Journal of Power Sources, *19* (1987) 325 - 335

PERFORMANCE CHARACTERISTICS OF Li/MnO_2–CF_x HYBRID CATHODE JELLYROLL CELLS

J. W. MARPLE

Eveready Battery Company, Inc., Westlake, OH 44145 (U.S.A.)

(Received April 21, 1986; in revised form November 17, 1986)

Summary

The performance characteristics of a hybrid cathode system containing manganese dioxide and carbon monofluoride are described. This novel cathode mixture provides a synergistic effect offering the most beneficial performance properties of each material. Cylindrical jellyroll cells constructed with this cathode system possess: high energy density, high initial cell voltage (no voltage delay), high rate capability, moderate material cost, stable discharge reaction products, a safe, non-noxious electrolyte, and excellent shelf properties. Performance characteristics are compared with CF_x, MnO_2 and SO_2–lithium cells.

Introduction

A solid cathode, lithium battery system has been developed at Eveready Battery Company [1] which possesses an energy density greater than MnO_2, SO_2 or CF_x and approaches that of liquid cathode thionyl chloride cells. This solid cathode is a hybrid which takes advantage of the beneficial characteristics of manganese dioxide and fluorocarbon cathode materials. Inherent in its design are important advantages over other single component, solid cathode systems. Key limitations of MnO_2 and CF_x solid cathode cells are minimized. For example, one constraint of large, cylindrical CF_x cells is the high price of fluorocarbon materials. Battery grade CF_x costs range from 30 to 60 times that of MnO_2. On the other hand, the MnO_2 cathode suffers from rate capability limitation.

In addition, the mixed component, MnO_2–CF_x hybrid cathode cell developed at Eveready, compares very favorably with other high energy density lithium systems. Energy densities of 11 W h in^{-3} (670 W h dm^{-3}) have been achieved in 2/3A size cells employing MnO_2–CF_x hybrid cathodes (Fig. 1). The energy density advantage of this system is most remarkable when compared with other well established lithium systems. For example, the energy density of a Li–MnO_2 jellyroll 2/3A cell is 7 - 8 W h in^{-3} (420 - 490 W h dm^{-3}) and for Li–SO_2 5 - 6 W h in^{-3} (300 - 370 W h dm^{-3}). Figures 2, 3

0378-7753/87/$3.50

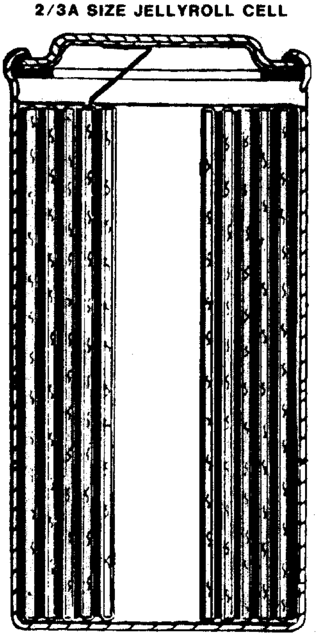

Fig. 1. Cross-section of a 2/3A size jellyroll cell. Dimensions: Dia., 0.640 in.; height, 1.300 in.; volume, 0.418 in^3. Cell input capacities: MnO_2, 1440 mA h; MnO_2–CF_x, 1760 mA h; CF_x, 1850 mA h; SO_2, 1100 mA h. Cell weights: MnO_2, 15.7 g; MnO_2–CF_x, 14.5 g; CF_x, 13.2 g; SO_2, 12.0 g.

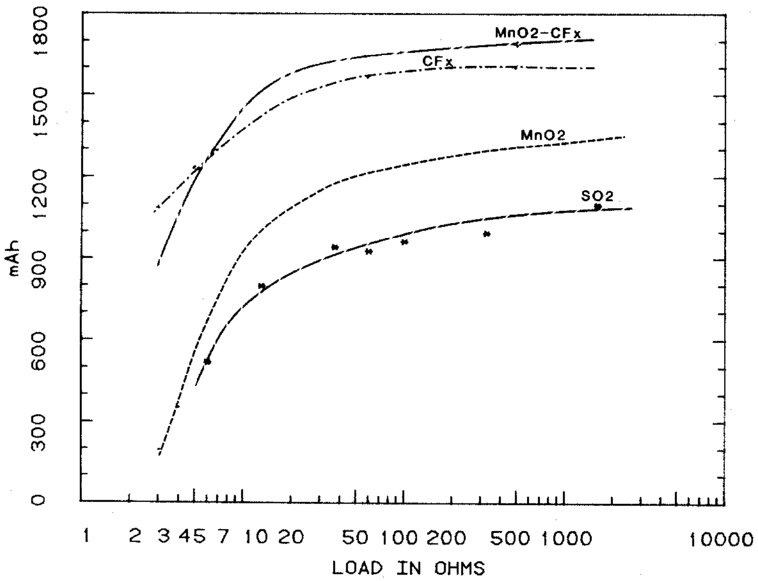

Fig. 2. Comparison of output capacities *vs.* discharge loads for 2/3A size cells.

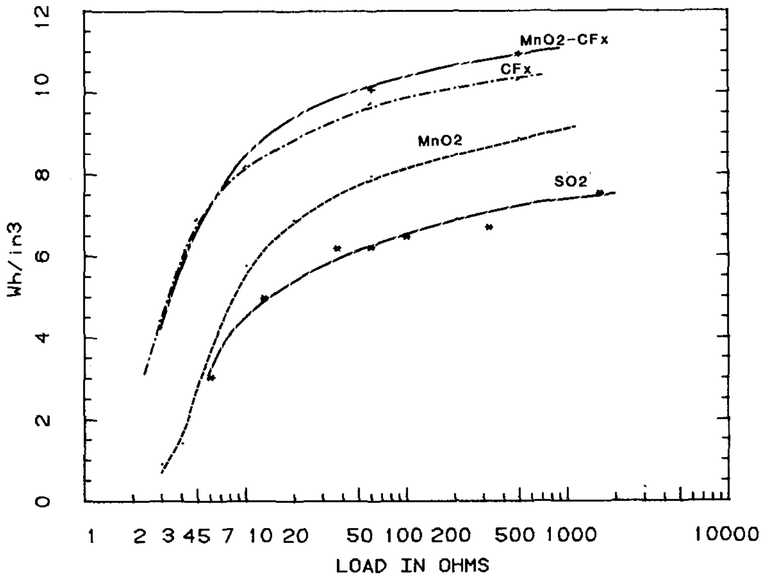

Fig. 3. Comparison of energy densities *vs.* discharge loads for 2/3A size cells.

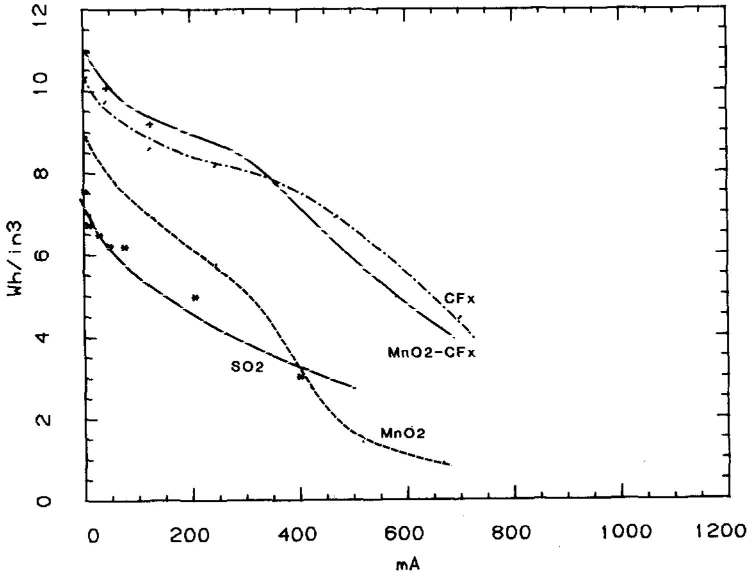

Fig. 4. Comparison of energy densities *vs.* discharge drain currents for 2/3A size cells.

and 4 provide a performance *versus* drain comparison of MnO_2, CF_x and SO_2 with the hybrid. The 2/3A cell can be rated on a 60 ohm continuous discharge. Figures 5, 6 and 7 provide a performance comparison with other lithium systems. The output capacity of the Li/(MnO_2–CF_x) is superior to the other systems in terms of: duration of service, ampere hours and watt hours to a 1.8 V cut-off.

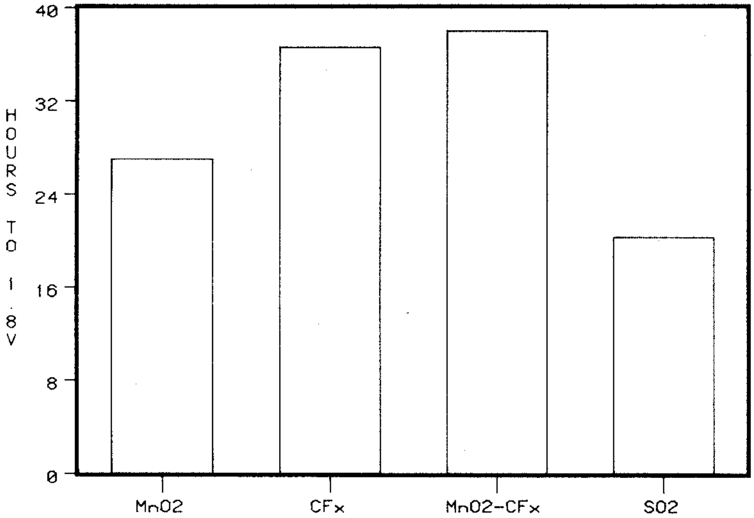

Fig. 5. Comparison of the duration of discharge to 1.8 V, for 2/3 size cells, tested on 60 Ω continuous discharge.

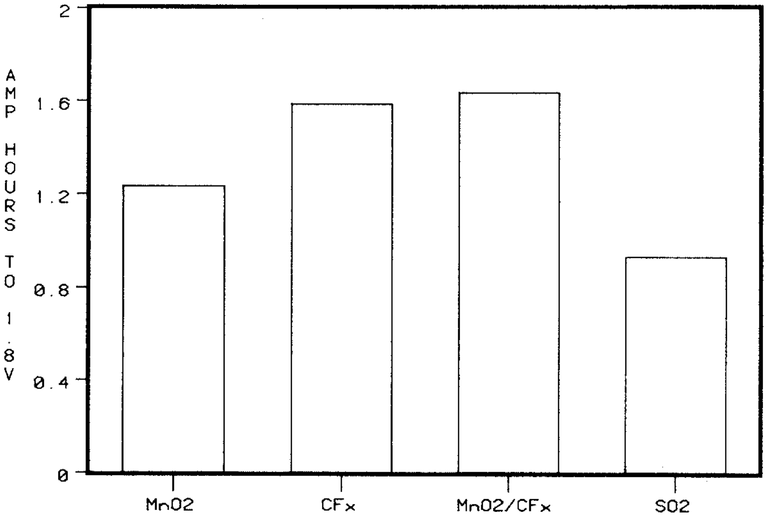

Fig. 6. Comparison of cell capacities to 1.8 V for 2/3A size cells tested on 60 Ω continuous discharge.

Experimental

Performance characteristics of MnO_2, CF_x and MnO_2–CF_x cathodes were evaluated in 2/3A size (0.640 in. × 1.300 in.) cells. Figure 1 provides a cross-sectional view of the cell showing typical cathode inputs and cell dimensions. Manganese dioxide was purchased from Mitsui Toatsu Chemicals

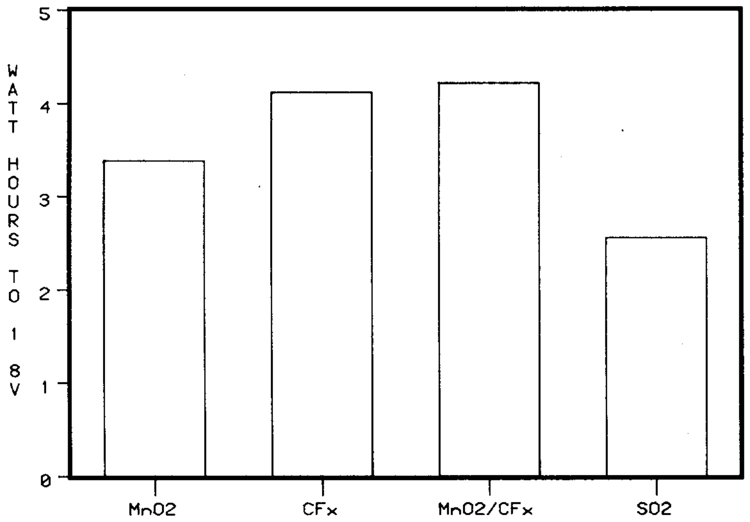

Fig. 7. Comparison of the power delivered to 1.8 V for 2/3A size cells tested on a 60 Ω load.

Inc., type TSV. The polycarbon fluoride was battery grade quality, purchased from Daikin Industries Ltd. The MnO_2 was heat treated in accordance with standard procedures [2]. The binder was a Teflon dispersion manufactured by DuPont. Cathode materials were formed on stainless steel woven wire and dried at 120 °C under vacuum for 16 h. Anodes consisted of battery grade lithium foil, purchased from Foote Mineral Co., pressed onto stainless steel expanded metal. Electrodes were encapsulated in mircoporous polypropylene separator obtained from Celgard Business Unit. Wound jellyroll cells were filled with electrolyte composed of: 0.5 M $LiCF_3SO_3$, 0.5 M $LiClO_4$ and 50/50 vol.% propylene carbonate and dimethoxyethane [3]. The electrolyte was purchased from Ferro Corp. in accordance with Eveready Battery Co. specifications. Cells were constructed in dry-air atmosphere boxes maintained at a moisture level below −55 °C dew point. Cell closures consisted of crimped seals utilizing molded gaskets of polybutylene terephthalate. Cathodes were evaluated over a range of conductor levels: 0 - 10% acetylene black or graphite and poly carbon fluoride levels of from 0 to 30 wt.%.

Results and discussion

Typical MnO_2 jellyroll cells display a rapid decline in performance efficiency at 1 - 3 mA cm^{-2}. Examination of this rate limitation using reference electrodes has shown cathode polarization to be the prime cause of decreased cell capacity. Similarly constructed CF_x($x = 1 \pm 0.05$) cells can be operated at 5 - 7 mA cm^{-2} before exhibiting rapidly declining performance. As a means of improving the performance of MnO_2 cells, various levels of fluorocarbon additions were evaluated. It was found that 20 wt.% CF_x provided the most desirable combination of performance, shelf and cost characteristics. At 20 wt.% CF_x the cell is a true hybrid, with CF_x contributing 48% of the cell input capacity and MnO_2 52%.

At CF_x levels greater than 20 wt.%, the advantages gained from the higher energy density poly carbon fluoride are offset by a decrease in cathode apparent density and electrode discharge efficiency. The admixture of large particle size MnO_2 and smaller particle size CF_x results in a high physical density cathode structure which is compromised as CF_x levels exceed 20 wt.%.

The performances of cathodes containing 10, 20 and 30 wt.% CF_x were evaluated by comparison with nonhybrid MnO_2 and CF_x cathodes. Table 1 provides a comparison of cell performance. These data clearly show the significant stepwise improvement in MnO_2 cell capacity which is observed at 10% and 20% CF_x levels. At the 30% CF_x level cell performance is only marginally improved over the 20% level. Secondly, the data also illustrate the advantage of MnO_2–CF_x mixtures over MnO_2 alone as a function of current density. For example, on a 10 Ω discharge, cells containing 20% CF_x provide 60% more capacity than MnO_2 cells and 38% more capacity on 500 Ω discharge. At the 500 Ω drain cell discharge, capacity approaches the increase in cathode input. At a 10 Ω drain cell discharge, performance greatly exceeds the increase in cell input capacity. This improvement at higher drain rates can be attributed to decreased cathode polarization and resistivity, typical of MnO_2–CF_x cathodes. Table 1 also shows the advantage of 20 and 30% CF_x hybrid cathode cells over nonhybrid CF_x cells.

In addition to an A h per cost consideration, there may be other advantages in limiting CF_x content to approximately 20 wt.%. Above 23% CF_x, hybrid cathode cells become primarily CF_x cells based on capacity. Thus, properties such as the natural stability of the MnO_2 system may be diminished and characteristics of the CF_x system could become prevalent. For example, corrosion of stainless steel components at the cathode potential, and voltage delay characteristics often associated with CF_x cells, may become more predominant.

Advantages of MnO_2–CF_x over MnO_2

A hybrid cathode of CF_x and MnO_2 has two obvious advantages over MnO_2: increased energy density and improved high rate performance. Since CF_x can provide up to 2350 mA h cm^{-3} *versus* 1400 mA h cm^{-3} for MnO_2, cell capacities can be significantly improved by the partial substitution of CF_x for MnO_2. In addition, the fine particle size, 5 - 7 μm, of CF_x, and high lubricity are ideal for obtaining high density electrodes. The substitution of 20 wt.% CF_x for MnO_2 increases the cathode energy density by 35% over a standard MnO_2 cathode formulation. After providing for increased anode and electrolyte inputs, actual cell capacity is increased by 25%.

Proper heat treatment of MnO_2 results in approximately a two order of magnitude decrease in electrical resistivity, from 100 Ω cm to 1 Ω cm [4]. Thus, initially, MnO_2 is a good electrical conductor. As the MnO_2 is discharged

TABLE 1

Comparison of cell performance as a function of polycarbon fluoride content

Cathode formulation (%)		Hours to 1.80 V								
MnO_2	CF_x	10 Ω	Increase* (%)	Increase (%)	60 Ω	Increase* (%)	Increase (%)	500 Ω	Increase* (%)	Increase (%)
		4.0	—		27.0	—		240	—	
88	—			> 25			> 14			> 19
		5.0	25		30.8	14		286	19	
	10			> 35			> 27			> 19
		6.4	60		38.0	41		330	38	
	20			> 5			> 7			> 4
		6.6	65		40.2	48		340	42	
	30									
		5.8	45		36.6	36		312	30	
—	80									

*Increase in service in comparison to nonhybrid MnO_2 cells.

however, electrical conductivity decreases as a result of the build-up of low conductivity reaction products. By comparison, hybrid MnO_2–CF_x cathodes benefit from increased conductivity with depth of discharge. That is, as CF_x is reduced and converted to carbon, a growing conductive matrix is developed. As a result it has been found that a synergistic effect results in which greater MnO_2 efficiency is obtainable. Figure 8 provides a comparison of cathode efficiencies *versus* current density for MnO_2, CF_x and the hybrid cathode.

The advantage of the hybrid cathode over MnO_2 is most impressive on high drain rates. At 5 mA cm^{-2} hybrid cathodes have out-performed MnO_2 by 200%. As drain rates decrease, the performance advantage over MnO_2 approaches the level of increased cell input capacity.

Advantages of MnO_2–CF_x hybrid cathode over CF_x

MnO_2–CF_x hybrid cathode cells possess a number of advantages over CF_x cells. These are: greater cathode efficiency on most applications, higher initial voltage, reduced cathode material cost, and more flexibility in the choice of cell construction materials.

From a simple comparison of material energy densities there would appear to be little incentive or feasible means of matching the capacity of a CF_x cell with MnO_2 or a mixture of MnO_2 and CF_x. From a processing standpoint, however, CF_x suffers from two major drawbacks: (i) CF_x materials do not pack well, and (ii) CF_x initially acts as an insulator. Unlike heat treated MnO_2, CF_x is essentially an insulator prior to discharge, having a resistivity of 10^{12} Ω cm. Thus, to avoid voltage delay problems, substantial levels of voluminous acetylene black are required. In addition, as a result of the small

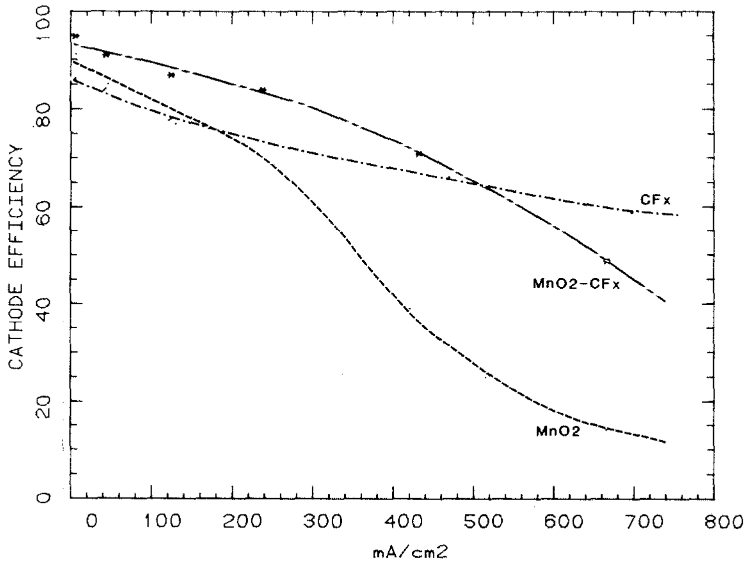

Fig. 8. Comparison of cathode efficiencies *vs.* discharge current densities for MnO_2, CF_x and MnO_2–CF_x, 2/3A size cells.

particle size of CF_x and the high concentration of conductor required, significantly higher binder levels are necessitated. A typical CF_x cathode contains 5% more volume of nonelectrochemically inactive materials than a hybrid cathode. Also, CF_x cathode mix material packing is physically limited to 55 - 60% *versus* 70 - 75% for a hybrid electrode.

In performance comparisons, hybrid cathode-containing cells were found to match or out-perform CF_x cells over a range of applications. Hybrid cathodes also have the advantage of a higher operating voltage than CF_x cathodes. Thus, on some higher voltage cut applications, hybrid cells significantly out-perform CF_x cells. In addition, this higher MnO_2 voltage is observed instantaneously upon load application. CF_x cells typically display a voltage delay or front-end-discharge voltage dip upon applying high drain rate loads. This initial voltage dip, typical of CF_x cells, is shown in Fig. 9. (This front-end voltage drop can be a drawback in some device applications.) By contrast, hybrid cathode cells display the high initial voltage characteristic of MnO_2 cells. For applications which require sustained high voltage performance, it has been found that the substitution of C_2F, while possessing a lower energy density than CF_x, can be advantageous. C_2F operates at approximately 200 mV higher voltage than CF_x. Cells constructed with MnO_2 and C_2F provide a flatter, nonstepped discharge voltage profile. This difference in voltage profiles is demonstrated in Fig. 10.

A secondary advantage of MnO_2–CF_x hybrids over CF_x cells is improved shelf stability and versatility in the choice of construction materials. It has been demonstrated that hybrid cells display shelf characteristics similar to MnO_2 cells. Service maintenance has averaged 95% after 40 days at 60 °C and

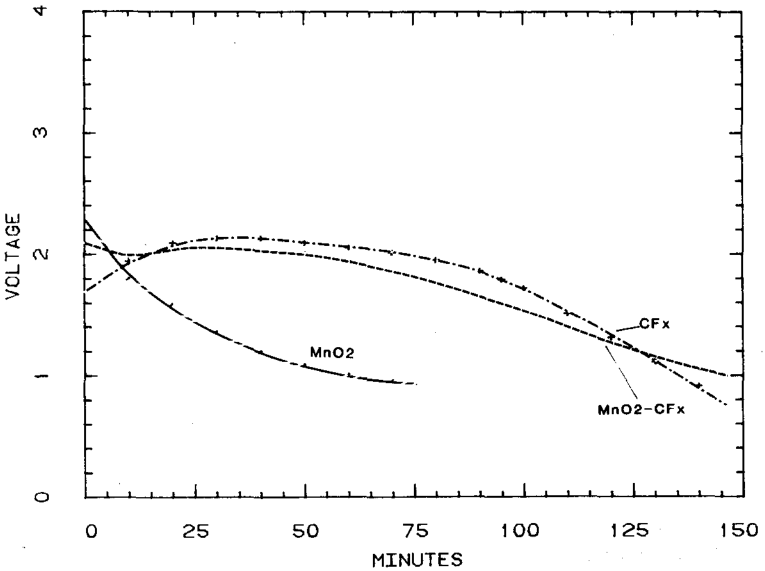

Fig. 9. Comparison of the high rate performance advantage, of 2/3A size cells possessing a polycarbon monofluoride cathode addition.

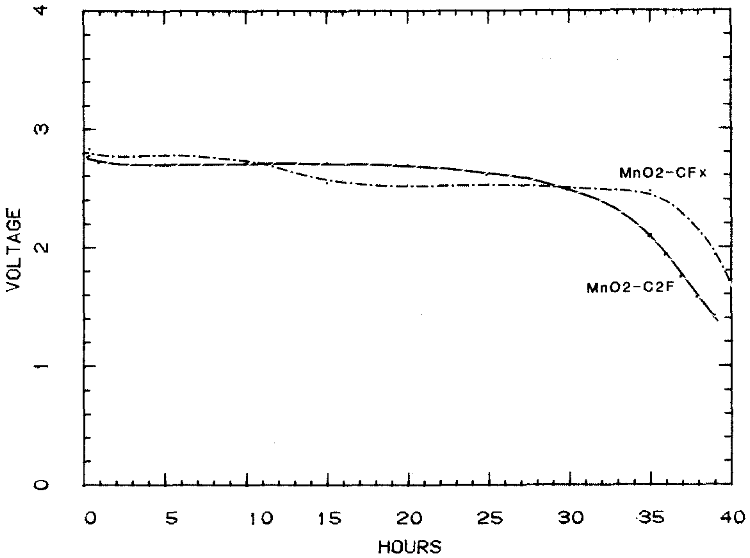

Fig. 10. Discharge characteristics of MnO_2–CF_x and MnO_2–C_2F cathodes in a 2/3A size cell tested on a 60 Ω load.

92% after 80 days at 60 °C. Performance characteristics of the hybrid cell after accelerated cell aging at 60 °C are shown in Fig. 11. By comparison, due to free fluoride associated with CF_x materials, CF_x cells often require more noble, corrosion-resistant cell components such as titanium to provide stable

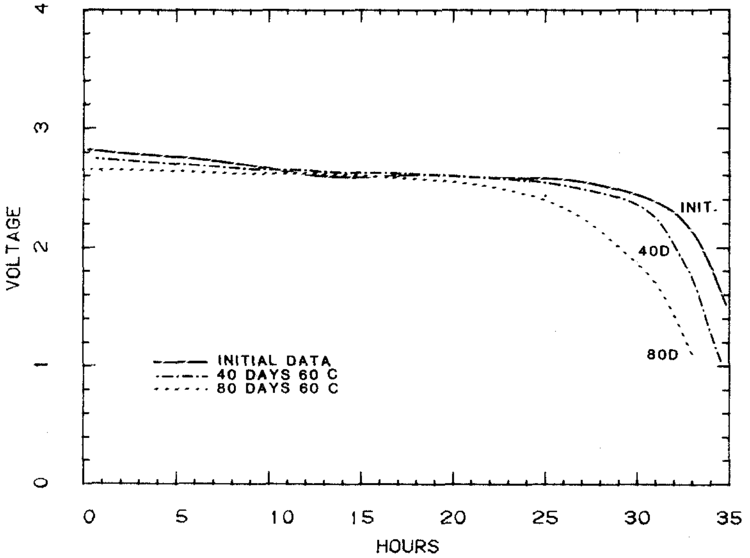

Fig. 11. Performance characteristics of MnO_2–CF_x hybrid cathode cells after elevated temperature storage. Cells stored for 40 and 80 days at 60 °C then discharged on 60 Ω at 21 °C.

shelf properties. In addition, it is generally accepted that CF_x cells require some degree of predischarge to improve shelf stability. Hybrid cathode cells provide excellent shelf life while using common stainless steel materials and without predischarge.

Cost is an important consideration in choosing any battery system. Since the hybrid MnO_2–CF_x cell contains less than half the amount of CF_x than that contained in an Li/CF_x cell, total cell cost favors the hybrid. Presently, the cost of CF_x is 30 - 60 times that of MnO_2.

Advantages of the MnO_2–CF_x hybrid over SO_2 cells

The MnO_2–CF_x hybrid jellyroll cell is superior to Li–SO_2 jellyroll cells in a number of areas: cell capacity, duration of discharge under constant load conditions, cell seal design flexibility, seal cost, and overall cell chemistry safety.

The capacity advantage of a 2/3A MnO_2–CF_x cell over SO_2 jellyroll cells is impressive. For instance, on a 60 Ω, standard rating drain the hybrid system provides 170% more output in ampere hours than SO_2. In addition, the hybrid cell provides approximately twice the service on a real time basis.

Higher internal cell pressure and the diffusion of SO_2 through common compression seal materials has necessitated that SO_2 cells be constructed with costly glass-to-metal seals [5]. By contrast, excellent shelf life and cell safety characteristics have been demonstrated for solid cathode, organic electrolyte cells using less costly compression seal designs.

An additional factor to consider in choosing any battery system is the safety aspect of an accidental cell venting. Vapors released by solid cathode, organic electrolyte battery systems tend to be less corrosive and less noxious than those associated with the SO_2 system. Under moderate abuse conditions, such as cell short circuiting, discharge to a low cell voltage, high rate discharge, and elevated temperature storage, the solid cathode system is substantially more stable than the Li–SO_2 system. Unlike the SO_2 system, solid cathode cells have demonstrated excellent stability under these conditions.

Acknowledgements

The author thanks A. Kozawa for his helpful discussions concerning material conductivity. Previous work on hybrid cathodes by A. Kozawa and V. Leger is gratefully acknowledged.

References

1 Violeta Leger, Nonaqueous cell having an MnO_2/polycarbon fluoride cathode, *U.S. Pat. No 4 327 166.*

2 Hironosuke Ikeda, Manganese dioxide as cathodes for lithium batteries, *Electrochem. Soc. Symp.*, Vol. 1, Cleveland, OH, 1975.

3 Violeta Leger, Nonaqueous cells employing heat-treated MnO_2 cathodes and a PC–DME–$LiCF_3SO_3$ electrolyte, *U.S. Pat. No. 4 419 423.*

4 Akiya Kozawa, Lithium–MnO_2 cells containing CF_x or C_2F in the cathode, *3rd Int. Meeting On Lithium Batteries, Kyoto, Japan, 1986, J. Power Sources, 20* (1987).

5 J. P. Gabano, *Lithium Batteries*, Academic Press, London, 1983.