Studies in lithium oxyhalide cells for downhole instrumentation
Use of lithium tetrachlorogallate electrolyte in Li/SOCl$_2$ cells

Mark M. Morrison

Sperry-Sun Drilling Services, P.O. Box 60070, Houston, TX 77205 (USA)

Nikola Marincic

Battery Engineering Inc., Hyde Park, MA 02136 (USA)

Abstract

Lithium/thionyl chloride cells containing lithium tetrachlorogallate electrolyte have been shown to provide improved performance during interrupted use with temperature cycling. In LiAlCl$_4$-containing cells, the effect, referred to as the 'early failure problem', is profound for temperature cycling above 70 °C and subsequent use at room temperature. This is mitigated when the solute is LiGaCl$_4$. Generally, the voltage delay for LiGaCl$_4$-containing cells is lower than for cells with lithium tetrachloroaluminate, is more reproducible, and the voltage on load is higher. The reduction of LiAlCl$_4$ at the lithium electrode under discharge at elevated temperature is suggested as the possible reason for the early failure problem.

Introduction

Lithium oxyhalide batteries have found extensive use in oilfield equipment used in the well bore, to provide power for applications such as computer memory backup, pressure–volume–temperature measurement, well inclination and direction, and measurement–while–drilling lithology measurements. Applications include use at temperatures from arctic conditions, for instrument functional test, to downhole oilwell conditions up to 150 °C, with discharge current requirements up to greater than 0.5 A in some pulsed discharge applications. Both wound element and bobbin configuration cells are in use. Cells used at elevated temperature are constructed using stainless-steel cases and glass-to-metal seals with welded construction, and the volume of the liquid depolarizer is less than what would be used for room temperature-use cells, to decrease the hydrostatic pressure at elevated temperature.

Bobbin-type lithium/thionyl chloride cells have found extensive use in downhole applications because of safety versus rate capability tradeoffs, decreased self-discharge (because of lower exposed electrode surface area) the relative ease in incorporating features to improve shock and vibration specifications, the relative ease of manufacture in a variety of sizes and shapes to meet widely varying customer requirements, and the relatively inexpensive materials and manufacturing costs. On the other hand, wound element cells show better rate capability and energy density at moderate rate discharge, and demonstrate less severe voltage delay problems due to the lower current density.

Our studies have shown that bobbin-type Li/SOCl$_2$ cells, containing 1.8 M LiAlCl$_4$ electrolyte salt, show significantly reduced operating voltages under load at room temperature after use at temperatures above about 70 °C. Ultimately, the cells may become virtually impossible to discharge at room temperature after extended use at elevated temperature. Once cells are heated back to 70 °C, they can be discharged to full capacity. If, during discharge at 70 °C or above, the temperature is decreased, the cells again fail. Studies on cells containing a lithium reference electrode show that the lithium negative electrode is severely polarized. Examination of the lithium electrode surface on cells that have shown the problem show that the lithium electrode surface is shiny and, based on the amount of lithium remaining, the lithium is present but unavailable for discharge. This performance problem, which we have referred to as the 'early failure problem', certainly limits use in applications where temperature cycling and interrupted discharge are important.

Battery reliability in downhole applications is essential to provide effective instrument performance. Downhole failure due to battery malfunction leads to instrument failure, failure of other components, and serious negative customer impact. In our experience, the early failure problem has led to numerous instrument failures and severe customer impact. This paper describes an approach to solve the problem.

The electrolyte solute in Li/SOCl$_2$ cells is known to be important to develop the structure of the passivating layer on the lithium electrode and causes depressed voltages on start-up of discharge, the 'voltage delay' problem. Various electrolyte salts have been investigated, including LiAlCl$_4$, Li$_2$B$_{10}$Cl$_{10}$, LiBCl$_4$, LiSbCl$_6$, Li$_2$O·2GaCl$_3$, and LiGaCl$_4$ [1–5]. Complex chloroborate salts are not sufficiently soluble and are not completely stable to SOCl$_2$ [3] while the hexachloroantimonate complex yields cells that give unsatisfactory discharge capacity [2]. The performance of cells with the gallium salts has been shown to yield improved discharge capacity at higher discharge rates, decrease the voltage delay problem, and decrease the cell pressure during discharge [2].

The fact that these studies appeared to give rate capabilities similar to cells containing LiAlCl$_4$, that GaCl$_3$ is a weaker Lewis acid, and that availability of gallium salts has improved in recent years, has made it more attractive to evaluate tradeoffs for this electrolyte.

Gallium salts have been added to Li/SOCl$_2$ cells containing aluminum salts to improve discharge capacity and voltage on load [6, 7]. Our studies on cells containing both tetrachloroaluminate and tetrachlorogallate have shown that the 'early failure problem' discussed above is present so long as the tetrachloroaluminate is present.

Experimental

Bobbin-configuration Li/SOCl$_2$ cells were prepared using carbon black/PTFE compounded cathodes contacted to the positive pin by means of an expanded nickel screen, lithium metal (Foote Mineral) swaged onto the stainless-steel can, and vacuum filled with thionyl chloride solutions by a fill-tube which formed the final cell seal. Electrolyte solutions were prepared by slowly adding lithium chloride to the solution of aluminum chloride or gallium chloride in thionyl chloride. Electrolyte solutions were refluxed over lithium metal strips. Infrared analysis insured the absence of moisture in the solution.

Cells were discharged by means of either resistors or an electronic load. The electronic load was designed to simulate a hypothetical RC charging circuit, with

current maximum 0.46 A and minimum 0.06 A with 2 s duration, with about 0.3 A s charge removed per pulse. Data acquisition programming provided minimum and maximum voltage on load, calculated resistance, and provided an easy method for monitoring capacity to a given resistance or end voltage. Cells were tested in conventional laboratory ovens with overtemperature protection and were conducted inside a safety vent hood for protection from the effects of cell venting.

Results and discussion

Performance of baseline cells containing 1.8 M LiAlCl$_4$ electrolyte

Li/SOCl$_2$ bobbin-configuration cells, as commercially available for downhole instrumentation, were discharged as detailed above to develop capacity data and to demonstrate problems after storage or use at various temperatures. Discharge capacity to a 3 V cutoff voltage under resistive load for baseline cells is detailed in Table 1 for discharge at room temperature.

Figures 1 and 2 show typical performance of cells which were previously discharged at 85 and 100 °C for 20 000 pulses at 0.3 A s/pulse (1.67 Ah capacity removed) and then subjected to discharge with the same load after cooling to 21 °C, showing minimum and maximum voltage on the electronic load.

Clearly under this condition, the cells cannot support the current requirement. This phenomenon has not been described previously to our knowledge, and has been referred to as the 'early failure problem'. Based on extensive experience in our laboratories, cells will support the load only if the temperature on discharge is increased to at least 70 °C. For most practical applications, such performance cannot be tolerated or accommodated. The severity of the 'early failure problem' — the decreased load voltage — has been shown in other experiments to be worse with more capacity removed at elevated temperature, worse at 100 than at 75 °C, and is worse at higher discharge currents. Cells constructed with mixtures of LiAlCl$_4$ and LiGaCl$_4$ show that the severity of the problem increases with the concentration of LiAlCl$_4$, although in cells containing 0.1 M LiAlCl$_4$, the problem was still significant.

Voltage delay was monitored following static storage at specified temperatures for 3 and 11.6 days using the electronic pulsed load, monitoring the voltage on load at 0.06 A and the cell resistance. Cell resistance was calculated from the minimum and maximum voltage and the maximum and minimum electronic load current using Ohm's law. Data are presented in Table 2.

TABLE 1

Room temperature capacity of Li/SOCl$_2$ cells as a function of electrolyte and resistive load to 3 V cutoff voltage

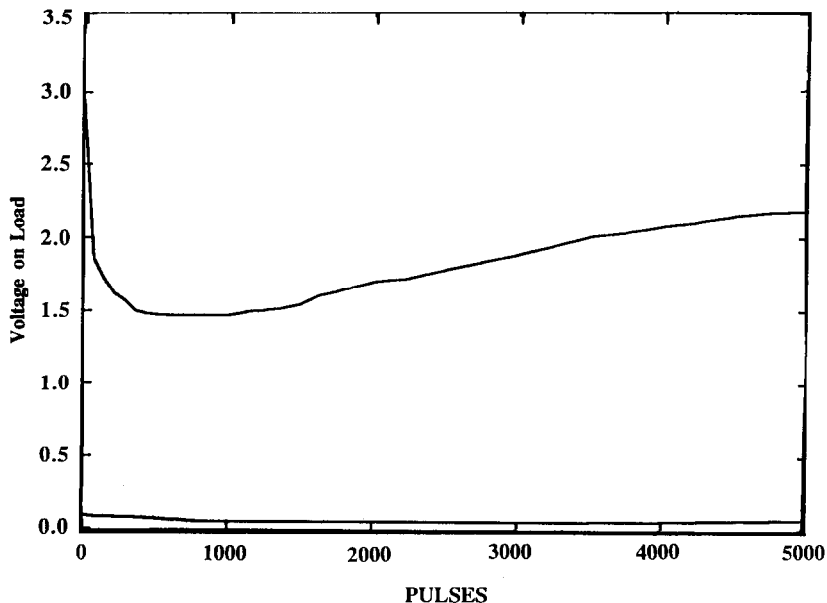| Load (Ω)	Capacity, Ah, for indicated electrolyte concentration LiGaCl$_4$				LiAlCl$_4$
	1.0 M	1.2 M	1.5 M	1.8 M	1.8 M
12	3.99	4.36	4.46	4.28	a
23.7	5.97	5.38	6.11	5.75	6.50
33.0	5.88	6.39	7.30	6.62	7.35
49.7	7.33	7.33	7.76	7.49	9.40

aDischarge rarely above 3 V.

Fig. 1. Voltage at the beginning and at the end of a pulsed discharge test; discharge at 21 °C. Discharge curve is for a Li/SOCl$_2$ cell containing 1.8 M LiAlCl$_4$ electrolyte. Cell previously discharged for 20 000 pulses at 85 °C. Details of discharge pulse are given in text. Top plot is for discharge voltage at 0.06 A, and lower plot for discharge voltage at 0.46 A.

Fig. 2. Voltage at the beginning and at the end of a pulsed discharge test; discharge at 21 °C. Discharge curve is for a Li/SOCl$_2$ cell containing 1.8 M LiAlCl$_4$ electrolyte. Cell previously discharged for 20 000 pulses at 100 °C. Details of discharge pulse are given in text. Top plot is for discharge voltage at 0.06 A, and lower plot for discharge voltage at 0.46 A.
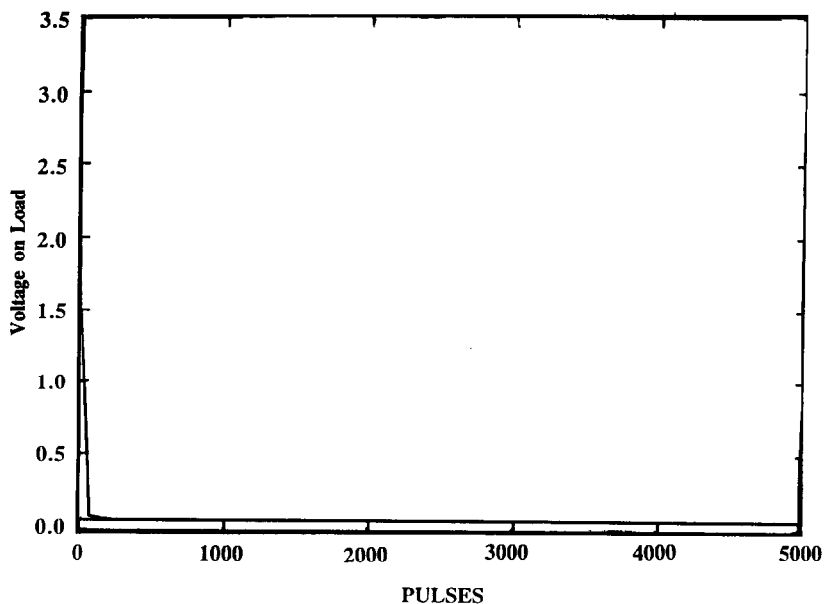
TABLE 2

Voltage delay after 3 and 11.6 day storage at specified temperature for baseline Li/SOCl$_2$ cells containing 1.8 M LiAlCl$_4$ electrolyte; voltage on load: 0.06 A, resistance calculated using Ohm's law: per text

Storage temperature (C)	Data at pulse number	After 3 days storage at specified temperature		After 11.6 days storage at specified temperature	
		Voltage on load (V)	Resistance (Ω)	Voltage on load (V)	Resistance (Ω)
55	0	3.02	ND[a](rep 1)	0.07	ND
	1000	3.25	1.7 (rep 1)	3.17	3.5
	3000	3.18	2.0 (rep 1)	3.30	1.4
	5000	3.07	2.5 (rep 1)	3.30	1.3
	0	1.56	ND (rep 2)		
	1000	3.28	1.9 (rep 2)		
	3000	3.19	2.6 (rep 2)		
	5000	3.16	2.7 (rep 2)		
75	0	3.29	1.3 (rep 1)	0.07	ND
	1000	3.27	1.4 (rep 1)	3.23	2.0
	3000	3.22	1.7 (rep 1)	3.18	2.6
	5000	3.13	2.4 (rep 1)	3.12	3.2
	0	3.54	1.3 (rep 2)		
	1000	3.23	1.8 (rep 2)		
	3000	3.13	2.6 (rep 2)		
	5000	3.14	2.5 (rep 2)		
85	0	3.33	3.3 (rep 1)		
	1000	2.54	6 (rep 1)		
	3000	3.15	2.6 (rep 1)		
	5000	3.12	2.8 (rep 1)		
	0	3.54	1.5 (rep 2)		
	1000	3.18	2.8 (rep 2)		
	3000	3.14	2.9 (rep 2)		
	5000	3.16	2.7 (rep 2)		
100	0	3.26	1.6 (rep 1)	3.48	2.0
	1000	3.28	1.6 (rep 1)	3.26	1.5
	3000	3.14	2.9 (rep 1)	3.24	1.6
	5000	2.98	4.2 (rep 1)	3.22	1.7
	0	3.53	1.6 (rep 2)		
	1000	3.34	1.5 (rep 2)		
	3000	3.28	1.7 (rep 2)		
	5000	3.24	1.9 (rep 2)		
110	0	3.49	1.7 (rep 1)		
	1000	3.29	1.8 (rep 1)		
	3000	1.92	5.5 (rep 1)		
	5000	2.17	ND (rep 1)		

TABLE 2 (*continued*)

Storage temperature (C)	Data at pulse number	After 3 days storage at specified temperature		After 11.6 days storage at specified temperature	
		Voltage on load (V)	Resistance (Ω)	Voltage on load (V)	Resistance (Ω)
	0	0.06	ND (rep 2)		
	1000	3.05	4.3 (rep 2)		
	3000	2.99	4.6 (rep 2)		
	5000	2.97	4.8 (rep 2)		
150	0	ND		3.20	4.8
	1000	ND		2.72	2.8
	3000	ND		2.75	3.2
	5000	ND		2.75	3.4

[a]ND: no data.

Data presented confirm that the worst condition that causes the voltage delay phenomenon for baseline cells is extended storage at 55 °C [8]. It should be noted that based on user's observations, such conditions are not uncommon during ordinary shipping in steel drums during summer months for batteries in use in the southern USA and Gulf of Mexico, tropical, and subtropical regions where oil well drilling is often carried out. Based on the voltage delay data presented in Table 1, which includes several repetitions for test runs for 3 days, considerable performance variability is common.

Performance of cells containing 1.0, 1.2, 1.5, and 1.8 M LiGaCl₄ electrolyte

Results of discharge capacity tests on resistive loads for cells containing various concentrations of $LiGaCl_4$ are presented in Table 1 with data on baseline cells. While the discharge capacity data versus electrolyte concentration cannot be assumed to be statistically significant, the observed trend is that under many use conditions the obtained discharge capacity for cells with 1.5 M $LiGaCl_4$ electrolyte appears to surpass that of cells with other $LiGaCl_4$ concentrations, and, at least at higher rates of discharge, exceeds that of the baseline 1.8 M $LiAlCl_4$ electrolyte cells.

Figures 3 and 4 show typical performance of cells with gallium electrolyte which were previously discharged at 85 and 100 °C for 20 000 pulses at 0.3 A s/pulse as detailed above, and then attempted to discharge with the same load after cooling to 21 °C, showing minimum and maximum voltage on the electronic load. Under these conditions there is no difficulty in continuing the discharge. Under no condition of temperature cycling have we observed the 'early failure problem' for cells containing only $LiGaCl_4$ electrolyte.

Results of voltage delay experiments on cells containing 1.5 M $LiGaCl_4$ electrolyte (Table 3) show that the voltage delay problem observed with these cells is significantly improved at all temperatures up to 150 °C at which the performance is comparable. A direct comparison is given in Fig. 5 for voltage delay after 11.6 days storage at 55 °C for a cell containing 1.5 M $LiGaCl_4$ and a cell containing 1.8 M $LiAlCl_4$.
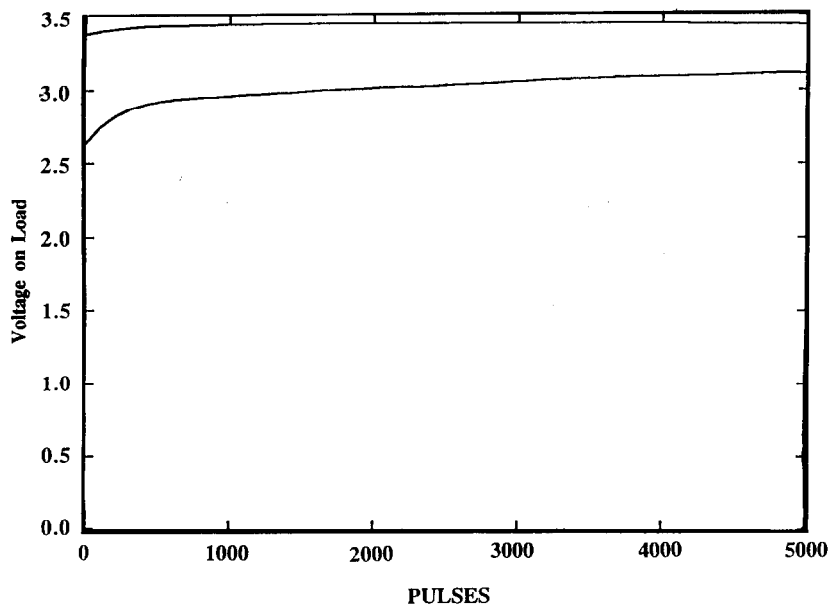
Fig. 3. Voltage at the beginning and at the end of a pulsed discharge test; discharge at 21 °C. Discharge curve is for a Li/SOCl$_2$ cell containing 1.5 M LiGaCl$_4$ electrolyte. Cell previously discharged for 20 000 pulses at 85 °C. Details of discharge pulse are given in text. Top plot is for discharge voltage at 0.06 A, and lower plot for discharge voltage at 0.46 A.
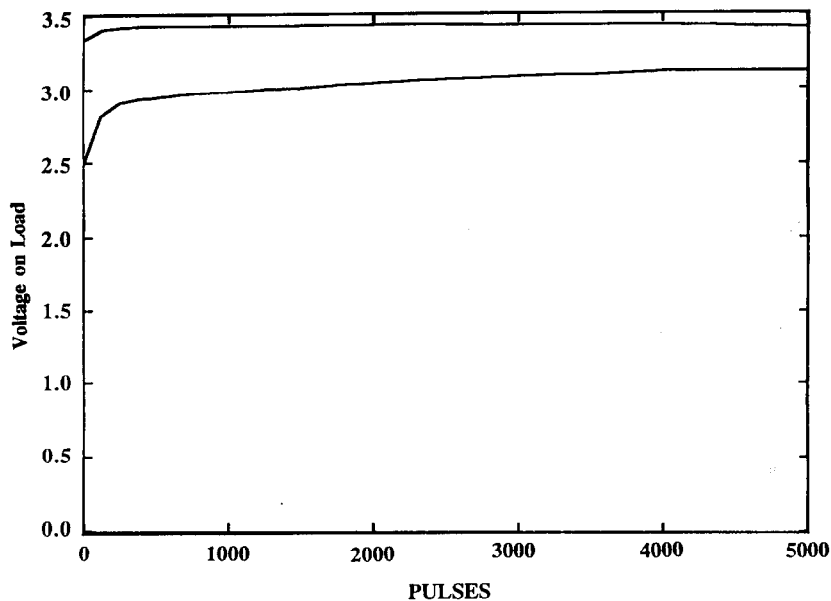

Fig. 4. Voltage at the beginning and at the end of a pulsed discharge test; discharge at 21 °C. Discharge curve is for a Li/SOCl$_2$ cell containing 1.5 M LiGaCl$_4$ electrolyte. Cell previously discharged for 20 000 pulses at 100 °C. Details of discharge pulse are given in text. Top plot is for discharge voltage at 0.06 A, and lower plot for discharge voltage at 0.46 A.

TABLE 3

Voltage delay after 3 and 11.6 day storage at specified temperature for baseline Li/SOCl$_2$ cells containing 1.5 M LiAlCl$_4$ electrolyte; voltage on load: 0.06 A; resistance calculated using Ohm's law: per text

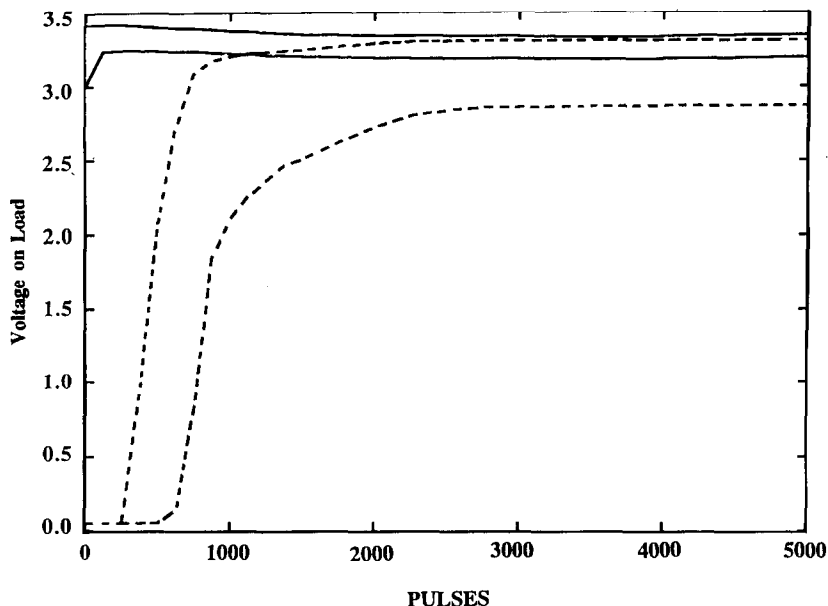| Storage temperature (°C)	Data at pulse number	After 3 days storage at specified temperature		After 11.6 days storage at specified temperature	
		Voltage on load (V)	Resistance (Ω)	Voltage on load (V)	Resistance (Ω)
55	0	3.37	0.93 (rep 1)	3.46	1.2
	1000	3.36	0.68 (rep 1)	3.39	0.46
	3000	3.36	0.64 (rep 1)	3.35	0.45
	5000	3.37	0.63 (rep 1)	3.36	0.45
	0	3.41	1.7 (rep 2)		
	1000	3.35	0.58 (rep 2)		
	3000	3.32	0.51 (rep 2)		
	5000	3.33	0.50 (rep 2)		
75	0	3.29	1.1 (rep 1)	3.49	0.96
	1000	3.29	0.99 (rep 1)	3.41	0.50
	3000	3.29	0.98 (rep 1)	3.36	0.50
	5000	3.29	1.0 (rep 1)	3.36	0.50
	0	3.34	1.9 (rep 2)		
	1000	3.34	0.75 (rep 2)		
	3000	3.32	0.62 (rep 2)		
	5000	3.33	0.59 (rep 2)		
85	0	3.35	2.0		
	1000	3.38	0.52		
	3000	3.33	0.50		
	5000	3.33	0.50		
100	0	3.32	1.0 (rep 1)	3.42	2.4
	1000	3.32	0.72 (rep 1)	3.37	0.68
	3000	3.31	0.66 (rep 1)	3.30	0.69
	5000	3.32	0.60 (rep 1)	3.31	0.70
	0	3.40	2.3 (rep 2)		
	1000	3.38	0.60 (rep 2)		
	3000	3.31	0.60 (rep 2)		
	5000	3.31	0.61 (rep 2)		
110	0	3.34	3.0		
	1000	3.34	0.67		
	3000	3.28	0.65		
	5000	3.29	0.65		
150	0	ND[a]	ND	3.23	3.8
	1000	3.03	4.1	3.24	4.3
	3000	3.05	4.1	3.28	3.8
	5000	3.04	4.2	3.28	3.8

[a]ND: no data.

Fig. 5. Comparison of voltage on pulsed discharge for Li/SOCl$_2$ cells containing 1.5 M LiGaCl$_4$ or LiAlCl$_4$ electrolyte following storage at 55 °C for 11.6 days. Details of discharge pulse are given in text. Solid lines are for cell containing LiGaCl$_4$, dashed lines are for cell containing LiAlCl$_4$. Top plots are for discharge voltage at 0.06 A, and lower plots for discharge voltage at 0.46 A.

Note that the problem with storage at 55 °C is absent for the cells with LiGaCl$_4$. The trends in the voltages on load during the initial stages of discharge seem to indicate that the electrolyte may be more stable with respect to the dissociation equilibria that yield products causing high open-circuit voltages in cells containing LiAlCl$_4$.

The cause for the 'early failure problem' in cells with LiAlCl$_4$ electrolyte is not known. We do not believe that the 'early failure problem' is due merely to some change to the morphology of the lithium passivating layer [9]. In our experience the passivation of the lithium electrode due to extended storage at elevated temperature, can be ameliorated by physical shock to the sides of the cell*. This does not seem to help the 'early failure problem'.

We hypothesize that during discharge at temperatures of 70 °C and higher, the aluminum that is plated onto the anode and alloys with the lithium metal. So long as the temperature is maintained above 70 °C, at the discharge conditions studied, the lithium metal diffuses to the surface of the anode and is discharged. When the cell temperature is decreased below 70 °C, the diffusion of the lithium is too slow to keep up with the discharge rate and the anode becomes polarized. This voltage drop at room temperature has been observed in Li(Mg)/SOCl$_2$ cells on discharge, except that the voltage stabilizes at a higher voltage than in cells with the early failure problem [10]. Further study is warranted.

---

*This is not a recommended procedure.

Acknowledgements

References

1 A. N. Dey, J. S. Miller and W. L. Bowden, *US Patent No. 4 177 329, RE31 414; US Patent No. 4 238 552.*

2 W. L. Bowden, J. S. Miller, D. Cubbison and A. N. Dey, *J. Electrochem. Soc., 131* (1984) 1768; in A. N. Dey (ed.), *Proc. Symp. Lithium Batteries, Washington, DC, USA, Oct. 1983,* The Electrochemical Society, Vol. 84-1, pp. 80–89.

3 C. R. Schlaikjer, *Proc. 28th Power Sources Conf., Atlantic City, NJ, USA, June 1978,* p. 241; *US Patent No. 4 202 240.*

4 A. N. Dey and C. R. Schlaikjer, *Proc. 26th Power Sources Conf., Atlantic City, NJ, USA, April–May 1974,* p. 47.

5 D. L. Chua, W. C. Merz and W. S. Bishop, *Proc. 27th Power Sources Conf., Atlantic City, NJ, USA, June 1976,* p. 33.

6 H. V. Venkatasetty, *US Patent No. 4 279 973; Jpn Kokai Tokkyo Koho, Jpn. Patent No. 81 165 275.* (Assigned to Honeywell.)

7 M. Kogure and M. Mizutani, *Jpn Kokai Tokkyo Koho, Jpn Patent No. 87 254 362; Jpn Patent No. 62 254 362; Jpn. Patent No. 87 254 363; Jpn. 62 254 363.* Y. Shimizu, *Jpn. Kokai Tokkyo Koho; Jpn. Patent No. 85 177 557-A2; Jpn. Patent No. 60 177 557; Jpn. Patent No. 85 177 556; Jpn. Patent No. 60 177 556; Jpn. Patent No. 85 177 555-A2; Jpn. Patent No. 60 177 555.* (Assigned to Japan Storage Battery.)

8 M. Babai, S. Bababigi and J. Bineth, in A. N. Dey (ed.), *Proc. Symp. Lithium Batteries, Washington, DC, USA, Oct. 1983,* The Electrochemical Society, Vol. 84-1, pp. 194–205.

9 W. P. Hagan, N. A. Hampson and R. K. Packer, *J. Power Sources, 24* (1988) 95.

10 P. Kane, N. Marincic, J. Epstein and A. Lindsay, in A. N. Dey (ed.), *Proc. Symp. Lithium Batteries, Washington, DC, USA, Oct. 1987,* The Electrochemical Society, Vol. 87-1, pp. 171–184.
   Further studies carried out at Sperry-Sun Drilling Services confirm the observation and show that the low voltage discharge of $Li(Mg)/SOCl_2$ cells is characterized by low internal resistance, indicating that the main discharge of the cell at low temperature is a discharge of the Mg.