

A RECHARGEABLE Li/Li_xCoO₂ CELL

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(Received November 14, 1986; in revised form January 16, 1987)

Summary

The Li/Li_xCoO₂ rechargeable cell has been studied in several solvents, and the preferred electrolyte is LiAsF₆ in methyl acetate. It is shown that this cell can deliver very high energy densities at rates of 1 - 10 mA cm⁻² over the wide temperature range of -40 °C to 25 °C. The cell is currently limited to around 20 charge/discharge cycles which is suitable for moderate cycle life practical rechargeable cell applications.

Introduction

The use of Li_xCoO₂ (0 < x ≤ 1) as the cathode in a rechargeable lithium cell was first proposed by Mizushima *et al.* [1]. The layered rocksalt structure of LiCoO₂ can theoretically deintercalate one mole of lithium per mole of oxide at cell voltages of 4 V or greater on charge, and deliver energy densities in excess of 1000 W h kg⁻¹ on discharge. Since the initial report of this high energy cathode by Mizushima *et al.*, the Li/Li_xCoO₂ cell remained a curiosity due, undoubtedly, to its characteristically high cathodic potentials which result in solvent oxidation. Mendiboure *et al.* [2] reported some cycling data for this high energy couple in LiClO₄-PC solutions, but their work mainly focused on the phase transitions occurring within Li_xCoO₂. They reported the upper stability of the electrolyte as 4 V.

In recent work on vanadium oxide intercalating cathodes which are also characterized by high cathodic potentials, it was found that simple esters exhibit superior stability to most other solvents such as ethers, cyclic esters, and lactones [3, 4]. The present communication reports new results for the Li/Li_xCoO₂ cell using LiAsF₆ in methyl formate and methyl acetate as the electrolyte systems. Cells were characterized electrochemically over the temperature range -40 °C to 25 °C.

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Experimental

Methyl formate (MF) received from MC/B was purified by distillation from P_2O_5 , and the Alfa Chemicals 99+% product was distilled after drying with 4A molecular sieves for at least 24 h. The electrolytic conductance of the latter purified solvent was $1.6 \times 10^{-8} \text{ S cm}^{-1}$ at 25 °C. Methyl acetate (MA) obtained from MC/B or Aldrich Chemical (99+% pure) was similarly treated, and the purified solvent had an electrolytic conductance of $1.4 \times 10^{-7} \text{ S cm}^{-1}$. The water content of both solvents was less than 20 ppm (Karl Fischer method), and methanol was not detected by GC analysis.

$LiAsF_6$ (USS Agri Chemicals Electrochemical Grade) was dried at 60 °C for 24 h and not treated any further. $LiBF_4$ (Foote Mineral Co.) was used as received. All other salts were commercial AR grade products dried at 60 °C under vacuum for 48 h. Li_xCoO_2 was prepared by thermal decomposition of a pelletized mixture of Li_2CO_3 and $CoCO_3$ at 900 °C in air.

The initial product was ground, pelletized, and reheated to 900 °C for 20 h twice more. The final product was examined by X-ray, and the results were found to be in excellent agreement with the JCPDS standard. The stoichiometry of the solid was determined by atomic absorption analysis for Li and Co, and the material analyzed as $Li_{0.85}Co_{0.97}O_2$ [5]. The material prepared in ref. 1 analyzed as $Li_{0.99}Co_{1.01}O_2$.

X-ray analysis of Li_xCoO_2 pretreated with water followed by vacuum drying at 60 °C for 24 h showed no change in the diffraction pattern, thus indicating that the lithiated oxide does not readily react with water. Cathodes were prepared from a mixture of 80.5 mass% Li_xCoO_2 , 9.8 mass% Shawinigan black carbon (SAB), and 9.7 mass% Teflon emulsion. The mixture was rolled into thin sheets and sintered at 280 °C under vacuum for one hour. The sintered cathodes were pressed (to 20 psi) onto both sides of Exmet nickel screen (5Ni 7 - 3/0) or Exmet aluminum screen (5Al 7 - 3/0).

Laboratory cells consisted of a wick cell configuration utilizing flag electrodes in a pressure reaction vessel. Electrodes were sealed in Celgard 2400 polypropylene separator material, and lithium anodes on each side of the cathode were separated with a porous fiberglass separator (wick). A lithium strip served as the reference electrode.

All cells were cathode limited containing about 4 times excess lithium. The polarization at the lithium anode varied between 1 and 8 mV depending upon temperature and current density. The reported efficiencies are therefore based solely on the cathode, and are reported in moles of lithium per mole of oxide with 100% efficiency corresponding to $1 F \text{ mol}^{-1}$.

For methyl formate cells, the electrolyte was either $2 \text{ mol dm}^{-3} LiAsF_6 + 0.4 \text{ mol dm}^{-3} LiBF_4$ or $2 \text{ mol dm}^{-3} LiAsF_6$; no difference was observed with either electrolyte composition. Additions of $LiBF_4$ have been found beneficial in other oxide systems, particularly at high temperatures [3, 5]. For studies with methyl acetate, 2.4 - 2.7 $\text{mol dm}^{-3} LiAsF_6$ solutions were used.

All cells were thermostatted in a Tenney environmental chamber, and cycled at constant current with an ECO model 545 galvanostat.

Results

The specific conductance of pure Li_xCoO_2 ($x \approx 0.9$) was measured by the van der Pauw four probe technique (*e.g.*, see ref. 6). For these measurements, a 1.27 cm dia. pellet was used which was prepared by compression to 1400 psi. The results are given in Table 1 which also includes specific conductances for LiAsF_6 solutions in MF and MA over the temperature range $-40^\circ\text{C} - 25^\circ\text{C}$.

TABLE 1

Specific conductance of lithiated cathode and electrolyte solutions as a function of temperature
Units are S cm^{-1} .

t ($^\circ\text{C}$)	Li_xCoO_2 ($x = 0.9$)	2 M LiAsF_6 + 0.4 M LiBF_4 in MF	2 M LiAsF_6 in MA
25	0.005 13	0.043	0.025
0	0.002 23	0.031	0.013
-10	0.002 04	0.027	0.010
-30	0.001 16	0.018	0.005
-40	—	0.013	0.004

Since Li_xCoO_2 is prepared in the discharged state, the cells were initially charged at a rate of 0.5 mA cm^{-2} to upper limits of 4.5 - 5 V *versus* Li. The best results were obtained by setting the upper voltage limit at 4.5 V. Typical initial charge acceptance corresponded to around $0.7 + F \text{ mol}^{-1}$. Upon discharge, the lower potential limits were varied between 2.5 and 1.5 V *versus* Li.

Initial cell studies in MF and MA solutions employed Exmet nickel screen and Ni wire as current collectors at both anode and cathode. However, corrosion of the nickel at the cathode was severe, leading to rapid loss in capacity and electrolyte degradation after 2 - 5 cycles. These problems were eliminated by utilizing Exmet aluminium screen and Al wire as current collectors at the cathode, nickel still being used for anode fabrication.

For methyl formate solutions with, or without, LiBF_4 , initial charging to about $0.8 F \text{ mol}^{-1}$ resulted in irregularities in the voltage-time curves, indicating solvent decomposition which was visually confirmed by the appearance of an amber color in the electrolyte. Upon discharge at low rates (0.5 mA cm^{-2}), cell capacities were around $0.36 - 0.46 F \text{ mol}^{-1}$ which degraded rapidly upon further cycling. Studies using MF solutions were terminated at this point.

The results using methyl acetate solutions contrasted those utilizing methyl formate. Rate capabilities are excellent and cycle life is satisfactory although no attempt has yet been made to optimize either cathode structure or solvent composition to extend the cycle life beyond around 20 cycles. In all cycling studies presented below, cells were always charged at 0.5 mA cm^{-2} at $25 \text{ }^\circ\text{C}$ while the discharge rates and temperatures were varied. Figure 1 shows the initial charge/discharge for $\text{Li}/\text{Li}_x\text{CoO}_2$ in 2.4 mol dm^{-3} $\text{LiAsF}_6\text{-MA}$ at $25 \text{ }^\circ\text{C}$, and a discharge rate of 2.0 mA cm^{-2} . The potential-capacity curve for the 1 mA cm^{-2} rate is identical with that for the 2 mA cm^{-2} discharge rate. Figure 2 shows the rate capability of the $\text{Li}/\text{Li}_x\text{CoO}_2$ cell at $25 \text{ }^\circ\text{C}$, and Fig. 3 shows the effect of temperature at a constant discharge rate of 2.0 mA cm^{-2} . A numerical summary of the data shown in Figs. 1 - 3 is given in Table 2. The data in this Table show that the $\text{Li}/\text{LiAsF}_6\text{-MA}/\text{Li}_x\text{CoO}_2$ system is not only capable of delivering excellent capacities at high discharge rates up to 10 mA cm^{-2} , but it can do so over a wide temperature range of $-40 \text{ }^\circ\text{C}$ to $25 \text{ }^\circ\text{C}$.

The relation between capacity and cycle number is shown in Fig. 4 where the temperature is constant at $25 \text{ }^\circ\text{C}$ and the discharge rate is fixed at 2.0 mA cm^{-2} . After the first 13 cycles some capacity was recovered by setting the lower limit to 2.0 V . Only moderate gains in capacity were observed by further lowering of this limit to 1.5 V after 19 - 20 cycles. From ref. 2 it is known that the intercalation and deintercalation of Li^+ in Li_xCoO_2 is highly reversible, and structurally stable upon cycling. The observed degradation in capacity shown in Fig. 4 appears to be mainly due to solvent oxidation [8].

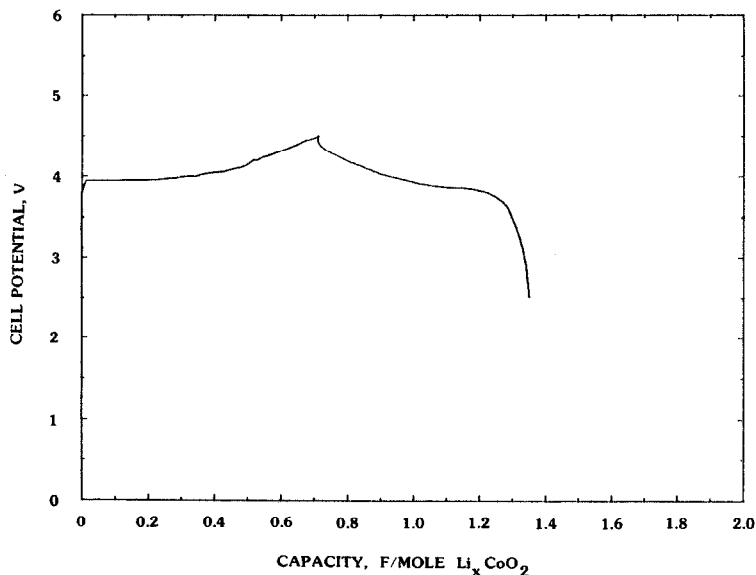


Fig. 1. First charge/discharge cycle for $\text{Li}/2.4 \text{ M LiAsF}_6\text{-MA}/\text{Li}_x\text{CoO}_2$ cell at $25 \text{ }^\circ\text{C}$. Initial OCV = 3.07 V . Charge/discharge rates: 0.5 and 2.0 mA cm^{-2} , respectively.

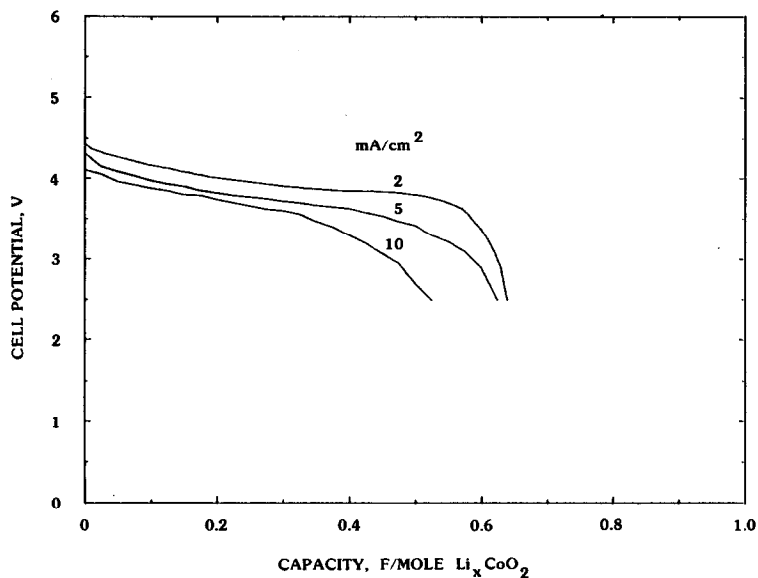


Fig. 2. Discharge curves for Li/2.4 M LiAsF₆-MA/Li_xCoO₂ cell at 25 °C at various rates. All curves are initial discharges except for 10 mA cm⁻² which was measured on the second discharge cycle.

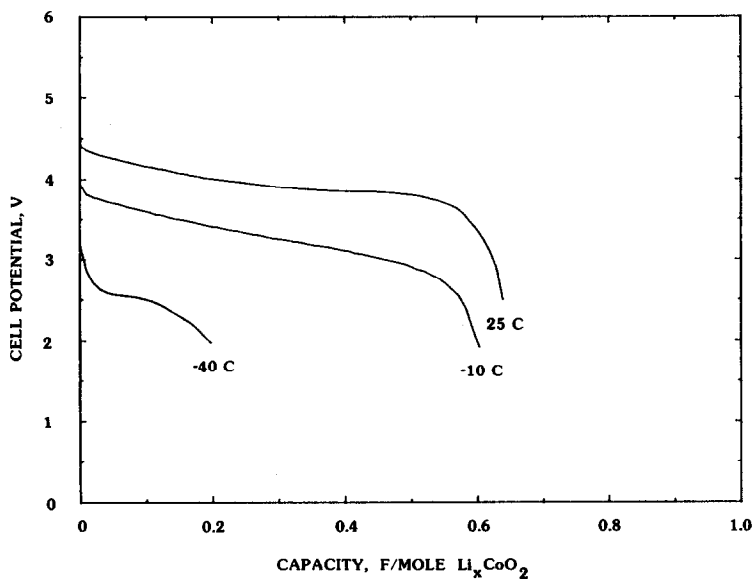


Fig. 3. Discharge of Li/2.4 M LiAsF₆-MA/Li_xCoO₂ cell at 2.0 mA cm⁻² as a function of temperature. 25 °C and -10 °C results are for the initial discharge, and -40 °C results were obtained on the second discharge.

TABLE 2

Discharge results for first and second cycles^a

t (°C)	Discharge rate (mA cm ⁻²)	Capacity (F mol ⁻¹)	Discharge cut-off potential (V)	Average discharge potential (V)	Energy ^b density (W h kg ⁻¹)
25	1.0 - 2.0	0.64	2.5	3.90	688
25	5.0	0.62	2.5	3.70	633
25	10.0	0.53	2.5	3.60	517
-10	2.0	0.60	2.0	3.30	603
-40	2.0	0.20	2.0	2.50	135

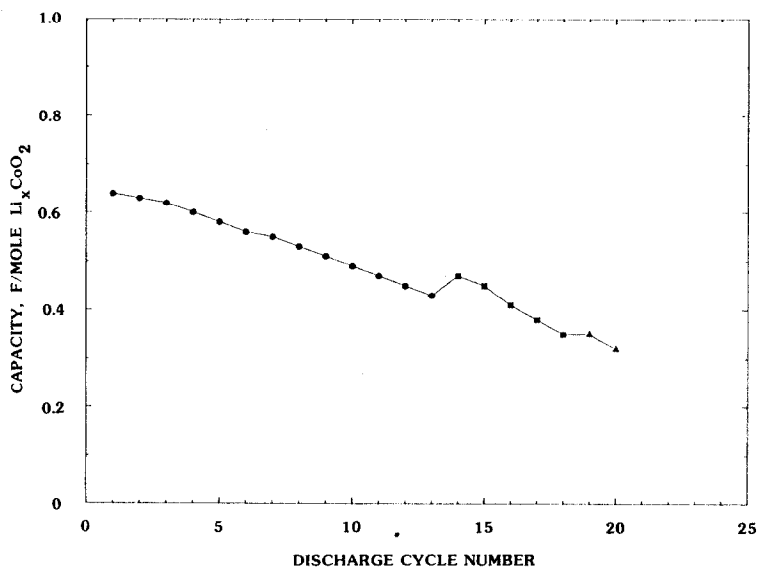
^aCharge voltage cut-off limit was 4.5 V.^bExperimental energy densities are based on mass of active materials.

Fig. 4. Li/2.4 M LiAsF₆-Li_xCoO₂ cell capacity as a function of discharge cycle. Temperature is constant at 25 °C, and charge/discharge rates are 0.5 and 2.0 mA cm⁻², respectively. Voltage limits for the first 20 cycles are : cycles 1 - 13, 4.5 - 2.5 V; cycles 14 - 18, 4.5 - 2.0 V, cycles 19, 20, 4.5 - 1.5 V.

Although it has been reported that methyl acetate solutions offer only limited cycle life capabilities with the lithium electrode [7], the present results demonstrate that methyl acetate solutions are indeed suitable for moderate cycle life, rechargeable cell applications. A more quantitative definition of the actual lithium cycling efficiencies achievable with methyl acetate solutions will be obtained once practical hardware cells have been manufactured and tested.

Conclusions

The present results indicate that using $\text{LiAsF}_6\text{-MA}$ electrolytes, the $\text{Li}/\text{Li}_x\text{CoO}_2$ cell is capable of providing high energy densities over a wide temperature range. Initial discharge rates and capacities (over the first 5 - 10 cycles) are comparable with some primary lithium systems which may be unique for a rechargeable system. In practical hardware, assuming a 33% realization of the experimental energy densities based on active materials (Table 2), the $\text{Li}/\text{LiAsF}_6\text{-MA}/\text{Li}_x\text{CoO}_2$ cell can deliver between 230 and 170 W h kg^{-1} at current densities of 2 - 10 mA cm^{-2} at room temperature. At a discharge rate of 2.0 mA cm^{-2} , the practical energy densities of 200 W h kg^{-1} and 45 W h kg^{-1} are achievable at temperatures of -10°C and -40°C , respectively.

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