

## A rechargeable Li/Li<sub>x</sub>CoO<sub>2</sub> cell incorporating a LiCF<sub>3</sub>SO<sub>3</sub>-NMP electrolyte

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### Abstract

Preliminary cell performance of a rechargeable Li/Li<sub>x</sub>CoO<sub>2</sub> cell at room temperature and 80 °C with a LiCF<sub>3</sub>SO<sub>3</sub>-NMP electrolyte has been evaluated. The results indicate that the cells using *N*-methyl-2-pyrrolidinone (NMP) solution at room temperature can deliver energy densities of 100-110 W h/kg at 1 mA/cm<sup>2</sup> discharge rate over 100 cycles while the cells at 80 °C or those using propylene carbonate (PC) solution can only last 40 cycles. Cathode preparation is discussed in terms of reaction time, number of firings, particle size, and type of binder. This is the first report to be published on the use of a LiCF<sub>3</sub>SO<sub>3</sub>-NMP electrolyte in rechargeable lithium cells.

### Introduction

The utilization of Li<sub>x</sub>CoO<sub>2</sub> as a cathode material for high energy rechargeable batteries was initially proposed by Mizushima *et al.* [1] in 1980. Lithiated cobalt oxide with a layered rock-salt structure was employed as a cathode material in several rechargeable Li cells [2-5] and non Li cells [6, 7].

Li<sub>x</sub>CoO<sub>2</sub> possesses a high cell-open voltage (3-4 V) and a theoretical energy density of 1110 W h/kg, one of the highest among all known cathode materials, which makes it an attractive cathode material for rechargeable Li cells. However, excessively large values of cell voltages can lead to electrolyte breakdown if the electrochemical stability window of the cell is overstepped. Electrolyte instability limits cell cycle life as shown by the Li/Li<sub>x</sub>CoO<sub>2</sub> cell using LiAsF<sub>6</sub> in methyl acetate which can only last around 20 cycles [3].

The solvent properties of *N*-methyl-2-pyrrolidinone (abbreviated as NMP) have been reviewed by Breant [8]. Anodic stability of LiClO<sub>4</sub>, NaBF<sub>4</sub>, and KPF<sub>6</sub> in NMP has been evaluated by Eichinger [9]. So far, no report on the use of a LiCF<sub>3</sub>SO<sub>3</sub>-NMP electrolyte in ambient temperature rechargeable Li cells has ever been published.

The major goals of our work are to improve cycle life and safety of Li/Li<sub>x</sub>CoO<sub>2</sub> cells. This paper describes our efforts to develop a new LiCF<sub>3</sub>SO<sub>3</sub>-NMP electrolyte system and to study the effect of cathode preparation on cell performance. Cathode preparation is discussed in terms of reaction time, sintering stage, particle size, and type of binder employed. This is the first report to be published on the use of a LiCF<sub>3</sub>SO<sub>3</sub>-NMP electrolyte in a rechargeable Li cell such as the Li/Li<sub>x</sub>CoO<sub>2</sub> system. Due to page limitation, the effects of reactant ratio and charge cutoff potential on cell capacity and cycle number will be reported elsewhere.

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## Experimental

### *Preparation of electrolyte*

*N*-methyl-2-pyrrolidinone (NMP) and propylene carbonate (PC) were obtained from Merck. Both solvents were treated with different drying agents such as sodium metal,  $\text{CaH}_2$ , or molecular sieve 4A. After drying with magnetical stirring for 12 h under an inert atmosphere, NMP was fractionally distilled over a drying agent at 51 °C and 4 mm Hg while PC was twice distilled at 95 °C and 5 mm Hg. The water content of the resulting distillates was measured by a Mitsubishi CA-03 moisture meter. The purity of NMP was also monitored by cyclic voltammetry, IR spectroscopy and conductivity measurement, using a BAS-100A electrochemical analyzer, a Jasco 200-A IR spectrophotometer, and a YSI-34 conductance meter, respectively.

$\text{LiCF}_3\text{SO}_3$  salt from Anderson Physics was dried by heating it at 100 °C under vacuum for 1 day and its water content was found to be below 200 ppm. All salts, solvents and electrolyte preparations were handled either in a glovebox or by Schlenk-tube technique.

### *Preparation of cathode*

Lithium dioxycobaltate(III) ( $\text{LiCoO}_2$ ) was synthesized by decomposing a pelletized, stoichiometric mixture of cobalt(II) carbonate (Koch-Light Laboratories) and lithium carbonate (Ferak Chemicals) in air at 900 °C for 24 h [1]. The mixture was first heated in an alumina crucible at a rate of 5 °C/min to 900 °C. The initial product was treated by either rapid quenching or slow cooling to room temperature, followed by grinding, pelletizing and reheating to 900 °C for 18 h. The final powder product was analyzed by X-ray diffraction (XRD) method using a Siemens D-500 X-ray diffractometer with  $\text{Cu K}\alpha$  radiation and scanning from 10 degree ( $2\theta$ ) to 80°. The XRD results were in excellent agreement with the JCPDS standard. The Li content of  $\text{Li}_x\text{CoO}_2$  was determined using a Kontron NS-35 ion-coupled plasma-atomic emission spectrometer.

The Li cobalt oxide cathode contained 80 wt.%  $\text{LiCoO}_2$ , the balance being 10 wt.% each of carbon black and binder. Four types of binders obtained from Aldrich were employed in this work: (i) ethylene(50%)/propylene/diene(8%)monomer (EPDM); (ii) ethylene(70%)/propylene/diene(4%)terpolymer (EPDT); (iii) polyethylene oxide (PEO); (iv) Teflon aqueous solution, 30%. The solvent for EPDM and EPDT was *n*-hexane and tetrahydrofuran (THF) for PEO. In the case of Teflon solution, water was the obvious solvent. The cathode constituents were well mixed with the proper amount of solvent and then rolled onto both sides of a nickel screen (1 cm×1 cm) with a thickness of about 0.5 mm. The cathode was then heated at 250 °C for 1 h under argon atmosphere to remove moisture and increase binding strength, followed by pressing at a pressure range of 900 to 1800 kg/cm<sup>2</sup>.

### *Cell tests*

The glass test cell consisted of a Li anode (1 cm×1 cm), a Teflon block separator, a  $\text{LiCoO}_2$  cathode (1 cm×1 cm), and 1 M  $\text{LiCF}_3\text{SO}_3$ -NMP electrolyte. Two electrodes with a distance of 8 mm were separated by a Teflon block which was placed above the electrolyte level. Nickel strips were used as current collectors. The cells were galvanostatically cycled to the desired depths using an Amel model 545 galvanostat-electrometer (charge voltage: 4.20 V; charge current density: 0.5 mA/cm<sup>2</sup>; discharge voltage: 1.50 V, and discharge current density: 1.0 mA/cm<sup>2</sup>).

## Results and discussion

The use of an aprotic solvent in ambient temperature rechargeable Li batteries is necessary, because Li metal is extremely sensitive to water or any substances involving active hydrogen. The removal of water from a solvent is mandatory when preparing an electrolyte.

The results of using different drying agents for the removal of water from NMP are summarized in Table 1 in terms of the data from conductivity measurement, IR spectroscopy, cyclic voltammetry, and moisture measurement. In general, the water content in NMP was greatly reduced through the use of molecular sieves 4A, sodium metal, or  $\text{CaH}_2$ .

As far as solvent conductivity is concerned, water is more conductive than NMP. Thus, the higher the conductivity, the higher the water content of NMP. As indicated in Table 1, the lowest conductivity,  $1.71 \mu\text{S}/\text{cm}$ , was shown by NMP dried with molecular sieves 4A.

There are strong IR absorptions in the region of  $3400\text{--}3600 \text{ cm}^{-1}$  and  $2800\text{--}3000 \text{ cm}^{-1}$  attributable to the stretching vibrations of the O–H bonds of water and the C–H bonds of NMP, respectively. The ratio of the intensities of these two absorptions is used as an indicator of water content in NMP. Again, NMP dried with molecular sieves 4A gives the best performance and has the smallest ratio.

The low background current curve with no appreciable peak from current–voltage indicates that there is very minimal electroactive material present in NMP after drying.

The water content of NMP after being dried with molecular sieves 4A was 110 ppm, significantly lower than those dried with sodium metal and  $\text{CaH}_2$ , which had values of 432 and 217 ppm, respectively. The drying agents in order of decreasing effectiveness: molecular sieves  $4A > \text{CaH}_2 > \text{Na}$ , was consistent with those results from conductivity and IR spectroscopic data. A similar trend was found for the purification of PC. After being dried with molecular sieves 4A, PC contained 110 ppm of water.

The XRD powder diffractograms of some typical  $\text{LiCoO}_2$  samples are shown in Fig. 1, indicating that  $\text{LiCoO}_2$  was best prepared by decomposing a mixture with a 1:2 mole ratio of  $\text{Li}_2\text{CO}_3$  and  $\text{CoCO}_3$  at  $900^\circ\text{C}$  for 24 h, followed by one more firing at  $900^\circ\text{C}$  for 18 h. The XRD patterns of the  $\text{Li}_x\text{CoO}_2$  materials were consistent with those derived from a hexagonal unit cell of  $\text{LiCoO}_2$ . The observed lattice parameters

TABLE 1

Comparison of NMP purification methods using various drying agents

Drying agent	Distillation condition	Water content <sup>a</sup> (ppm)	IR <sup>b</sup> ratio	CV	Conductivity ( $\mu\text{S}/\text{cm}$ )
Molecular sieves	4 mm Hg, b.p. $51^\circ\text{C}$	B: 1039 A: 110	L	no peak	1.71
Na, metal	4 mm Hg, b.p. $52^\circ\text{C}$	B: 1040 A: 432	H	no peak	1.85
$\text{CaH}_2$	4 mm Hg, b.p. $51^\circ\text{C}$	B: 1040 A: 217	M	no peak	1.75

<sup>a</sup>B: before drying, A: after drying.

<sup>b</sup>L: low, H: high, M: medium.

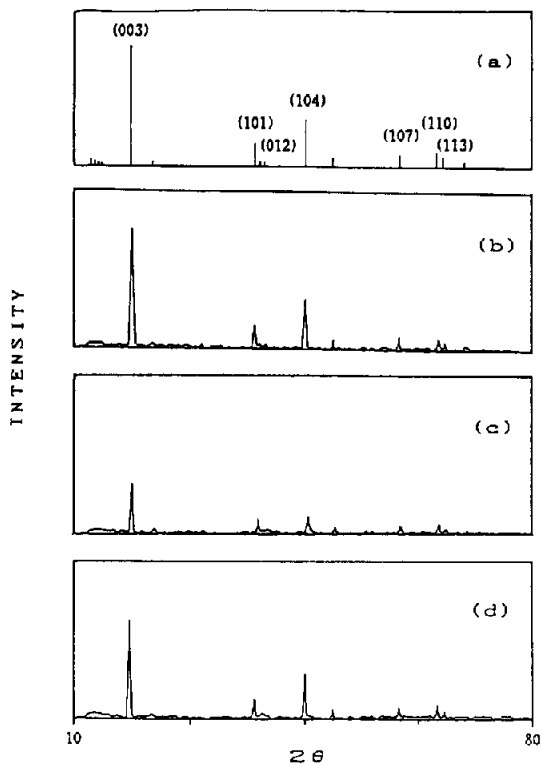


Fig. 1. Some XRD powder diffractograms of  $\text{LiCoO}_2$ : (a) JCPDS standard; (b) after two firings,  $\text{Li}_2\text{CO}_3:\text{CoCO}_3=5:3$ ; (c) only one firing,  $\text{Li}_2\text{CO}_3:\text{CoCO}_3=5:3$ , and (d) after two firings,  $\text{Li}_2\text{CO}_3:\text{CoCO}_3=1:2$ .

of  $\text{Li}_x\text{CoO}_2$  ( $a=2.811 \text{ \AA}$ ,  $c=14.09 \text{ \AA}$ ) compared with those from the references [1, 10–12] showed that the stoichiometry of Li,  $x$ , was very close to 1.

The conductivity of a  $\text{LiCoO}_2$  pellet at room temperature,  $2.5 \text{ mS/cm}$ , was measured by the four-probe method, because a single crystal of  $\text{LiCoO}_2$  was not available. The above value indicates that the  $\text{LiCoO}_2$  material has a conductivity similar to a semiconductor. From the Arrhenius plot, the activation energy for conduction,  $0.42 \text{ eV}$ , can be calculated for  $\text{LiCoO}_2$ . The value is close to  $0.33 \text{ eV}$  reported by Molenda *et al.* [4] but considerably lower than  $1 \text{ eV}$ , the value found for most other cathode materials. This implies that  $\text{LiCoO}_2$  possesses electronic conductivity.

The performance of  $\text{Li}_x\text{CoO}_2$  as a cathode material depends upon both intrinsic and extrinsic properties, such as the method of preparation, particle size, electrode porosity, and type of binder. With respect to the method of cathode preparation, various approaches have been attempted by varying the reaction time, number of firings, powder treatment, cooling method, powder density, and distribution of particle size; results are given in Table 2. The sintering temperature was set at  $900 \text{ }^\circ\text{C}$ , because the product showed poor crystallinity below this temperature and possible decomposition above  $900 \text{ }^\circ\text{C}$ .

In general, there was no obvious trend in the composition of  $\text{Li}_x\text{CoO}_2$  with respect to these preparation parameters, but the  $x$  value was close to 1, ranging from 0.93

TABLE 2

The effects of cathode preparation on the physical properties and chemical composition of  $\text{Li}_x\text{CoO}_2$

Reaction time and number of firings	Powder <sup>a</sup> treatment	Cooling <sup>b</sup>	Particle distribution ( $\mu\text{m}$ )	Density ( $\text{g}/\text{cm}^3$ )	Composition
20 h+20 h+20 h	G	S	5-20	4.768	$\text{Li}_{0.34}\text{CoO}_2$
20 h+20 h+20 h	G	R	5-20	4.711	$\text{Li}_{0.38}\text{CoO}_2$
20 h+20 h+20 h	P	S	1-10	4.498	$\text{Li}_{0.36}\text{CoO}_2$
20 h+20 h+20 h	P	R	2-12	4.481	$\text{Li}_{0.37}\text{CoO}_2$
24 h+18 h	G	S	1-8	4.747	$\text{Li}_{0.33}\text{CoO}_2$
24 h+18 h	G	R	1-12	4.832	$\text{Li}_{0.38}\text{CoO}_2$
24 h+18 h	P	S	1-5	4.908	$\text{Li}_{0.36}\text{CoO}_2$
24 h+18 h	P	R	1-5	4.732	$\text{Li}_{0.33}\text{CoO}_2$

<sup>a</sup>G: grinding, P: pelletizing.

<sup>b</sup>S: slow cooling to room temperature, R: rapid cooling to room temperature.

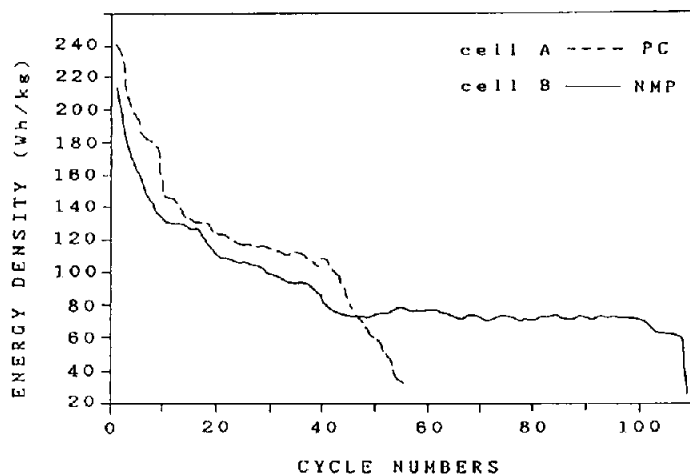


Fig. 2. The performance of  $\text{Li}/\text{LiCoO}_2$  cells using a PC or NMP electrolyte at room temperature.

to 0.99 as discussed earlier. Materials sintered in two stages had a higher powder density and a narrower range of particle distribution with smaller sizes than those sintered in three stages. Similar results were observed for the pelletized materials. A treatment of rapid cooling in air for the final product usually led to a lower powder density than slow cooling.

Figure 2 illustrates the electrolyte effect of PC and NMP on the cycle life and energy density of a  $\text{Li}/\text{LiCoO}_2$  cell, which has been charged to 4.2 V at  $0.5 \text{ mA}/\text{cm}^2$ . Both curves display an initial sharp drop in energy density within 10 cycles and another sharp drop at the end of cycle life, i.e., about 40 cycles for cell A with a PC electrolyte and about 100 cycles for cell B with an NMP electrolyte. The first drop may be due to the interaction of the electrolyte and the electrode materials, and the second drop may be due to anode failure or cathode instability. Although cell A has slightly higher

energy density than cell B (a difference of about 20 W h/kg), it can only last 40 cycles. On the other hand, cell B can maintain a steady energy density of about 80 W h/kg from 40 cycles to 100 cycles. Obviously, cell B outperforms cell A in terms of cycle life.

The temperature effect on cell performance is illustrated in Fig. 3, which shows that the Li/1 M LiCF<sub>3</sub>SO<sub>3</sub>-NMP/LiCoO<sub>2</sub> cell had only about 40 cycles at 80 °C versus 100 cycles at room temperature. On cycling at 80 °C, the electrolyte solution turned black and viscous around 30 cycles, indicating rapid deterioration, while at room temperature the color did not change until 80 cycles. However, the cell at 80 °C had a much higher energy density during a cell life of 40 cycles.

The addition of a binder to powdered cathode materials can keep the cathode in good shape during cycling but may cause a decrease in cathode conductivity and a subsequent energy loss. Thus, the selection of a proper binder is an important step in cathode preparation. Figure 4 displays cell performance of cathodes employing an EPDM, EPDT, PEO or Teflon binder. In general, cells using the above binders had longer cycle life than those not using these binders. All cells exceeded 100 cycles except for the cell containing an EPDT binder which lasted only 62 cycles. They also suffered an initial sharp decrease in energy density during the first 10 cycles, especially, the cell using a PEO binder which continued to drop until it reached 20 cycles.

Overall, the cell with an EPDM binder provided the best cell performance with an average energy density of 100 W h/kg, followed by the cells using EPDT and Teflon binders which had energy densities of 90 and 70 W h/kg, respectively. Although the cell containing a PEO binder was quite stable after 20 cycles, its energy density of 50 W h/kg was too low for high energy battery application.

The effect of the particle size of LiCoO<sub>2</sub> powders on cell performance is clearly shown in Fig. 5. As expected, the two cells with small particles, 2 and 8 μm, outperformed the cell with large particles, 15 μm. The energy densities of the first two cells were close to 110 W h/kg while the latter was 40 W h/kg only. Large cathode particles resulted in low surface area and loose contact of the cathode and probably caused the significant reduction in energy density. Generally speaking, the smaller the particle size of the cathode powder, the longer the cell cycle life.

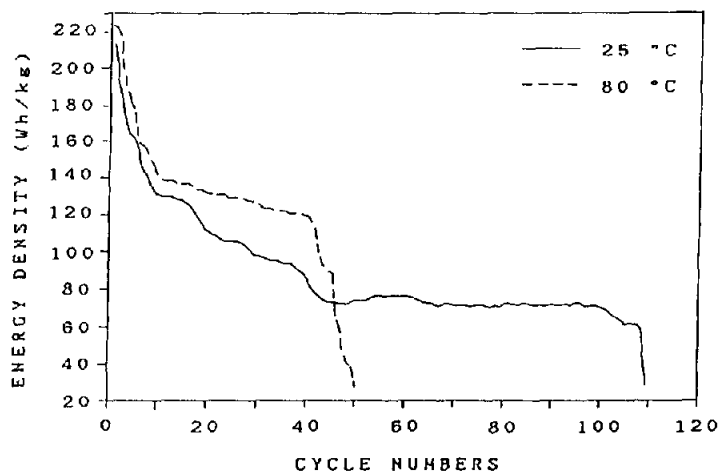


Fig. 3. The effect of temperature on Li/LiCoO<sub>2</sub> cell performance.

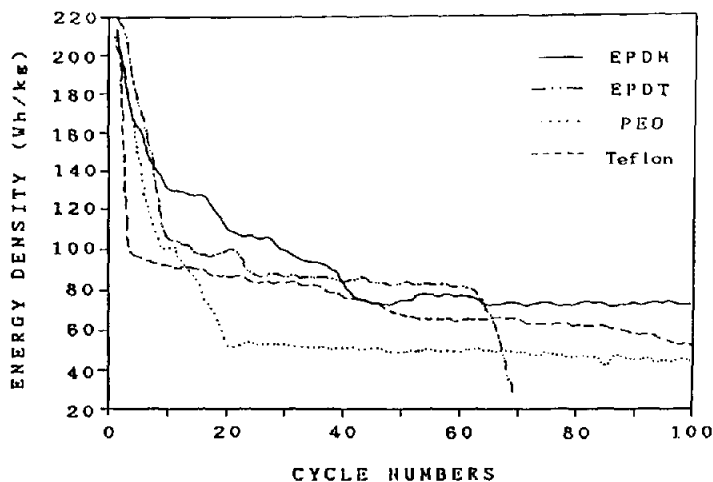


Fig. 4. The performance of Li/LiCo<sub>2</sub> cells using various binders.

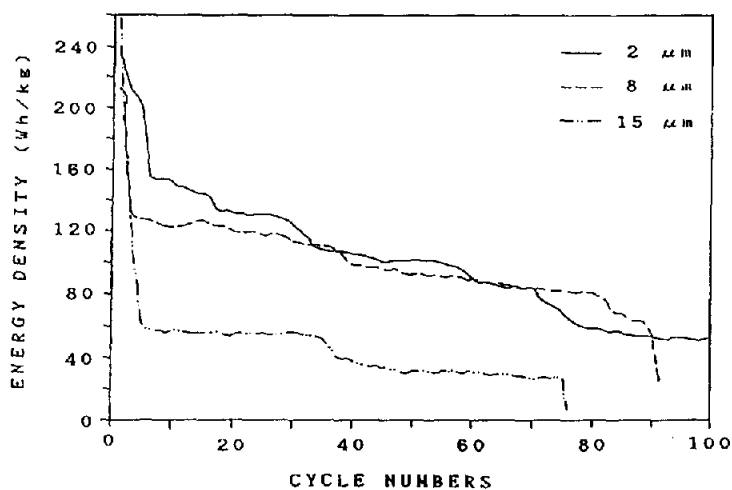


Fig. 5. The effect of cathode particle size on Li/LiCo<sub>2</sub> cell performance.

## Conclusions

The preliminary cell performance of a rechargeable Li/Li<sub>x</sub>CoO<sub>2</sub> cell using a LiCF<sub>3</sub>SO<sub>3</sub>-NMP electrolyte at room temperature provided 100 cycles with 100–110 Wh/kg at 1 mA/cm<sup>2</sup> discharge rate, and was much more promising than that of cells using other electrolyte systems. NMP was effectively dried in molecular sieve 4A prior to its use. Although the energy density of this cell is lower than usual LiCoO<sub>2</sub> cells, the practicality of this new electrolyte system has yet to be explored and improved.

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