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BUTTON-TYPE LITHIUM BATTERY USING COPPER OXIDE AS A CATHODE

TAKASHI IIJIMA, YOSHINORI TOYOGUCHI, JOJI NISHIMURA and HIROMICHI OGAWA

Central Research Laboratories, Matsushita Electric Industrial Co., Ltd., Moriguchi, Osaka (Japan)

Summary

A button-type lithium battery with a nominal voltage of 1.5 V was studied by employing CuO with improved performance as a cathode. The effects of several additives to CuO were examined and the results revealed that CuO heated with a small quantity of Li_2CO_3 at high temperatures could be used as an excellent cathode material. The operating voltage, utilization of CuO and shelf-life of the lithium–copper oxide battery have been improved with the use of the Li-doped CuO.

Introduction

Much attention has been paid to lithium batteries using organic electrolytes because of their high energy density and long shelf-life. At present, several lithium batteries using $(CF)_n$ and MnO_2 as cathodes are being manufactured for commercial applications such as watches and portable calculators [1, 2]. The lithium batteries developed to date operate at a voltage of about 3 V. Lithium batteries operating at a voltage of about 1.5 V are also available using other suitable cathode materials and they can be compatible with conventional aqueous batteries in respect of voltage.

Various materials have been studied as cathodes for 1.5 V lithium batteries, and their theoretical energy densities are summarized in Table 1. Among them, CuO has one of the highest faradaic capacities per unit volume. The value of 4.26 A h/cm^3 is about twice that of $(CF)_n$ and MnO_2 for 3.0 V lithium batteries. Thus, CuO appears to be a most suitable cathode material for a practical 1.5 V miniature type lithium battery in which high volumetric energy densities are particularly required.

With regard to the Li/CuO battery system, a cylindrical AA size cell was first reported by Lehman *et al.* [3]. CuO used for the cathode was prepared by thermal oxidation of a copper powder at high temperature (400 °C). This cell gave a volumetric energy density in excess of 400 - 600 W h/dm^3, compared with 250 - 270 W h/dm^3 for the alkaline manganese dioxide and 130 -

TABLE 1

Comparison of theoretical energy densities of cathode materials for lithium batteries

Material	Valency	Faradaic capacity		Cell reaction coupled with lithium
	(F)	(A h/g)	(A h/ml)	
CuO	2	0.67	4.26	$2Li + CuO \longrightarrow Li_2O + Cu$
FeS	2	0.61	2.90	$2Li + FeS \longrightarrow Li_2S + Fe$
FeS_2	4	0.89	4.45	$4Li + FeS_2 \longrightarrow 2Li_2S + Fe$
Pb_3O_4	8	0.31	2.85	$8Li + Pb_3O_4 \longrightarrow 4Li_2O + 3Pb$
Bi_2O_3	6	0.35	3.07	$6Li + Bi_2O_3 \longrightarrow 3Li_2O + 2Bi$
$(CF)_n$*	1	0.86	2.32	$nLi + (CF)_n \longrightarrow nLiF + nC$
MnO_2*	1	0.31	1.55	$2Li + 2MnO_2 \longrightarrow Li_2O + Mn_2O_3$

*Material for 3.0 V lithium batteries.

150 W h/dm^3 for the Leclanché cell at low and moderate current drains. Recently, similar AA and 1/2 AA size cells were designed by Broussely *et al.* [4]. Considerable increase of efficiency was obtained by using a better separator material and cell capacity was increased by minimizing the void volume inside the cell, leading to energy densities of 200 - 500 W h/dm^3 for the 1/2 AA size cell. Matsuda *et al.* [5] reported on the cathodic performance of the CuO electrode in propylenecarbonate containing 1M $LiClO_4$. The results of X-ray analysis of the CuO electrodes during the discharge showed CuO to be reduced stepwise; $CuO \longrightarrow Cu_2O \longrightarrow Cu$, though the detailed mechanisms have not been clarified. Ohzuku *et al.* [6] investigated the half-cell discharge characteristics for CuO and Cu_2O compared with those of numerous other metal oxides.

The present report summarizes our research on 1.5 V button-type lithium cells using CuO as a cathode. Additives to the CuO, electrode composition, and mixed solvent electrolytes were examined with a view to improving the discharge performances of the battery.

Experimental

Reagents

The CuO was a commercial reagent powder (G. R grade, made from $Cu(NO_3)_2$ by thermal decomposition). All compounds studied as additives to the CuO, were reagent grade products. The lithium was high purity (low sodium) sheet stored under dry argon (Foote Mineral Co). The solvents, propylenecarbonate (PC) and γ-butyrolactone (BL), were distilled with lithium metal under reduced pressure. 1,2-dimethoxyethane (DME) and tetrahydrofuran (THF) were stored over 4 Å molecular sieves for 24 h and distilled at normal pressure. The water remaining in the distilled solvents was checked with a Hiranuma digital Aquacounter (Model AQ-1) and maintained below 20 ppm. The $LiClO_4$ solute was freed from water by melting at 250 ℃

under vacuum. Anhydrous $LiBF_4$ was dried in a vacuum oven at 120 °C. The preparation of electrolytes was conducted in an argon drybox.

Cathode materials

Several additives to the CuO were surveyed to improve the discharge characteristics of the CuO. CuO powder was mixed with the additive and the mixture was heated for 8 h in air at a high temperature. The heat-treated powder was press moulded into a pellet at 790 MPa. The pellet was sandwiched between nickel sheet leads under pressure and its conductivity was measured with a digital conductance meter. Table 2 shows the effects of additives on the conductivity of CuO. The addition of Li at 800 °C as Li_2CO_3 or LiOH (samples 4 and 6) was markedly effective in increasing the conductivity of CuO. No significant changes in X-ray diffraction patterns were observed between CuO and CuO containing Li, as shown in Fig. 1. It seems that Li was completely doped into CuO which became a conductive, p-type semiconductor.

In order to evaluate these materials as cathodes for lithium batteries, preliminary tests were carried out using H-type glass cells. For the cathode, CuO (+Li) powder was pressed onto both sides of an expanded nickel grid. The anode was made from lithium metal sheet attached under pressure to an expanded nickel grid. The cathode, entirely surrounded by a nonwoven polypropylene separator, was inserted between lithium anodes. The couple of cathode and anodes was discharged in an electrolyte of 1M $LiClO_4$/PC + THF (1:1 volumetric ratio). Figure 2 shows the discharge curves of these cells at 20 °C. The cell employing CuO doped with Li as the cathode, showed the highest discharge voltage and the highest utilization. Consequently, CuO powder doped with Li, which was prepared by heating the mixture of CuO and Li_2CO_3 (100:1 mole ratio) at 800 °C for 8 h, was mainly used in the following experiments.

TABLE 2

Effects of additives on conductivity of CuO

Sample no	Additive to CuO	Treatment	Specific conductivity at 20 °C (ohm^{-1} cm^{-1})
1	CuO no additive	–	1 - 2 × 10^{-6}
2	CuO no additive	800 °C, 8 h	5 - 7 × 10^{-5}
3	CuO:Li_2CO_3(100:1 mole ratio)	400 °C, 8 h	2 - 3 × 10^{-4}
4	CuO:Li_2CO_3(100:1 mole ratio)	800 °C, 8 h	1 - 2 × 10^{-1}
5	CuO:LiOH(100:2 mole ratio)	400 °C, 8 h	3 - 4 × 10^{-4}
6	CuO:LiOH(100:2 mole ratio)	800 °C, 8 h	2 - 3 × 10^{-1}
7	CuO:K_2CO_3(100:1 mole ratio)	800 °C, 8 h	2 - 3 × 10^{-5}
8	CuO:$Al(NO_3)_2$(300:1 mole ratio)	800 °C, 8 h	4 - 5 × 10^{-5}

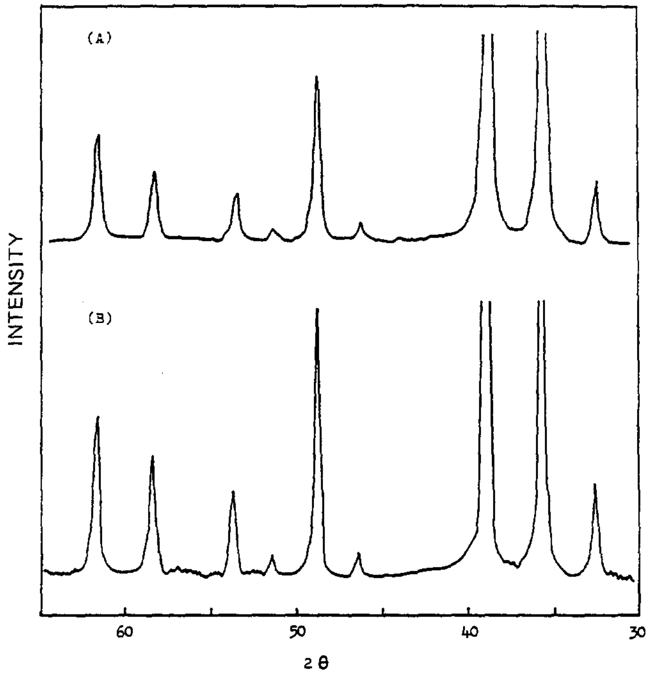

Fig. 1. X ray diffraction patterns (Cu Kα; Ni filter) of CuO powders. (A) untreated CuO powder (Sample 1 in Table 2). (B) Li doped CuO powder (Sample 4 in Table 2)

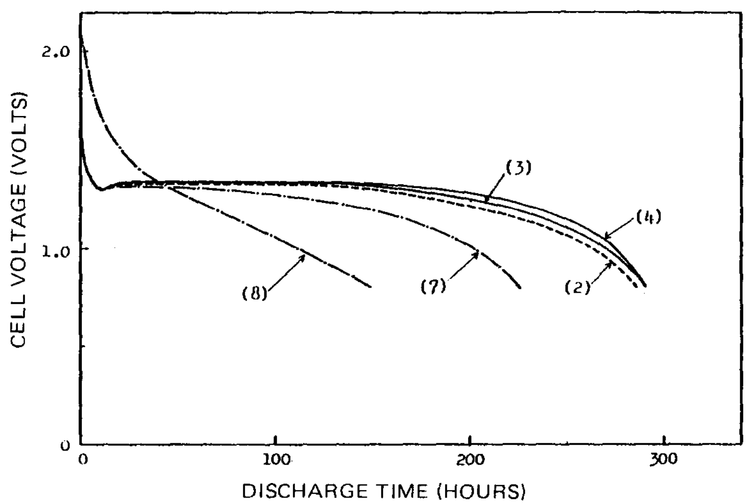

Fig. 2. Effects of additives to CuO on discharge performances under 2.5 mA/cm^2 at 20 °C. (The number by the curve corresponds to that in Table 2.)

Button cells

Button-type cells of two sizes (11.6 mm dia., 5.4 mm height and 11.6 mm dia., 4.2 mm height) were used for testing the cell performances.

The construction of the cells is shown in Fig. 3. The cell cases were made from nickel-plated steel and the sealing grommet was polypropylene. The cathode was a press moulded pellet of CuO (+Li) powder while the anode was a pellet punched from a lithium sheet. Nickel sponge inserted between the lithium anode and the top case functions both as an absorbent of electrolyte and as an electron conductive lead. Microporous polypropylene sheet (Celgard, 0.025 mm thick) was used as a separator.

Results and discussion

Button-type cells (11.6 mm dia., 4.2 mm height) were used to test the composition of the cathodes. CuO heated with Li_2CO_3 and CuO untreated were examined as cathode materials. Acetylene black and graphite were tested as conductive components. When using acetylene black, a binder such as polytetrafluoroethylene was necessary for the pellet to be moulded. The mixed solvent of PC + THF (1:1 volumetric ratio) with the solute of 1M $LiClO_4$ was used as the electrolyte.

The characteristics of cathodes and the cells employing them are summarized in Table 3. The conductivity of the Li-doped CuO pellet was higher than that of the untreated pellet, even when it was mixed with 1 wt.% of acetylene black. Graphite seemed to be superior to acetylene black as the conductive cathode component because the graphite significantly increased the conductivity of the pellet without a binder.

The impedance of button-type cells was proportional to the resistance of the pellets. As was expected, the cell using Li-doped CuO as cathode exhibited a higher utilization of CuO and also showed better retention of discharge capacity after storage at 60 °C for 1 month than the cell using untreated CuO, as shown in Fig. 4.

Various mixed solvents of cyclic esters (PC, BL) and ethers (DME, THF) with solutes of $LiClO_4$ and $LiBF_4$ were studied as organic electrolytes. Fig-

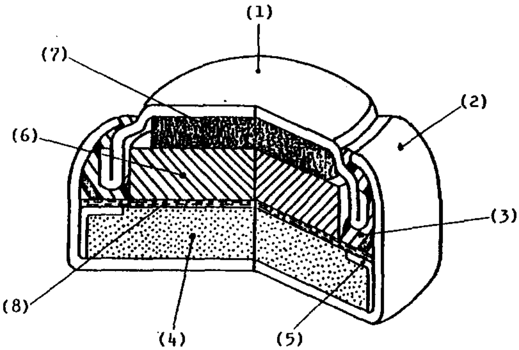

Fig. 3. Construction of button type cell. (1) Top case; (2) cell case; (3) sealing grommet; (4) cathode; (5) cathode ring; (6) anode; (7) nickel sponge; (8) separator.

TABLE 3

Characteristics of the cells employing various compositions of cathodes

Sample number		1	2	3	4	5
Composition of cathode (wt.% ratio)	CuO	100 (untreated)	100 (Li doped)	100 (untreated)	100 (Li doped)	100 (Li doped)
	Conductive component	1 (A.B)	1 (A.B)	5 (graphite)	5 (graphite)	–
	Binder	8	8	–	–	–
Moulded pellet (theoretical capacity 180 mA h)	Thickness (mm)	0.78	0.77	0.75	0.72	0.70
	Resistance (ohm)	2000	23	7	5	25
Size of cell			11.6 mm dia., 4.2 mm high			
Impedance of cell (ohm)		250	92	74	68	120
Discharge performance under 3 kΩ load at 20 °C	Voltage operated (V)	1.11	1.17	1.23	1.27	1.14
	Capacity delivered (mA h)	134	156	144	151	168
	Utilization of CuO (%)	74	83	80	85	91

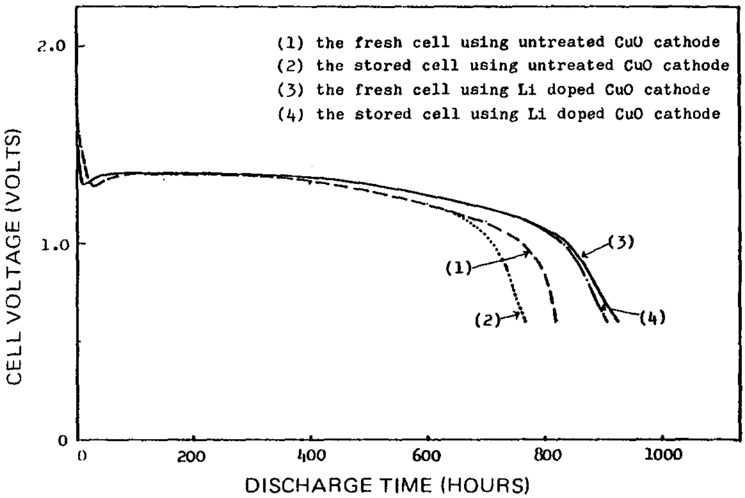

Fig. 4. Discharge curves under 6.5 kΩ load at 20 °C after storage at 60 °C for 1 month for button cells 11.6 mm dia., 4.2 mm high.

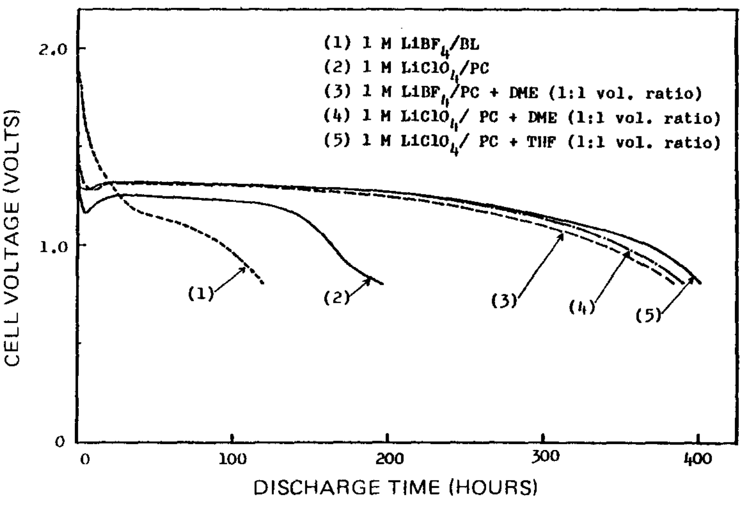

Fig. 5. Effects of electrolytes on discharge performances under 3 kΩ load at 20 °C. Cell size: 11.6 mm dia., 4.2 mm high.

ure 5 shows typical discharge curves of the cells (11.6 mm dia., 4.2 mm height) which employed the mixed electrolytes compared with those of cyclic esters alone. These results showed that the mixed solvents (PC + THF, or DME) were most effective in improving discharge performance under relatively high rates. As a solute, $LiClO_4$ was slightly superior to $LiBF_4$ with regard to operating voltage and utilization of CuO.

As the discharge reaction ($2Li + CuO \longrightarrow Li_2O + Cu$) proceeds, the CuO cathode gradually swells as it produces fine particles of Cu. Thus the cell accommodating a cathode with too much CuO was observed to swell during discharge. Figure 6 shows the relationship between amount of cathode and the swelling of the cells during discharge. From the above experiments, a suitable amount of cathode was determined to be 250 mA h for a cell of dimensions, 11.6 mm dia., 5.4 mm height. Below that amount, the cell showed an acceptable amount of swelling. Based on similar experiments, 180 mA h was determined to be the suitable amount for a cell of the smaller dimensions, 11.6 mm dia., 4.2 mm height.

Discharge characteristics of prototype batteries

Figure 7 shows the typical discharge curves of button-type cells (11.6 mm dia., 5.4 mm height) under 3, 6.5 and 30 kΩ loads at 20 °C. Fairly flat discharge curves were obtained with high utilizations of 85% - 90%.

The influence of temperature on the discharge curves is shown in Fig. 8. The utilization of cathode active material discharged under a 6.5 kΩ load is nearly 100% at 45 °C and about 75% even at a low temperature of −10 °C.

The discharge performances of these cells were tested after being stored at 20 °C for 6 months, at 45 °C for 3 months and at 60 °C for 1 month. To compare them with fresh cells, these cells were discharged at 20 °C under a 6.5 kΩ load after being stored at the elevated temperature. As shown in Fig. 9, no appreciable decrease in cell performance was observed even after storage at the highest temperature.

The typical discharge characteristics of the lithium–copper oxide battery were compared with those of a commercial alkaline manganese, a mercury oxide and a silver oxide battery. As shown in Fig. 10, the button-type cells of the same size were discharged under a relatively low rate of 20 μA

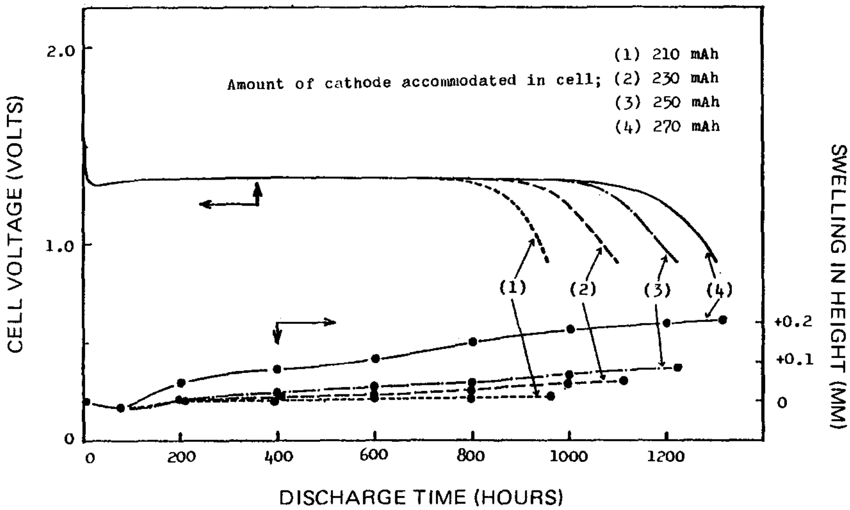

Fig. 6. Relationship between amount of cathode and swelling of cells (11.6 mm dia., 5.4 mm high) during discharge under 6.5 kΩ load at 20 °C.

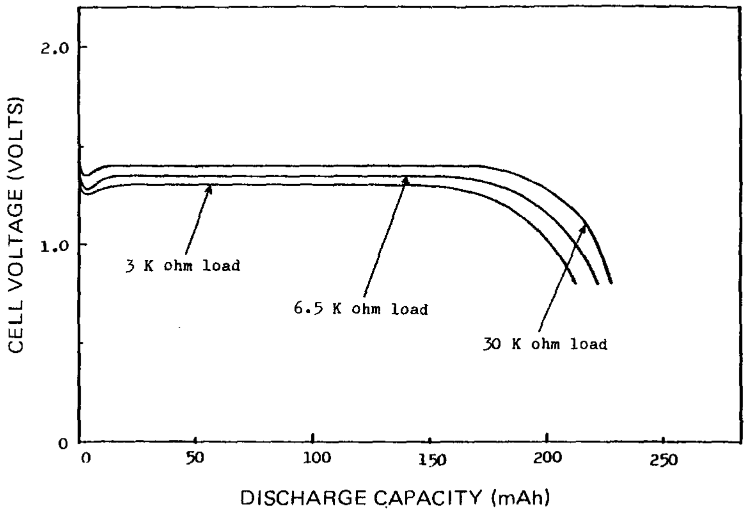

Fig. 7. Typical discharge curves under various fixed loads at 20 °C for button cells 11.6 mm dia., 5.4 mm high.

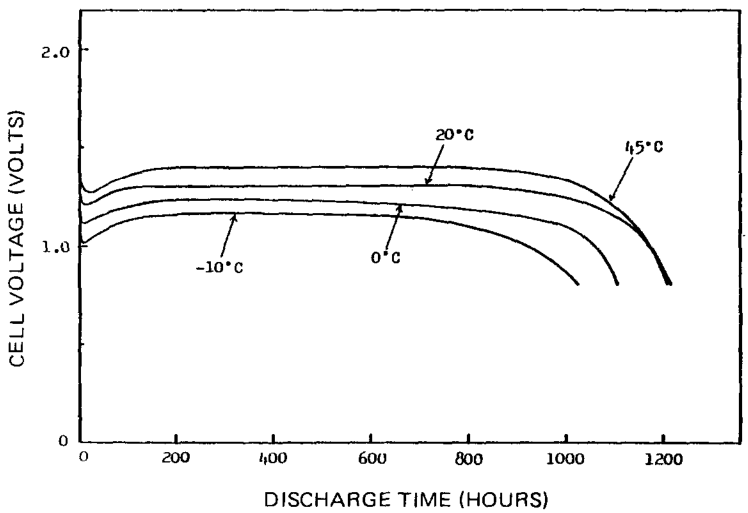

Fig. 8. Influence of temperature on discharge curves under 6.5 kΩ load for button cells 11.6 mm dia., 5.4 mm high.

at 20 °C. Table 4 summarizes energy densities in mW h obtained from these cells. The results indicated that the lithium–copper oxide cell delivered the highest energy, 345 mW h, and did so at operating voltages compatible with those of conventional aqueous batteries.

Conclusion

A lithium button-type cell with a nominal voltage of 1.5 V was studied by using a lithium-doped-copper oxide cathode system. The operating volt-

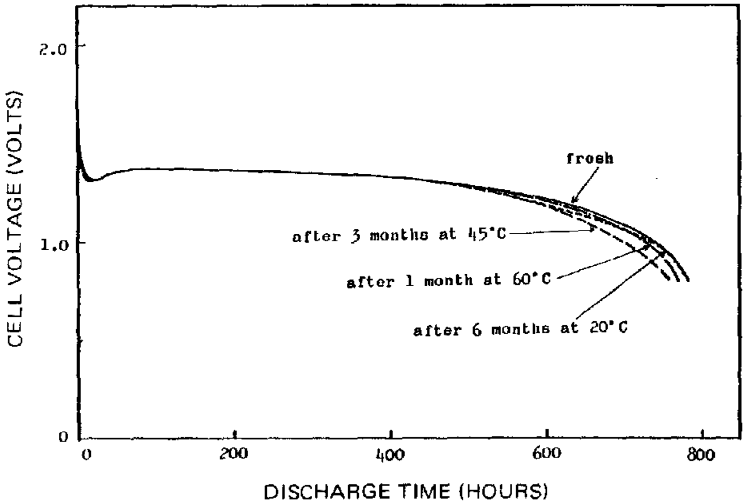

Fig. 9. Effect of storage on discharge performance under 6.5 kΩ load at 20 °C for button cells 11.6 mm dia., 4.2 mm high.

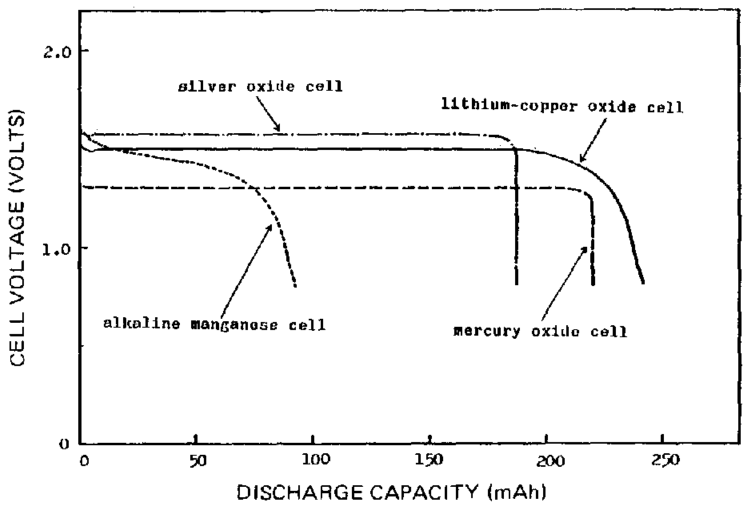

Fig. 10. Comparison between typical discharge curves of the Li/CuO cell and those of conventional aqueous cells at 20 μA at 20 °C. Button cell size: 11.6 mm dia., 5.4 mm high.

age and utilization of CuO, as well as the shelf-life of the battery, were improved by employing CuO doped with Li. On the basis of this study of suitable electrode composition and mixed organic electrolytes, button-type batteries with high energy density were developed which appear to be most promising lithium batteries and which are also compatible with the voltages of conventional systems. Further work to develop other, smaller size cells with a similar configuration is presently being conducted and commercial

TABLE 4

Comparison of energy densities between Li/CuO cell and those of conventional aqueous cells discharged under 20 μA at 20 °C.

Type of cell	Operating voltage (V)	Energy delivered (mW h)
Lithium–copper oxide	1.5	345
Silver oxide	1.55	295
Mercury oxide	1.35	297
Alkaline manganese	1.5	90

application tests of these cells are being carried out to evaluate them as power sources for digital, LCD and analogue watches.

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