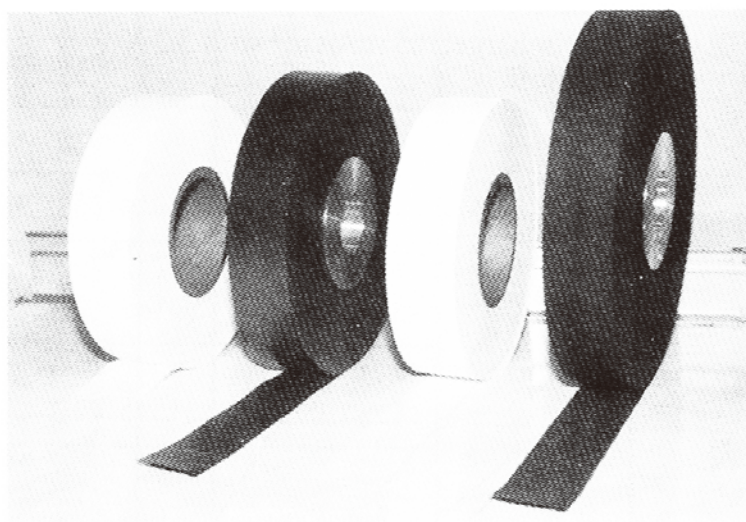


Fig. 7 Photograph of electrodes and separator used for lithium ion rechargeable batteries.

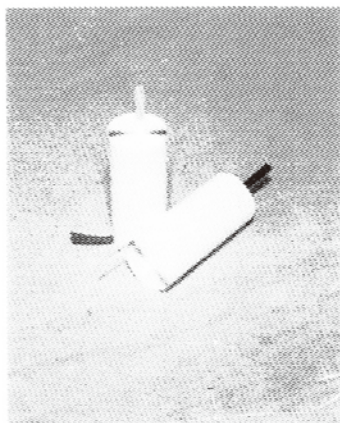


Fig. 8 Photograph of a cell element wound into jellyroll.

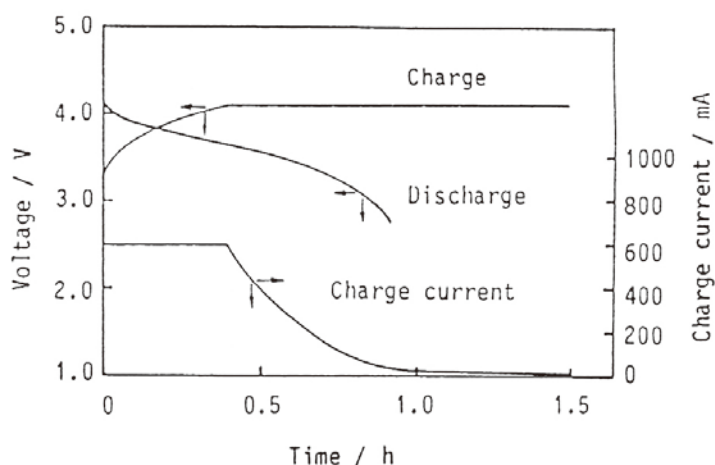


Fig. 9 Typical charge and discharge voltage profile of  $\text{Li}_\alpha\text{C}/\text{Li}_{1-\alpha}\text{CoO}_2$  AA-size cells. Charge: 600 mA with max. limit of 4.1 V. Discharge: 400 mA with 2.75 V cutoff.

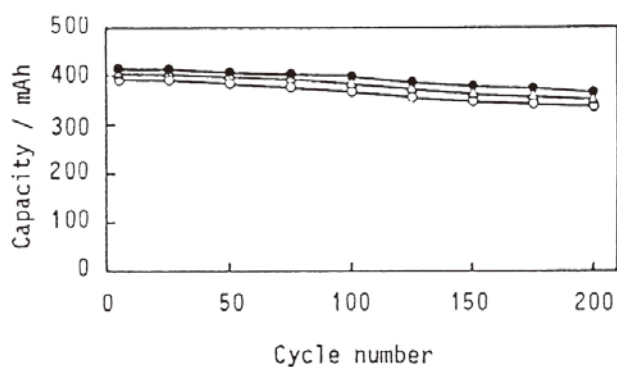


Fig. 10 Capacity vs. cycle number for  $\text{Li}_\alpha\text{C}/\text{Li}_{1-\alpha}\text{CoO}_2$  AA-size cells. Discharge: with 2.75 V cutoff at 200 mA (○), 40 mA (△) and 20 mA (●).

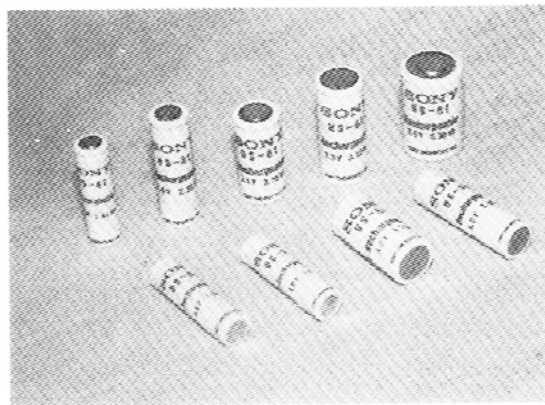


Fig. 11 Lithium ion rechargeable batteries



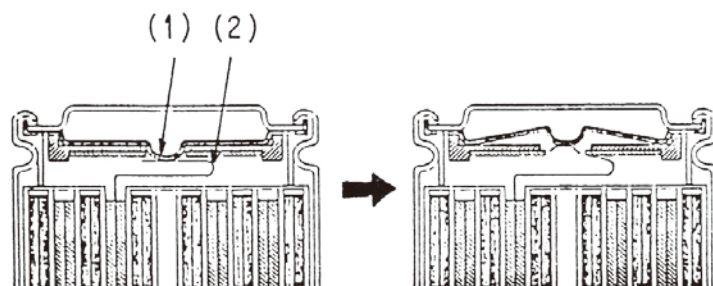


Fig. 12 Schematic of anti-overcharging mechanism showing how charging end for safety in case of lost control of charging limit voltage  
 (1) aluminum burst disks  
 (2) aluminum lead

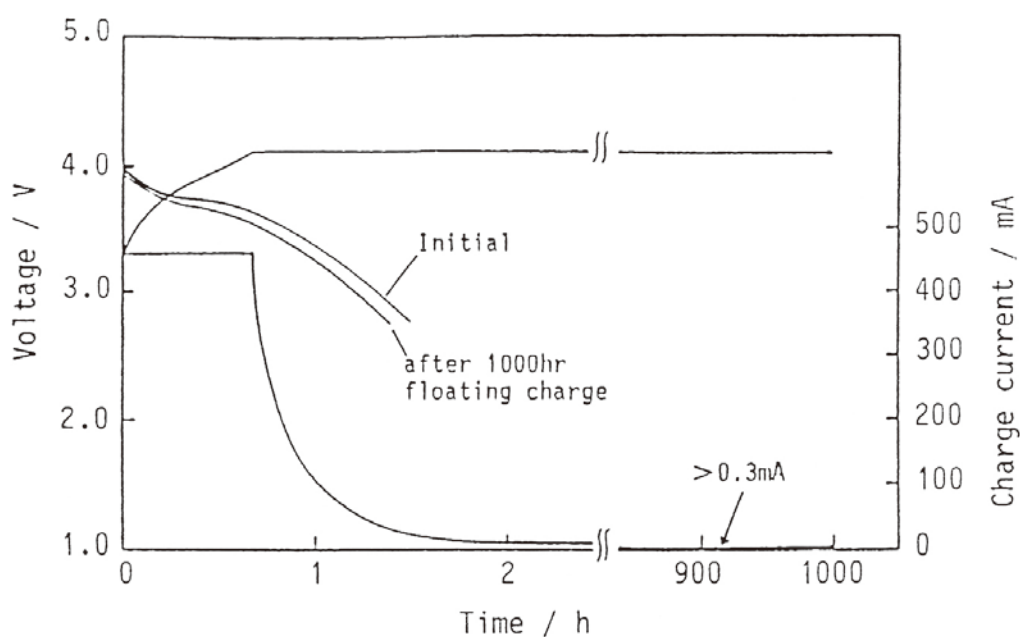


Fig. 13 Floating characteristics at 60° C. Initial Charging current: 460 mA  
 Max. limit of charging: 4.1 V  
 Discharge: 250 mA with 2.75 V cutoff