

# The Reduction of Sulfuryl Chloride at Teflon-Bonded Carbon Cathodes

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## ABSTRACT

Polarization and discharge curves were measured for sulfuryl chloride reduction at Teflon-bonded carbon cathodes fabricated using a number of different carbon powders. Lithium chloroaluminate was utilized as electrolyte solute. At moderate current densities cathode polarization tends to normalize with respect to Brunauer, Emmett, Teller (BET) surface area of the carbon. Cathode life increases with increased porosity of the electrode. The porosity is required for good accommodation of product LiCl. A formulation incorporating both high BET area and porosity was developed and found to provide good electrochemical performance against lithium counterelectrodes. When sulfuryl chloride is reduced at the optimized cathode (against a lithium anode), the main products of reaction are LiCl (which is quantitatively deposited within the electrode's pores) and SO<sub>2</sub>. This suggests the overall cell reaction:  $2\text{Li} + \text{SO}_2\text{Cl}_2 \rightarrow 2\text{LiCl} + \text{SO}_2$ . The addition of Cl<sub>2</sub> or SO<sub>2</sub> to the electrolyte causes decrease or increase of cathode polarization, respectively. This may be taken as evidence that the reduction, at moderate current densities, occurs through a Cl<sub>2</sub> intermediate resulting from heterogeneous decomposition of SO<sub>2</sub>Cl<sub>2</sub>. Reduction of undissociated SO<sub>2</sub>Cl<sub>2</sub> may occur at high current densities or after the active area of the electrode is significantly reduced through deposition of product LiCl.

The potential usefulness of sulfuryl chloride for lithium inorganic electrolyte cells was recognized a number of years ago (1-3). However, development of a practical lithium-sulfuryl chloride cell has generally been assigned lower priority, by both governmental and industrial organizations, than the corresponding lithium-thionyl chloride system. One reason for the relative inattention to sulfuryl chloride cell technology has been the observed dissipation of the apparent high voltage and capacity advantage (observed at low current densities) when experimental cells utilizing Teflon-bonded carbon (Shawinigan black) cathodes are discharged at high rates (4). It was the purpose of this work to improve the performance-limiting Teflon-bonded carbon cathode and to gain mechanistic insights which will suggest further refinements in technology. The present work was performed using neutral lithium chloroaluminate solution (1.5 molar) in which lithium anodes are fairly stable and which is therefore suitable for primary cell use. As is the situation for the analogous thionyl chloride system, acidic (e.g., AlCl<sub>3</sub>-rich) solutions allow higher voltages and cathode service life under load, but are suitable only for reserve cell use.

## Experimental

**Preparation of electrolyte.**—Sulfuryl chloride was refluxed over Li ribbon for several hours and then distilled under a positive pressure of argon, retaining the middle fraction. Lithium aluminum chloride was prepared by fusion of the salts as described previously (5). The 1.5M solutions were prepared in an argon atmosphere, in a glove box, and were stored in a tightly stoppered bottle. Electrolyte was used within a day of preparation or argon-degassed just before use.

**Preparation of cathodes.**—"Uncompressed" cathodes were prepared as described previously (5) by wet-blending of du Pont TFE-30 emulsion, carbon powder, and a sufficient amount of water to yield a stiff paste. The latter was then applied to a 2.5 × 2 cm Exmet

(Exmet Corporation) support. The latter support was prepared by welding two thicknesses of (Type 5 Ni7-2/0) screen together, with the mesh out of registration so as to provide maximum tortuosity for good anchoring of the Teflon-carbon mixture and to provide high electronic conduction. While still moist, the electrode was pressed to whatever thickness (depending on the particular carbon powder used) required for a final thickness of 0.89 ± 0.05 mm after vacuum drying for approximately 24 hr at 99°C. All cathodes were trimmed to the 2.5 × 2 cm dimensions of the Exmet support.

"Compressed" (the fabrication procedure finally developed for United Carbon) cathodes were prepared as described above, but compressed to an intermediate thickness of 1.56 mm while still moist. After vacuum drying the electrode was pressed in a 0.635 mm frame and after re-expansion (due to electrode resiliency) had a final thickness of 0.89 mm. The "uncompressed" electrodes made with Shawinigan black or Darco G-60 were of good, uniform appearance and possessed good adherence after the vacuum drying step. The uncompressed electrodes made of Columbia or United Carbon were badly cracked and fragile after the drying stage. The compressed United Carbon electrodes presented a good appearance and were sturdy.

**Preparation of cells.**—Cells were assembled in an all-Teflon jig with the planes of the electrodes parallel to the bottom of the jig. The cathode was placed between two Li anodes. An Li foil electrode placed in the same plane as the cathode served as reference. A 0.36 mm thick glass "filter-paper" provided mechanical separation between the cathode and the Li counterelectrodes facing it on each side. The lithium anodes were fabricated by pressing nickel Exmet into a 1.3 mm thick lithium foil and trimming to the same (2.5 × 2 cm) length and width as the cathodes. After assembling the cell and adding electrolyte, a Teflon weight was applied to the cell to help maintain good contact between the cell components. Unless otherwise specified, the electrolyte volume was 5 cm<sup>3</sup>. Electrical connections were made to Pt wires sealed in the cap of a glass outer container having a standard taper ground glass joint, and the cell assembly was then

Key words: polarization curves, discharge curves, cathode polarization.

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enclosed in the outer container. All assembly steps were accomplished in the glove box.

**Electrochemical measurements.**—Discharge and polarization curves were recorded on a Moseley Strip Chart Recorder at  $22^\circ \pm 2^\circ\text{C}$ . The discharge curves were obtained while applying constant current from a power supply. The polarization curves were measured by applying predetermined constant currents (starting from  $0.02\text{ mA/cm}^2$ ) for a period of 3 min before recording each cathode potential.

**Cathode porosity determination.**—The percent porosity is defined as the percent of wet cathode volume available for absorption of  $\text{SO}_2\text{Cl}_2$ . The volume of  $\text{SO}_2\text{Cl}_2$  absorbed was determined by weighing a cathode before and after immersion in  $\text{SO}_2\text{Cl}_2$  and "blotting" on a glass surface. The wet volume of the cathode was determined by measuring its lineal dimensions with calipers. The porosity measurements were conducted in the glove box.

**Chemical analysis.**—The solubility of lithium chloride at  $25^\circ\text{C}$  in  $\text{SO}_2\text{Cl}_2$  was determined by preparing a saturated solution at  $30^\circ\text{C}$ , allowing equilibration/precipitation to proceed for several days at  $25^\circ\text{C}$ , and then weighing the  $\text{LiCl}$  residue after taking  $10\text{ cm}^3$  of solution to dryness.

Determination of sulfur chloride-insoluble chloride in discharged cathodes was accomplished as follows. The cathode was extracted with five  $20\text{ cm}^3$  volumes of  $\text{SO}_2\text{Cl}_2$  (with vigorous magnetic stirring) during a 24 hr period. The cathode was then vacuum-dried, first at room temperature and then at  $100^\circ\text{C}$ . The cathode was then extracted with a total volume of  $100\text{ cm}^3$  of water and aliquots of the extract titrated potentiometrically with standardized silver nitrate solution.

Aluminum was determined quantitatively to correct for occluded lithium aluminum chloride in the sulfur chloride-insoluble (lithium) chloride cathode product residue. The aurintricarboxylate colorimetric method (6) was employed, and aluminum concentrations were read off from a Beer's law plot at the absorption maximum of  $525\text{ m}\mu$ .

**Volumetric determination of ( $\text{SO}_2$ ) gas release during cell discharge.**—The cell was prepared for discharge as described above. Before use, a volume of electrolyte was presaturated with  $\text{SO}_2$  for 45 min by bubbling the gas through the solution. To minimize gas-supersaturation effects, only  $2\text{ cm}^3$  of the presaturated electrolyte were inserted in the cell. After assembling the cell and closing the gas-tight glass outer envelope, the latter was flushed with  $\text{SO}_2$  through its two stopcocks. The glass envelope was then connected to a manifold and gas burette assembly by means of standard taper joints. Before opening the stopcock separating the cell from the manifold-burette assembly, the latter was evacuated and backfilled with  $\text{SO}_2$ . Measurements were made more or less frequently depending on observed rate of change of volume, and a rate of gas release was derived from each pair of adjacent volume determinations.

**Determination of solubilities of  $\text{SO}_2$  and  $\text{Cl}_2$  in  $\text{SO}_2\text{Cl}_2$ .**—In an alkaline aqueous solution,  $\text{SO}_2$  or  $\text{Cl}_2$

when individually dissolved can be titrated through iodimetry or iodometry, respectively (7). If both gases are introduced into an alkaline solution, they will react, resulting in quantitative oxidation of the  $\text{SO}_2$ , by  $\text{Cl}_2$ , to  $\text{SO}_4^{--}$  and  $\text{Cl}^-$  plus the balance of the component present in higher normality. Therefore, only the excess of equivalents may be determined iodometrically/iodimetrically for such a mixture. Pure sulfur chloride can be expected to behave like a stoichiometric mixture of  $\text{SO}_2$  and  $\text{Cl}_2$  when dissolved in alkaline solution as was confirmed.

Solutions of either gas in  $\text{SO}_2\text{Cl}_2$  were prepared by bubbling the gas through the liquid for  $\frac{1}{2}$  hr. A  $1\text{ cm}^3$  aliquot of either of the solutions was then placed in an ampul which was supported above  $40\text{ cm}^3$  of 1-5M aqueous KOH solution in a flask with a gas-tight stopper. The ampul was dropped into the KOH solution and the latter shaken vigorously. A sample of argon-saturated  $\text{SO}_2\text{Cl}_2$  gave a negligible iodimetric or iodometric blank determination. Iodimetric/iodometric determinations were conducted on the saturated solutions of the pure gases.

### Results and Discussion

**Dependence of cathode polarization and discharge capacity on cathode physical properties.**—A Teflon content of 16% was chosen for preliminary comparative evaluation purposes, because it was found to provide adequate coherence of the Teflon-carbon mixtures and adherence to the screens even though this is not the optimum Teflon loading for each individual carbon powder.

Table I identifies the carbon powders used in formulating cathodes, along with their BET surface areas. Shawinigan black possesses the lowest area of the entries listed, but has been a frequent choice of lithium battery technologists because of its good mechanical working properties and porosity. The latter quality is due in part to its extensive chain-like microstructure. Darco G-60 is a relatively high-area activated charcoal. The United and Columbia carbon blacks listed possess particularly high surface areas and were originally produced for use in experimental aqueous primary cells (8, 9).

The cathodes were compared at the same thickness ( $0.89\text{ mm}$ ) (rather than at the same weight) since that allows the best comparison with respect to overall performance of a practical cell. The carbon loadings obtained reflect the different packing tendencies of the Teflon-carbon mixtures when accommodating to the same volume. Previous studies revealed that the BET surface area of such electrodes is approximately the same as that of the original carbon utilized (10). On that basis, Table I presents the BET areas for the electrodes computed from the powder areas and the carbon loadings (of representative electrodes). Because the variations in carbon loadings of the electrodes tend to compensate for the variations in surface areas of the powders, the only large variation in electrode BET area is that for Shawinigan black when compared with the other three carbons.

The electrode porosity or, more precisely, the ability to absorb  $\text{SO}_2\text{Cl}_2$  depends on the original microstructure of the powder and its interaction with the Teflon

Table I. Teflon-bonded carbon cathodes (16% TFE)

Type of carbon	Derivation	BET surface area of carbon: meter <sup>2</sup>			% electrode porosity
		Carbon loading* (g/cm <sup>3</sup> )	Per gram of carbon powder	Per cm <sup>2</sup> of electrode geometric area <sup>a</sup>	
Shawinigan—50% compressed	Decomposition of acetylene	0.0194	66	1.38	87
Darco G60	Steam-activation of charcoal	0.0048	301	14.4	64
United XC-6310-4	Decomposition of oil	0.0146	1000	14.6	81
Columbia HR 1670	Decomposition of oil	0.0104	1200	12.5	78

\* Based on (length x width) area of electrode, one side.

binder. As already mentioned above, the latter properties are particularly favorable for Shawinigan black and probably account for the higher than average cathode porosity listed in the table and the fact that the electrodes have a sturdy and uniform appearance. The Darco cathodes have the lowest porosity and fair mechanical integrity. The Columbia and United carbon cathodes prepared by this method are cracked and fragile, but possess medium porosity. When swollen with electrolyte, the latter electrodes acquired a more uniform appearance.

Figure 1 shows the polarization curves obtained for the four different carbon samples, with the recorded current density based on the geometric cathode area (length  $\times$  width, one side). From the practical point of view, it can be concluded that the United carbon would provide the best and Shawinigan black the poorest initial voltage in a practical cell.

The results of Fig. 1 are replotted in Fig. 2 but with the current densities computed from the total currents and the BET carbon areas of the electrodes. It is now apparent that polarization for three of the carbons (covering more than an order of magnitude's spread in BET area) is very similar in the range of currents where "activated" processes predominate. The Darco cathode shows significantly more polarization than the other three in that range. This may possibly be attributed to the fact that Darco G-60 is an "activated charcoal" with part of the BET area intragranular in nature and consequently not readily accessible to solid/liquid reactions. The steep decline of cathode potential at high current densities may be attributed [as applies also to the similar thionyl chloride cath-

ode (10, 11)] to transport limitations in pores partially blocked by a solid product of cell discharge.

Cathodes made from the four different carbon samples were discharged at a constant current density of 5 mA/cm<sup>2</sup> in cells containing the "standard" 1 mm of electrolyte/cm<sup>2</sup> of cathode geometric area. The "full discharge capacities" were determined from the discharge curves by drawing the appropriate tangents near the "knee" of the curves. In Fig. 3, the capacities are plotted against the percent porosity values taken from Table I. The relationship is approximately linear for the particular current density employed. The slope can be conceptualized as incorporating a pore "choking coefficient" as proposed by Marincic (11) for the thionyl chloride cathode. The similarity exists because the same major product of cathode reaction (LiCl) is involved in both cases as discussed below. It may also be anticipated, as observed for the thionyl chloride cell (12), that the distribution of LiCl in the cathode, and its effect on the discharge curve, will vary with the current density.

From Fig. 1 and 3 it can be concluded that Shawinigan black affords the best cathode capacity, but the poorest cathode voltage. United Carbon black, which affords the highest cathode voltage performance, provides second-best capacity. The latter carbon black was selected for further experimentation.

*Improvement of the United Carbon cathode.*—Figure 4 presents discharge curves for experimental modifi-

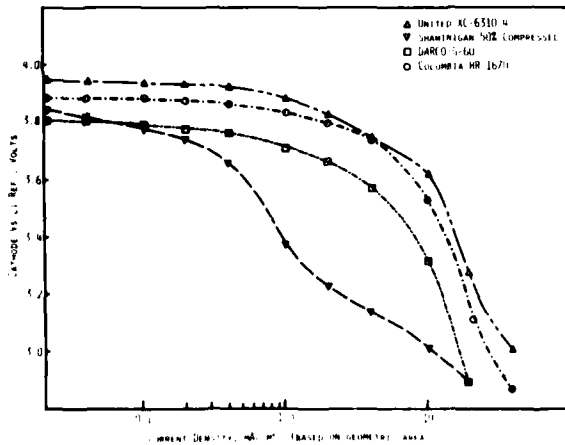


Fig. 1. Polarization curves for Teflon-bonded carbon cathodes (16% TFE, uncompressed).

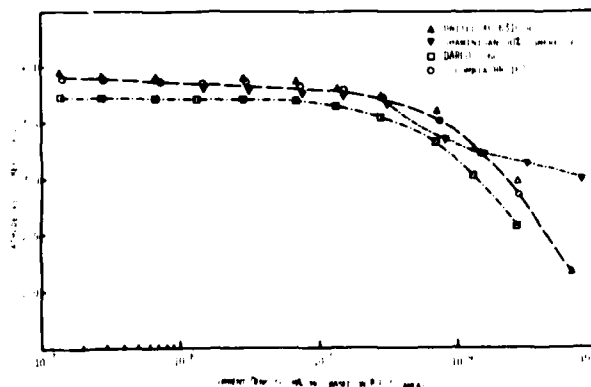


Fig. 2. Polarization curves for Teflon-bonded carbon cathodes (16% TFE uncompressed) normalized with respect to BET area.

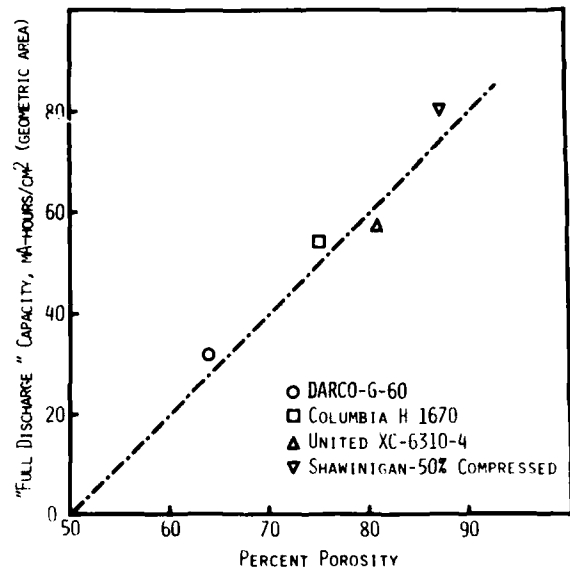


Fig. 3. Capacity-porosity relationship for Teflon-bonded carbon cathodes (16% TFE, uncompressed).

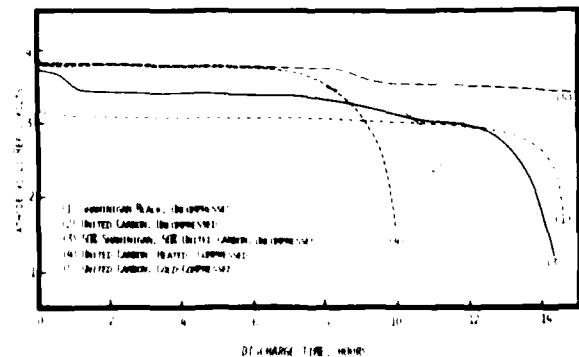


Fig. 4. Discharge curves ( $I = 5 \text{ mA/cm}^2$ ) for differently formulated cathodes.

cations of the cathode fabrication process (16% TFE) for comparison with those obtained by the original ("uncompressed") process (curves 1 and 2). All cathodes were constructed to the same final thickness (0.89 mm), but incorporated different amounts of carbon. Admixture of the two carbons (curve 3) results in the high capacity associated with Shawinigan black, but only part of the increased voltage associated with United Carbon black. Also, the physical integrity of the electrode is not good. Heat-compression of the United Carbon cathode at 300°C (curve 4) greatly improves its sturdiness and slightly improves the voltage, but causes decreased capacity. The "cold-compression" process (curve 5) results in a cathode of highest discharge voltage and longest life. This cold-compressed United Carbon formulation was therefore selected for further optimization.

Figure 5 shows the discharge curves obtained, at a current density of 5 mA/cm<sup>2</sup>, for different concentrations of TFE in the dried United Carbon-Teflon mixtures. A maximum in cathode life ("full discharge capacity") is obtained for a TFE concentration of 10.7%. Duplicate runs for 9.7% and 10.7% are presented to show typical variation of results attributable to fabrication technique variability.

The 10.7% formulation was selected for the further investigations reported below. A typical electrode had a carbon loading of 0.024 g/cm<sup>2</sup> and a porosity of 87%. The electrode swelled 11% when immersed in electrolyte.

**Solubilities of LiCl, SO<sub>2</sub>, and Cl<sub>2</sub> in sulfolyl chloride.**—The solubility of LiCl in sulfolyl chloride at 25°C was determined to be less than 0.009M. This corresponds to a solubility product of less than  $8 \times 10^{-5}$  and leads to the conclusion that LiCl is, practically speaking, insoluble in the 1.5M lithium chloroaluminate concentration of our electrolyte.

The solubilities of Cl<sub>2</sub> and SO<sub>2</sub> at 24° were determined to be 0.62 and 1.09 molal, respectively, when individually dissolved in pure SO<sub>2</sub>Cl<sub>2</sub>. The analysis for SO<sub>2</sub> correlates well with published results (13) for other temperatures.

**Analysis of cell discharge products.**—A discharged cathode, after rinsing in sulfolyl chloride and drying, was crushed and analyzed with an x-ray spectrometer. Diffraction lines were obtained for LiCl only. Two cathodes, A and B (formulated with 6.7% and 10.7% TFE, respectively), were discharged to a cut-off potential of 2V, treated as described in the Experimental section above, and analyzed for both Cl<sup>-</sup> and Al<sup>3+</sup>. Table II presents the results of the analyses, assuming that all chloride in the cathode is either LiCl or

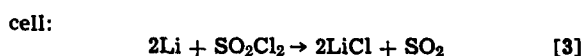
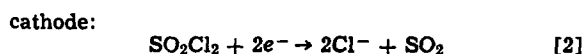
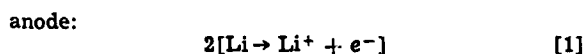
Table II. Chloride determination for discharged cathodes

	Cathode A	Cathode B
Total equivalents of Cl <sup>-</sup> determined argentometrically	0.0146	0.02035
4 × equivalents of Al <sup>3+</sup> determined colorimetrically	0.00093	0.00103
Equivalents of Cl <sup>-</sup> as LiCl	0.0137	0.0193
Equivalents of electricity consumed in cathode discharge	0.0141	0.0189

LiAlCl<sub>4</sub>. It can be seen that agreement between the equivalents of charge passed and LiCl formed is within 2%, which is taken as evidence that LiCl is the only ionic product of cathode discharge for the predominant discharge reaction. Quantitative precipitation of the LiCl in the cathode is a result of its insolubility as already noted above. In this respect the situation is identical to that for thionyl chloride cells (14).

One of the possible non-ionic products of cell discharge is elemental sulfur, as proposed previously (2). A cathode was fully discharged (20 hr) at a current density of 5 mA/cm<sup>2</sup>. Extraction of the vacuum-dried cell components with CS<sub>2</sub> yielded only 15 mg of a yellow waxy substance with no distinct melting point. The substance dissolved in benzene and, therefore, was apparently not sulfur.

The simplest cell discharge reaction involving LiCl as the ionic product would produce SO<sub>2</sub> as the neutral product. Cells were always observed to develop positive pressure during discharge. The resulting gas phase contained SO<sub>2</sub> and Cl<sub>2</sub> which are, in any case, present above an SO<sub>2</sub>Cl<sub>2</sub> volume (15). To avoid the difficulty of analyzing for SO<sub>2</sub> released in the presence of Cl<sub>2</sub>, volumetric determination of gas release during discharge was made after saturating the solution with SO<sub>2</sub>. This procedure has the benefit of suppressing Cl<sub>2</sub> release while forcing electrochemically produced SO<sub>2</sub> into the gas phase. The results of a determination appear in Fig. 6. The figure compares the observed rate of gas production with that anticipated based on the reactions



$$E^\circ = 3.909\text{V (30}^\circ\text{C)}$$

A "background" production of gas of approximately 0.06 cm<sup>3</sup>/min was measured at open circuit. That "background" may, for instance, correspond to initial reaction (corrosion) of the fresh lithium electrode

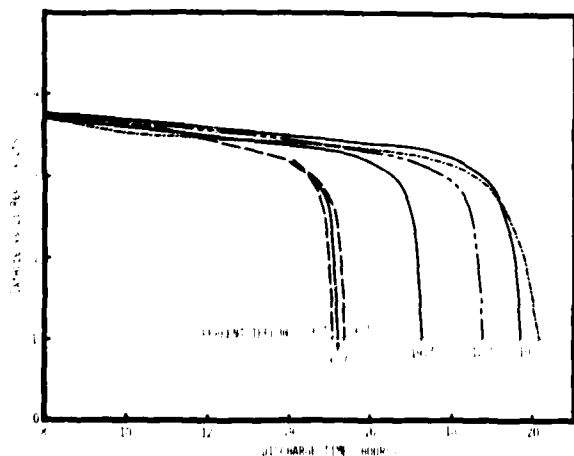


Fig. 5. Discharge curves ( $i = 5 \text{ mA/cm}^2$ ) for cathodes formulated with varying amounts of TFE (uncompressed).

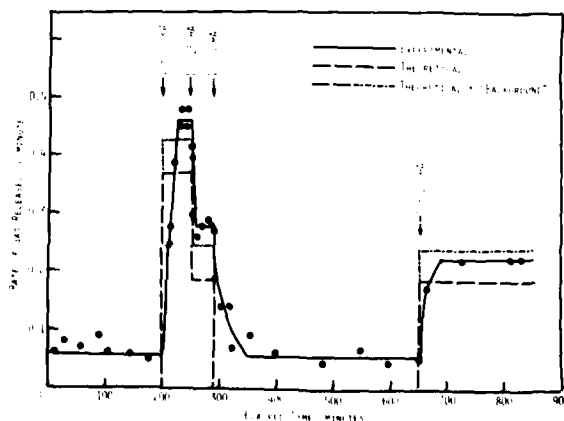


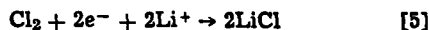
Fig. 6. Gas release during cathodic reduction of SO<sub>2</sub>Cl<sub>2</sub>.

surface with the solvent. When the "background" and theoretical rates are added, they compare fairly well with the experimental rates eventually established when the current is increased or decreased. The results imply that the cell reactions proceed, at least largely, according to Eq. [1] and [2].

**Effect of dissolved gases on cathode discharge.**—Sulfuryl chloride dissociates readily into  $\text{SO}_2$  and  $\text{Cl}_2$  (15), and that reaction may be suspected of playing a role in the cell electrochemistry. The equilibrium constant at  $30^\circ\text{C}$  is 0.0288 for the reaction



The chlorine produced by reaction [4] could then be consumed as follows cathode:



The standard potential,  $E^\circ$ , for reaction [5] vs. an Li reference electrode is 3.979V ( $30^\circ\text{C}$ ). However, the activity of  $\text{Cl}_2$  in solution will always be equal to or less than dictated by the equilibrium constant of Eq. [4] and, therefore, always lower than unity. Correspondingly, the cell potential can never exceed that of Eq. [3] unless molecular  $\text{Cl}_2$  is introduced from an external source.

Reaction [4] could proceed either homogeneously or heterogeneously. However, for pure  $\text{SO}_2\text{Cl}_2$ , the homogeneous reaction is slow, while the heterogeneous decomposition is relatively rapid at a carbon surface (15).

Figure 7 compares the polarization curves obtained when the electrolyte is saturated with either argon,  $\text{SO}_2$ , or  $\text{Cl}_2$ . Results for solutions prepared in the glove box and stored for a few days resemble the "argon-saturated" example. Clearly,  $\text{Cl}_2$  and  $\text{SO}_2$  serve to enhance or diminish the current, respectively, at any particular cathode potential. The effect of  $\text{Cl}_2$  saturation demonstrates that molecular  $\text{Cl}_2$  is kinetically more active than  $\text{SO}_2\text{Cl}_2$  in this electrolyte, although reduction occurs well below the appropriate thermodynamic cell potential (3.979V). Since  $\text{SO}_2$  is itself not reduced at these high potentials, and since it could not produce any significant decrease in  $\text{Cl}_2$  bulk concentration over that in the argon-saturated solution, it is proposed that it exerts its effect on the polarization curve by decreasing the surface concentration of the chlorine which (at moderate currents and high potentials) normally serves as an intermediate in the reduction of  $\text{SO}_2\text{Cl}_2$ . In practical situations, (small volume of electrolyte, extended periods of discharge) the electrolyte will become  $\text{SO}_2$  rich and the tendency for the results for the argon and  $\text{SO}_2$ -saturated electrolytes to converge (at higher currents) is also apparent from the figure.

Discharge curves (constant current of  $5 \text{ mA/cm}^2$ ) appear in Fig. 8. The results for the  $\text{SO}_2$ -saturated, argon-saturated, and "aged" electrolytes are almost

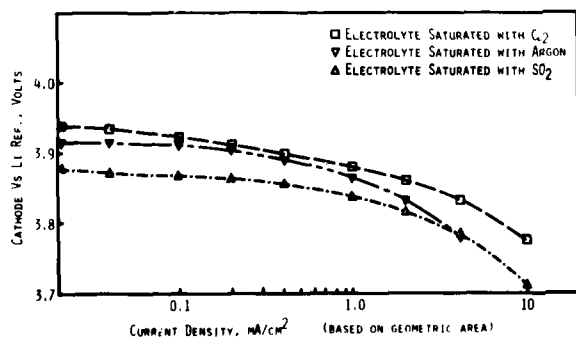


Fig. 7. Cathode polarization curves for optimized cathode electrolyte presaturated with different gases.

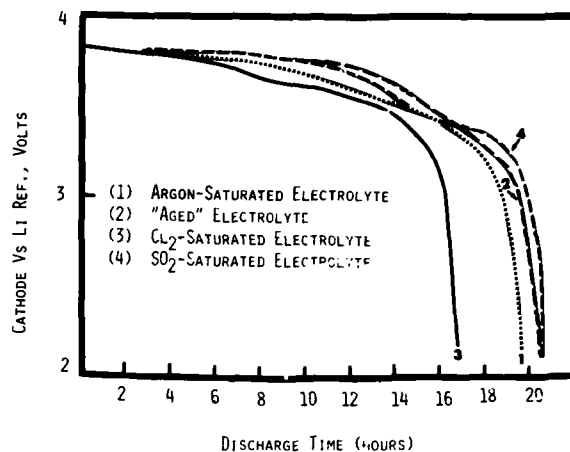


Fig. 8. Cathodic discharge curves ( $i = 5 \text{ mA/cm}^2$ ). Electrolyte saturated with different gases.

indistinguishable in the first few hours (as might be expected due to buildup of product  $\text{SO}_2$ ) in the first two cases. The variations during the later period of discharge are within the normal span for any particular (e.g., argon-saturated) starting condition. The significantly shorter discharge for  $\text{Cl}_2$  saturation was found reproducible. A possible explanation is that the direct reduction of chlorine from the bulk of the solution occurs near the outer surface of the electrode and has a greater tendency to clog pores than the heterogeneously produced  $\text{Cl}_2$  intermediate which would be produced and consumed throughout the electrode volume.

The discharge curves for cells with either argon/ $\text{SO}_2$ -saturated or "aged" electrolyte exhibit an intermediate voltage decline suggesting a two-step reduction. This is probably analogous to the two-wave reduction observed by Behl (16) during voltage-sweep studies of carbon microelectrodes. Behl attributed the first and second waves to reduction of  $\text{Cl}_2$  and undissociated  $\text{SO}_2\text{Cl}_2$ , respectively. A similar interpretation for the second transition in the discharge curve is tentatively adopted here. The transition to reduction of molecular  $\text{SO}_2\text{Cl}_2$  might come about as the available surface area available to catalyze  $\text{SO}_2\text{Cl}_2$  dissociation is diminished through coating with product  $\text{LiCl}$ .

**Dependence of discharge curves (optimized United Carbon cathodes) on electrolyte volume and current density.**—Figure 9 presents discharge curves for several current densities at the "standard" ratio of electrolyte volume to cathode geometric area of  $1 \text{ ml/cm}^2$ .

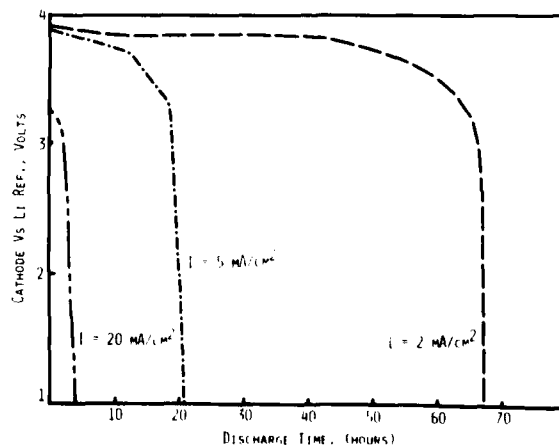


Fig. 9. Discharge curves for optimized cathode

As for thionyl chloride cells, the efficiency of cathode utilization tends to drop off with increased current density. The relatively efficient discharge current density of 2 mA/cm<sup>2</sup> was selected for exploring the effect of varying the electrolyte volume. Curves for several different volume/area ratios appear in Fig. 10. From such curves, a charge *Q* was estimated for "full discharge" and for discharge to a first "high voltage" transition point and the results plotted in Fig. 11. Based on Eq. [3], the values of charge, and the volume of solution in the cell, a "percent solvent utilized" was derived and plotted in Fig. 11. For volume/area rates of 0.14 or less, cell components are visibly incompletely wetted at the beginning of the experiment. No attempt has yet been made to analyze the rather sharp dependence on electrolyte volume/area ratio. Maximum solvent utilizations at "high voltage" and for "full discharge" were not observed to exceed 20% and 30%, respectively.

Let us consider how the 20% "high voltage" efficiency compares with the percentage of equivalents of Cl<sub>2</sub> available from the dissolved phase only. Corresponding to the Cl<sub>2</sub> (0.62 molal, as reported above) in a saturated solution at 24°C, 7.8% of the reducible equivalents are available from predissolved Cl<sub>2</sub>. For degassed sulfuryl chloride, allowed to dissociate to equilibrium with the gas phase, the partial pressure of Cl<sub>2</sub> is approximately 0.05 atm [based on the vapor pressure of SO<sub>2</sub>Cl<sub>2</sub> and dissociation constant of SO<sub>2</sub>Cl<sub>2</sub> at 30°C (15)]. The corresponding percentage of equiv-

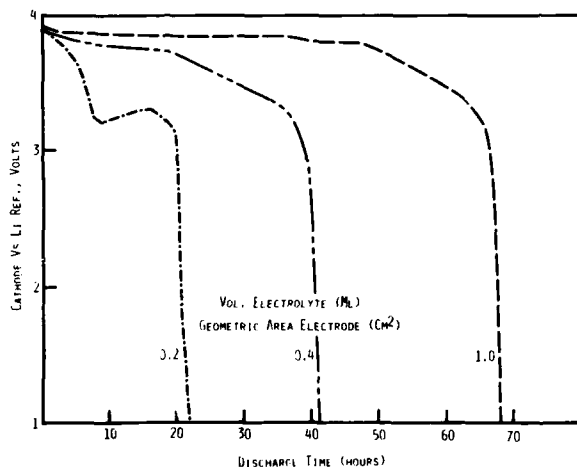


Fig. 10. Discharge curves for optimized cathode using various volumes of electrolyte.

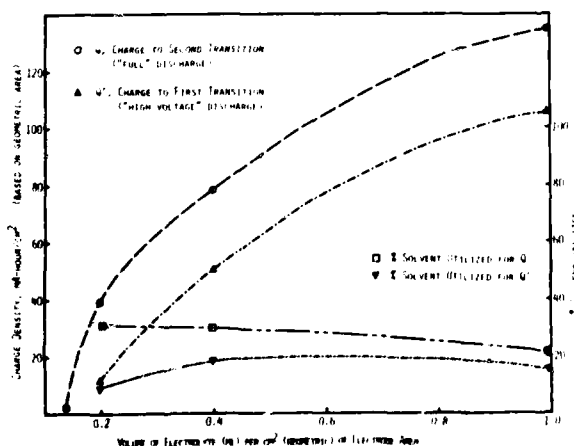


Fig. 11. Dependence of cathodic charge and solvent utilization on electrolyte volume.

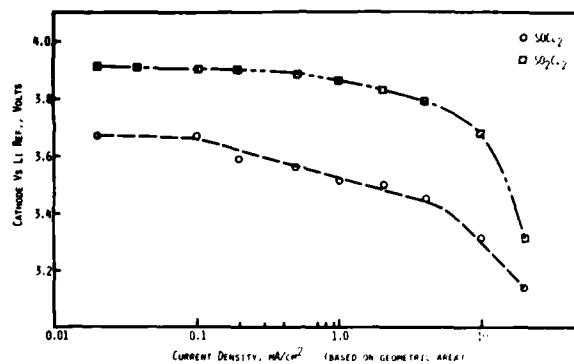


Fig. 12. Comparison of cathodic polarization curves for SO<sub>2</sub>Cl<sub>2</sub> and SOCl<sub>2</sub>.

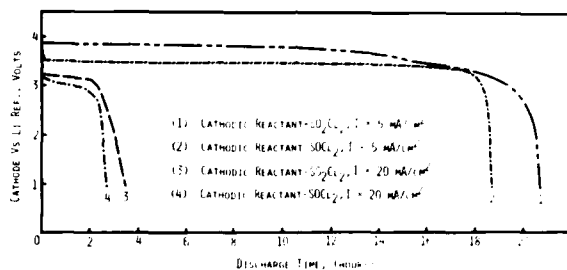


Fig. 13. Comparison of cathodic discharge curves for SO<sub>2</sub>Cl<sub>2</sub> and SOCl<sub>2</sub>.

alents available from Cl<sub>2</sub> can be as low as 0.4% (if Henry's law is obeyed). Hence the "high voltage" solvent utilization reported above cannot be attributed to a "reservoir" of Cl<sub>2</sub> resulting from dissociation of the solvent before cathodic discharge is begun, but must be supplied during the cathodic process.

**Comparison of SO<sub>2</sub>Cl<sub>2</sub> with SOCl<sub>2</sub> cathodes.**—The polarization and discharge curves are compared in Fig. 12 and 13, respectively, for cathodes utilizing SOCl<sub>2</sub> and SO<sub>2</sub>Cl<sub>2</sub> and an electrolyte volume/cathode geometric area of 1 ml/cm<sup>2</sup>. Shawinigan black cathodes were used as representing the "state-of-the-art" for SOCl<sub>2</sub> and the optimized United Carbon cathodes were utilized for SO<sub>2</sub>Cl<sub>2</sub>. It can be seen from the figures that SO<sub>2</sub>Cl<sub>2</sub> appears to offer an advantage in terminal voltage over SOCl<sub>2</sub> at high current densities, if the optimized cathodes are utilized. The comparison may be expected to vary, of course, for different proportions and concentrations of electrolyte, different temperatures, etc.

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