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Coordination in thionyl chloride solutions of alkali metal salts

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Table I. Calculated values for $R(\text{SnO}_2)$, (R/R_c) , and t as functions of the active area (s) for the WO_3 system, neglecting the electrolyte resistance and assuming colored WO_3 to be a good electronic conductor. A square display with $w = 0.5$ cm is considered and the other numerical values are taken as follows: $V_0 = 0.5\text{V}$; $(Q/s) = 6$ mC/cm²; $z = 1$; $V_m = 45$ cm³; $E_y = 1\text{V}$; $D = 10^{-10}$ cm²/sec; $R_{sq} = 20\Omega$; $d = 2000\text{\AA}$. The value given to R_{sq} corresponds to the best presently achievable trade-off between the electrical and optical properties of the SnO_2 film. Dependent numerical values: $t_c = 4$ sec; $t_d = 0.246$ sec; $(R_c s) = 26.1 \Omega\text{cm}^2$; $(\alpha/s^2) = 4.60 \cdot 10^{-4}$ F/ Ωcm^4

Linear scaling factor	$s(\text{WO}_3)$ (cm ²)	$R(\text{SnO}_2)$ (Ω)	(R/R_c)	t_{calc} (sec)
0.1	0.01	100	0.038	0.27
1	1	10	0.38	0.42
10	10 ^a	1	3.8	1.8
32	10 ^a	0.32	12	4.7
100	10 ^a	0.1	38	14

containing a TiO_2 pigment and equilibrated at 65 or 70% relative humidity and 22°C, corresponding to about 30 or 40 weight percent (w/o) H_2O with respect to dry polymer, respectively (6). A carbon paper counterelectrode was used whose potential was about +0.65V vs. NHE. The WO_3 film was colored by injection of 6 mC/cm² and bleached by short-circuiting the device. The current vs. time curve was recorded and used to define the bleaching time as shown elsewhere (7). The experiments were performed at ambient temperature.

Table II shows the effect of increasing the surface area of WO_3 on the bleaching time for the geometry defined in Fig. 5 with an electric contact on only one side. The agreement between the measured response time and the calculated one is very good at small

Table II. Comparison of experimental and calculated response times. Except for R_{sq} the numerical values indicated in Table I were used. R_e , electrolyte resistance; R_{tot} , total resistance of the cell

$s(\text{WO}_3)$ (cm ²)	$R(\text{SnO}_2 + \text{contact})$ (Ω)	R_e (Ω)	R_{tot} (Ω)	R_{tot}/R_e	t_{exp} (sec)	t_{calc} (sec)
0.028	70	50	120	0.13	0.3	0.3
1.6	20	5	25	1.53	0.6	0.9
3.9	8	0.6	8.6	1.28	0.9	0.8
	25	0.6	25.6	3.82	1.7	1.8
100	2.3	0.7	3	11.5	28	4.5
	15	0.2	15.2	58.2	85	20

surface areas. At high surface areas the experimental time is about four times slower than the calculated one. This most likely arises from the finite thickness of the WO_3 film (cf. [3]).

Conclusions

A simplified theoretical model for the response time of electrochromic displays has been used to show that the scaling-up of a practical WO_3 device will be limited by an increase of the response time with increasing active area. The response time of experimental devices was found to be in agreement with the theoretical predictions. Response times smaller than about 10 sec imply a maximum active area of about 1000 cm², at least for the simple geometry considered in Fig. 5. Additional difficulties encountered with large size displays are (i) the presence of a coloration and bleaching wave arising along the front electrode from nonuniform current distribution due to the appreciable resistance in the conductive layer, and (ii) the transient inhomogeneities of contrast due to nonuniform conductivities of the electronic and ionic conductors.

While the additional series resistance is predominant for large active surface areas, the diffusional impedance mainly determines the value of the response time for small active surface areas. In the latter case the response time will tend toward the asymptotic minimum defined by the diffusion parameters.

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Sources of Pressure in Lithium Thionyl Chloride Batteries

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ABSTRACT

The generation of pressure in Li/SOCl_2 batteries has been investigated. Hydrogen, sulfur dioxide, and nitrogen are the principal gases evolved. Reaction of lithium metal with protic species in the liquid electrolyte produces hydrogen gas on open circuit and more rapidly on discharge. Sulfur dioxide is a product of electrochemical discharge. Nitrogen, trapped in lithium metal as dissolved gas or as lithium nitride is released during discharge. In addition, smaller amounts of gas, trapped in cathode pores and adsorbed on the surface of carbon, are evolved when discharge products are deposited in the cathode. Hydrogen pressure is very sensitive to the care used in drying the electrolyte and cathodes. Alternate cycles of evacuation and backfill with SO_2 eliminate much of the moisture and trapped gas from the cell prior to filling with electrolyte.

Ten-thousand amp hour prismatic lithium/thionyl chloride batteries have found increasing use where large high energy density primary batteries are required (1-4). Since pressure can be a critical limiting factor in the design and optimization of large prismatic

batteries, considerable effort has been directed toward identifying the sources of pressure and methods for reducing pressure in Li/SOCl_2 batteries.

In early studies of Li/SOCl_2 batteries, it was assumed that pressure was primarily due to sulfur dioxide resulting from discharge (5-7). Although some metastable intermediates are suspected, the net electrochemical discharge is known to proceed as follows (6)

* Electrochemical Society Active Member.

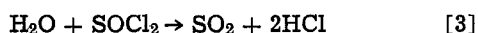
Key words: hydrogen, sulfur dioxide, nitrogen, intermittent discharge, Laplace's law.



The solubility of SO_2 in electrolyte is considerable, about 4 moles/liter of electrolyte at room temperature (8).

Formation of hydrogen gas proceeds in most galvanic cells where an electroactive metal is exposed to protic substances. For example, hydrogen is known to be formed through anode corrosion in Al/MnO_2 (9), Cd/NiOOH (NiCad) (10), Zn/MnO_2 (Leclanche) (11), and Pb/PbO_2 (lead acid) (12) batteries. The rate of this process is limited by the concentrations and diffusion rates of the protic substances in the electrolyte and by the permeability of any film coating the metal. Mechanical disruption of the film during discharge often increases permeability to protic species and hydrogen formation.

In Li/SOCl_2 cells, traces of water react with the electrolyte solute (LiAlCl_4) and solvent (SOCl_2) as follows (13, 14)



Infrared analysis of electrolyte and pure thionyl chloride shows that protons on $-\text{OH}$ groups are reduced to form hydrogen in the presence of lithium metal (15).

This paper discusses the results of a study carried out to determine the extent of these reactions in Li/SOCl_2 cells and the occurrences and sources of other gases which add to the total internal pressure.

Experimental

Six 10,000 A-hr prismatic Li/SOCl_2 cells were used for these studies in order to produce sufficient quantities of gas for accurate analyses. The prismatic cells were $45.7 \times 25.4 \times 31.8$ cm in size. The stainless steel cell walls were held rigidly by a casing of epoxy which was in turn held in an aluminum frame. Two fill ports were provided for electrolyte filling and gas sampling. A third opening held an adjustable pressure relief valve. All cells were routinely leak tested using a Veeco MS17 leak detector. They showed leak rates of less than 10^{-8} cm³ He/sec. The electrode configuration was similar to that described in Ref. (2), and at the current density of 0.9 mA/cm² used in this study, the cells were anode (lithium) limited. Total geometrical electrode surface area was 46,138 cm². After assembly, cells were purged with argon to minimize residual air and moisture and to provide a tracer gas.

Two of the 10,000 A-hr cells were purged with SO_2 gas just prior to filling with electrolyte. This was accomplished with alternate cycles of evacuation and SO_2 gas backfill.¹ The entire purge operation was performed in a closed system in order to exclude moisture and air. Mass spectroscopic analysis of the Matheson sulfur dioxide purging gas for contamination showed only 130 ppm nitrogen, 63 ppm oxygen, and 3.2 ppm argon.

The electrolyte consisted of 1.8M LiAlCl_4 in SOCl_2 . LiCl and AlCl_3 were obtained from Fluka and SOCl_2 from Mobay. The electrolyte solution was prepared and refluxed in the presence of lithium metal to minimize trace amounts of metals and hydrolysis products. The electrolyte was passed from the reflux unit to the cells through an enclosed system to minimize hydrolysis. Standard solutions of "wet" electrolyte with 12, 42, and 110 ppm water equivalents were prepared by slow addition of aliquots of distilled water followed by stirring for several days. Hydrolysis products were measured with infrared absorption spectrometry (13) and, unless otherwise noted, were kept below 12 ppm water equivalents. With the exception of the continuously discharged SO_2 purged cell, all cells were purged with helium after addition of electrolyte, to provide a reference gas. Cathodes were prepared from

Shawinigan acetylene black with a small amount of Teflon binder.

Cell discharge current, voltage, and temperature were monitored as well as ambient temperature. Pressures were measured with Data Instruments Model AB pressure transducers. Zero offsets were checked before each use, and linearity was verified. The cells were discharged with a constant resistive load, using large adjustable carbon resistors, at 40A, or about 0.9 mA/cm² of geometrical surface area. Discharges were carried out continuously or intermittently according to the following scheme: (i) discharge 10% of the total capacity, (ii) remove load for one week, (iii) discharge 10%, (iv) no load for 5 weeks, (v) discharge 10%, (vi) no load for three weeks, and (vii) discharge remaining capacity.

Gas samples were drawn periodically for analysis by mass spectrometry at Gallop Analytical Service, Berkeley, New Jersey. The quantity of gas withdrawn for each sample was small (125 cm³ at about 70 mm Hg) so that the total cell pressure remained constant within the sensitivity of the pressure transducers. Reported gas compositions assume ideal mixing of gases and a constant falling rate of the electrolyte level during discharge which was determined in a separate experiment. Samples of pure SO_2 and SOCl_2 vapor were submitted for analysis by mass spectrometry in order to obtain standard cracking patterns and sensitivities.

Results

Analyses of gases from continuously discharging 10,000 A-hr Li/SOCl_2 batteries show a typical pattern of changing composition as shown in Fig. 1. Exact partial pressures of these gases may vary 1-3 psi between cells treated identically. The combined experimental errors from volume approximations, pressure and mass spectrometer measurements led to experimental errors of less than 10% in most cases as judged from the variation in quantity of helium reference gas found in a given cell over the course of an experiment. The relative partial pressure of helium falls as the cell headspace increases and total electrolyte volume shrinks. Altogether, gas samples were drawn from 6 separate prismatic cell discharges. The resulting gas analyses are given in Tables I-III.

Table I shows the gas composition in a typical baseline untreated cell at the end of continuous discharge. The vapor pressure of thionyl chloride, 1.7 psi, is greatly reduced by soluble discharged products so that the gas is not detected after 30% discharge. Sulfur dioxide, as expected, is generated from the electrochemical discharge. Helium, the reference gas, remains constant for a given cell. In addition, substantial

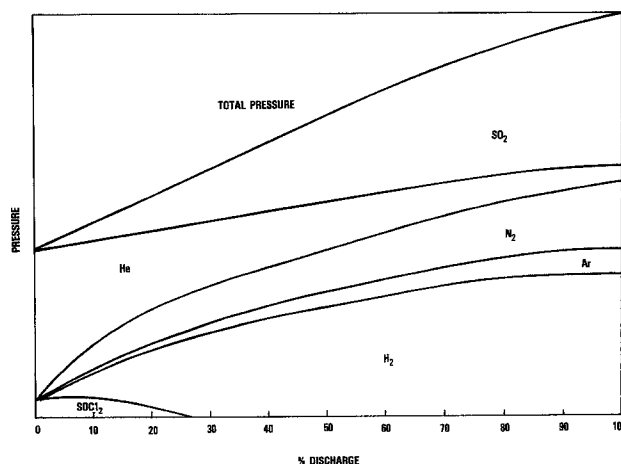


Fig. 1. Typical change in 10,000 A-hr cell gas composition with discharge. Relative gas pressures are represented by areas between lines. Head space increases from 1.9 liters to 5.9 liters during discharge.

¹ U.S. Patent No. 4,303,744.

Table I. Final gas composition of cells discharged continuously as shown in Fig. 2
(Total mols of gas $\times 10^3$)

	Baseline	SO ₂ purge ⁺
N ₂	150.0	190.0
O ₂	4.0	5.0
H ₂	170.0	100.0
He	47.0	ND
Ar	16.0	9.7
CO ₂	1.0	1.0
SO ₂	ND	ND
SO ₃	73.0	80.0
HCl	ND	ND

ND = Not detected.

Table II. Gas analyses of partially discharged Li/SOCl₂ cells before and after 73 days on open circuit as shown in Fig. 3
(Total mols of gas $\times 10^3$)

Initial water equivalents in electrolyte	12 ppm		40 ppm		110 ppm	
	Before	After	Before	After	Before	After
N ₂	46.0	39.0	47.0	41.0	40.0	35.0
O ₂	ND	0.70	ND	2.0	ND	1.9
H ₂	131.0	204.0	141.0	214.0	178.0	235.0
He	2.7	2.2	9.3	7.9	6.9	5.4
Ar	14.0	15.0	16.0	15.0	20.0	17.0
CO ₂	0.33	0.38	0.36	0.32	0.32	0.32
SO ₂	ND	ND	ND	ND	ND	ND
SO ₃	43.0	29.0	43.0	33.0	44.0	34.0
HCl	ND	ND	ND	ND	ND	ND

ND = Not detected.

Table III. Gas analyses of partially discharged Li/SOCl₂ cells before and after 6 days on constant current load as shown in Fig. 3
(Total mols of gas $\times 10^3$)

Initial water equivalents in electrolyte	12 ppm		42 ppm		110 ppm	
	Before	After	Before	After	Before	After
N ₂	40.0	77.0	32.0	96.0	31.0	72.0
O ₂	3.7	5.3	0.93	7.5	2.1	7.5
H ₂	368.0	658.0	364.0	613.0	401.0	697.0
He	1.8	2.1	6.2	7.7	4.2	4.9
Ar	12.1	17.5	13.0	21.0	16.0	21.0
CO ₂	0.45	1.2	0.56	1.6	0.46	1.4
SO ₂	ND	0.23	ND	0.056	0.48	ND
SO ₃	34.0	175.0	48.0	189.0	52.0	213.0
HCl	0.75	0.35	0.071	0.29	0.23	0.15

ND = Not detected.

amounts of hydrogen, nitrogen, and argon were detected along with minor amounts of oxygen, carbon dioxide, and sulfur trioxide.

The pressure increase in untreated cells discharged continuously is represented by the upper line in Fig. 2. Continuously discharged SO₂ purged cells showed pressure increases similar to the lower line in the same figure. Final gas compositions are shown in Table I.

The long-term effects of intermittent discharge were investigated in the same cell configuration, using the sequence given in the Experimental section. Figure 3 shows the increase in pressure observed during the extended periods of open circuit, both with and without the SO₂ purge. Pressure had become fairly constant within the sensitivity of the pressure transducer before completion of discharge in the fifth month. No difference in capacity or load voltage was observed between continuously and intermittently discharged cells.

Two additional cells were discharged according to the same intermittent scheme. The electrolyte in these

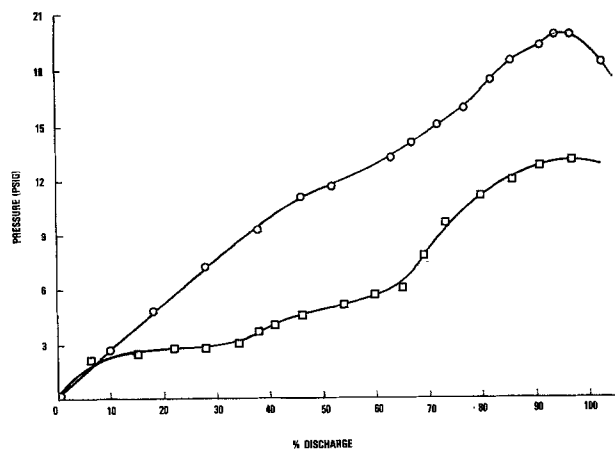


Fig. 2. Pressure increase in continuously discharged 10,000 A-hr cells: (□) with and (○) without SO₂ purge treatment.

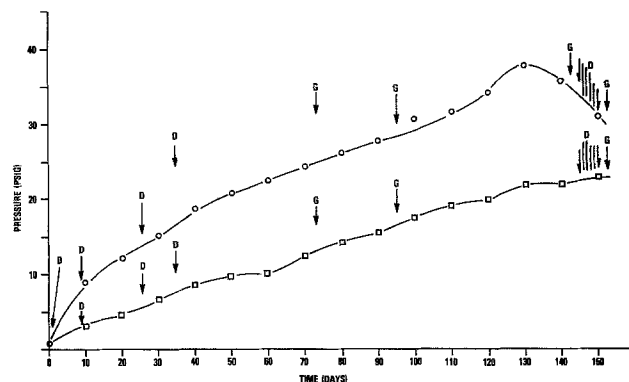


Fig. 3. Pressure increase in intermittently discharged 10,000 A-hr cells: (□) with and (○) without SO₂ purge treatment. Arrows indicate: (D) 24 hr discharge and (G) gas samples.

cells was doped with water to produce hydrolysis product contents of 42 and 110 ppm water equivalents. The discharge pressures of these cells are shown in Fig. 4 compared with the untreated baseline. No difference in running voltage or capacity was observed and none of the cells developed significant voltage delay. Initially, the pressure increases both on discharge and open circuit were proportional to the hydrolysis product content of the electrolyte. However, after about 15 days, the pressure increase was independent of the amount of water added. Gas analyses of the three cells represented in Fig. 4 before and after 73 days on open circuit and before and after 6 days on discharge are shown in Table II and III, respectively. This final

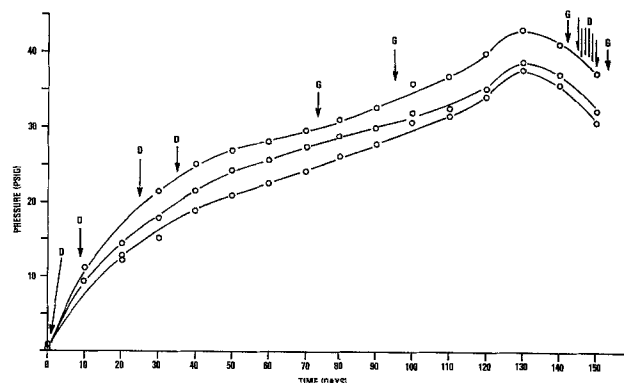


Fig. 4. Pressure increase in intermittently discharged 10,000 A-hr cells containing electrolyte doped with 12, 42, and 110 ppm water equivalents of hydrolysis products (lower, middle, and upper curves, respectively). Cell discharge scheme and gas sampling as in Fig. 3.

6 day discharge consumed the remaining capacity of the cells. Table IV gives the gas analysis for the SO₂ purged cell, which was intermittently discharged, before and after 73 days on open circuit and after complete discharge.

Discussion

Mass spectroscopy proved to be an accurate and useful means of identifying gaseous components within hermetically sealed cells. Duplicate analyses differed by less than 5%. The overall impression one receives from the data is that gases are generated in Li/SOCl₂ cells uniformly with the exception of SO₂ whose solubility in the thionyl chloride electrolyte is quite temperature sensitive. Therefore, despite the complexity of the various physicochemical processes involved, one can draw certain qualitative and, in the case of hydrogen, quantitative, conclusions.

The two candidates most often mentioned in the literature as possible discharge intermediates, SO (6, 16, 17) and SOCl (16, 17) were not detected by mass spectrometry in mixtures of gases over discharging Li/SOCl₂ cells. There is, however, occasionally a small quantity of SO₃ detected in unpurged cells. This may result from the redox reaction between an unstable intermediate such as SO and traces of O₂ remaining in the cathode pores.



Equation [4] would also help account for the near absence of oxygen in these cells. Table III shows that SO₂ increases with discharge while Table II shows no SO₂ gas generated over two months on open circuit.

SO₂ pressure depends on method of discharge. Final SO₂ contents vary from 70 millimols in the unpurged continuously discharged cell (Table I) to 213 millimols in the intermittently discharged cell (Table II). Final values of SO₂ content in the four intermittently discharged cells are substantially larger than those for the two continuously discharged cells. This observation supports the contention that SO₂ is actually the product of an intermediate reaction in the electrolyte which follows the initial electrochemical reduction of SOCl₂. The relatively constant value for SO₂ gas content over the 73 day period of open circuit (Tables II and IV) probably means that the process of discharge itself stimulates the breakdown of the intermediate. Thus, cells discharged intermittently or at very low rates are expected to produce more SO₂ gas.

Another major contributor to gas pressure in Li/SOCl₂ cells is H₂. Hydrogen was formed in untreated 10,000 A-hr cells during discharge at about 7.6×10^{-7} mols/day/cm² of geometrical electrode surface area. Since the lithium anode takes on a positive charge with the cell under load, negatively charged protic substances such as AlCl₃OH⁻ (see Eq. [2]) diffuse much faster to the lithium. A slower rate of about 2×10^{-8} mols/day cm² of hydrogen occurs during open circuit. These maximum rates of hydrogen gas generation

were both diminishing by the fifth month of intermittent discharge indicating that the cells' sources of protons were nearly exhausted. Thus, cells discharged intermittently or continuously at low rate are expected to produce hydrogen gas more rapidly. Cathode limited cells may continue to produce hydrogen after completion of discharge until all available protons are reduced. Fresh Li/SOCl₂ cells do not appear to develop significant hydrogen pressure, possibly because a brief discharge is required either to produce a more permeable passive film on the lithium or because a discharge product, such as SO₂ is required.

Infrared studies of wet solutions of LiAlCl₄ in SOCl₂ in the presence and absence of lithium metal show that one of the proton containing hydrolysis products, believed to be hydroxyaluminate, LiAlCl₃OH, reacts directly with lithium to produce hydrogen. The suggested reaction is



The rate of disappearance of the LiAlCl₃OH O-H stretch corresponds roughly to the observed rate of hydrogen generation on open circuit in a large cell. These results will be presented in a separate paper (15). Evidence for the aluminate product shown above is provided by surface x-ray photoelectron spectroscopy of lithium from discharged cells (18).

Further evidence for the origin of hydrogen is provided by analysis of gases evolved in cell stacks purged with sulfur dioxide (Fig. 1, Table I). The reduced partial pressure of hydrogen suggests that the purge has removed some volatile protic substance, such as water, prior to activation of the cells with electrolyte.

The solubility of H₂ in lithium metal is low (see below). Its solubility in SOCl₂ has not been measured but is expected to be quite low and there is no evidence for a room temperature reaction between hydrogen and thionyl chloride. Generated hydrogen thus necessarily concentrates in Li/SOCl₂ cells as a gas in locations which depend upon the geometry and orientation of the electrode stack.

Perhaps the most surprising result of the gas analyses of discharging cells was the detection of the evolution of argon and other trapped gases from the electrode stack as shown in Table III and IV. On open circuit, the quantities of both helium and argon remain fairly constant as shown in Table II and IV.

Surface active carbon such as Shawinigan acetylene black will always possess some adsorbed gas. Acetylene black provides a surface of about 60 m²/g. Both polar and nonpolar gas molecules may be adsorbed depending on the physical history of the material (19). It is for this reason that the SO₂ purge succeeds in reducing pressure in Li/SOCl₂ cells. Hydrogen pressure is reduced because of the replacement of adsorbed water by SO₂. The argon initially left in the dry electrode stack is also replaced by SO₂. Final SO₂ gas content, on the other hand, is not greatly affected (Table I and IV).

As trapped gases are released from the porous cathode, they are expected to increase pressure in sealed cells for two reasons. First, adsorbed gases on the surface of carbon possess extremely low vapor pressures. If forced off the surface by replacement with gas, liquid, or solid discharge products, these adsorbed gases will exert additional pressure, especially if their solubility in the electrolyte is low. Second, small trapped bubbles of gas, less than 1 micron in diameter and surrounded by liquid electrolyte, are under pressure. From Laplace's law (20) the pressure differential, ΔP , across a bubble-liquid interface is related to the diameter, d , of the bubble and surface tension, γ , of the liquid as follows

$$\Delta P = \frac{\gamma}{2d}$$

The surface tension of 1.8M LiAlCl₄ is estimated to

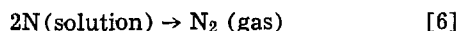
Table IV. Gas analyses of an SO₂ purged, intermittently discharged Li/SOCl₂ cell before and after 73 days on open circuit and after complete discharge as shown in Fig. 4
(Total mols of gas $\times 10^3$)

	Before	After	Final
N ₂	49.0	53.0	71.0
O ₂	2.2	7.3	ND
H ₂	102.0	140.0	444.0
He	1.5	1.4	1.5
Ar	6.1	6.7	11.0
CO ₂	0.28	0.40	1.6
SO ₃	ND	ND	ND
SO ₂	21.0	31.0	194.0
HCl	0.98	0.21	0.18

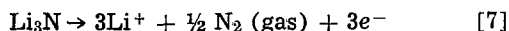
ND = Not detected.

be approximately 50 dynes/cm. Thus a 1.0 micron bubble trapped in the electrode stack would be compressed at a pressure of 0.3 atm or 4 psi above the surrounding medium. Actually, pore sizes on the order of 70Å have been detected by small angle x-ray scattering of carbon blacks (19). When the bubbles are forced to coalesce, unseated by solid discharge products, the gas expands exerting additional pressure. As with hydrogen, the distribution of these gases depends on the geometry and orientation of the electrode stack.

Substantial quantities of nitrogen are also generated on discharge (Table III and IV) but not on open circuit (Table II and IV). The absence of appreciable amounts of oxygen suggests that the evolved nitrogen is not the result of air contamination (barring some unusual reaction such as [5] which would quantitatively remove oxygen). It is more likely that the nitrogen comes from the lithium anode as it is discharged through one or both of the following mechanisms: dissolution of trapped or dissolved nitrogen



electrochemical oxidation of lithium nitride, a known surface contaminant



At end of discharge, 51-190 millimols of nitrogen gas are found. This corresponds to between 260 and 1000 ppm nitrogen present in the lithium metal at start of discharge.

The solid solubilities of nitrogen and hydrogen in lithium at their eutectic temperatures are 0.024 mol percent (m/o) at 180.24°C and 0.002 m/o at 180.41°C, respectively (21). The solubility of oxygen, on the other hand, is only 0.0009 m/o in liquid lithium at 200°C (22).

The high solubility of nitrogen suggests that in lithium batteries, some nitrogen is expected to be evolved during discharge unless this gas is scrupulously excluded from the lithium. Attempts to remove nitrogen from lithium by filtration have suggested that once this metal has been saturated with nitrogen, impurity levels below 0.08 m/o would be difficult to achieve (23).

Although the above discussion addresses sources of gases for one particular electrochemical power source, other lithium battery systems are expected to behave in a similar fashion. For instance, both the lithium/sulfuryl chloride and the lithium/sulfur dioxide batteries contain the requisite lithium anode and porous carbon cathode.

Summary

Four categories of gases contribute to pressure in lithium thionyl chloride cells: gases trapped by adsorption and absorption in the carbon cathodes and released as insoluble discharge products are deposited; hydrogen from reduction of hydrolysis products or other protic species both on discharge and open circuit; electrochemically generated sulfur dioxide evolved during discharge; and nitrogen released from the lithium anode during discharge.

The additional SO₂ gas present on five month intermittent discharge over continuous discharge provides evidence for a sulfur-containing intermediate. Intermittent discharge helps to break down this intermediate and to stimulate other gas producing processes.

Total pressures in continuously and intermittently discharged Li/SOCl₂ cells can be kept within manageable limits by careful control of lithium, electrolyte, and carbon purity and by purging the cells with SO₂ prior to activation with electrolyte.

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