

THE KINETICS OF THE REDUCTION OF THIONYL CHLORIDE

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Summary

The rate, reaction mechanisms, and the catalysis of the electrochemical reduction of thionyl chloride from anhydrous media, are discussed. Voltammetric measurements at stationary plane and rotated disc electrodes, using glassy carbon, graphite, or metal electrodes, have been made using thionyl chloride alone or at high dilution in supporting electrolytes. Porous carbon electrodes have been used to study stoichiometry and to determine how electrolyte concentration affects capacity.

Chemical analysis of cells after partial or complete discharge has established that without catalysis, the products are sulfur, sulfur dioxide, and lithium chloride. In both acid and neutral electrolytes, the reduction behaves as though it were diffusion controlled, whether the cathodes are porous carbon electrodes or rotated disc electrodes. The mechanism of the reduction likely involves several electrochemical and chemical steps, proceeding through unstable and metastable intermediates. The reduction is irreversible because the species initially produced rapidly decomposes. On decomposition, one of the intermediates produces thionyl chloride. The overpotential at either porous or nonporous electrodes can be lowered, and the capacity of porous electrodes increased, by high surface area carbons or by the use of catalysts. It is not known whether catalysts change the overall discharge stoichiometry.

In basic electrolytes, the first step in the reduction on a carbon surface appears to be first order with respect to the concentration of chloride ion and to involve only one electron. The species produced by the initial reduction is stabilized by chloride ion. As the chloride ion concentration is lowered, the initial reduction begins to involve more than one electron.

Introduction

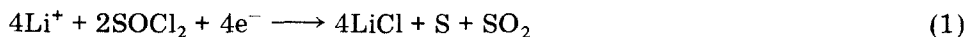
The performance of lithium/thionyl chloride electrochemical power sources has been of significant practical interest for more than fifteen years. While the kinetics and mechanism of the reduction of thionyl chloride on various types of carbon and metal surfaces have been studied, most of the effort has been empirical and designed to improve the capacity, rate capability, startup characteristic, storage capability, and safety of practical cells and

batteries. Occasionally in the literature, "mechanism" has come to be used interchangeably with "overall discharge reaction" [1, 2] rather than in its more traditional context.

Although fundamental studies may at times seem somewhat removed from practical matters, a clear understanding of the mechanism for the reduction of thionyl chloride on carbon, and the identification of the steps involving electron transfer could, for example, lead to the development of more efficient, less expensive, and more easily manufactured catalysts for lithium/thionyl chloride power sources. The study of reaction mechanisms is closely associated with the study of kinetics, since in any reaction the slowest step determines the overall rate. If the reaction mechanism is unknown, a kinetic study may be of help in deducing the mechanism. In this review paper, some of the available literature dealing with the kinetics and mechanism of the reduction of thionyl chloride, as well as the overall discharge reaction, and how many of the current ideas on this subject differ from each other, will be compared in terms of their significance to the further improvement in the performance of practical power sources.

The overall discharge reaction in the lithium/thionyl chloride cell

The reduction of the solvent on the cathode surface of an electrochemical power source containing lithium and thionyl chloride was first suggested by Gabano [3] to proceed according to



Analyses of 1.3 A h sealed cells by Bailey and Kohut [4] showed definitively that this single stoichiometry was valid for the reduction of thionyl chloride from 1 M $\text{LiAlCl}_4/\text{SOCl}_2$ on an uncatalyzed carbon electrode between -50 and $+71$ °C whether the cells were partially or totally discharged, or whether the loads were 75, 250, or 500 ohms. The lithium chloride was essentially insoluble and gradually filled the pores of the carbon electrode, while the sulfur dioxide and sulfur accumulated in the solution. Vallin *et al.* have studied the distribution of sulfur in cells discharged at various rates [5].

The existence and significance of discharge intermediates

The analyses by Bailey and Kohut were carried out in such a way that only the final products of discharge could be determined, and so did not address the question of the reaction pathway. Attempts were made to determine, quantitatively, whether the sulfur dioxide appeared in the electrolyte of a discharging cell at a rate commensurate with that predicted by eqn. (1). Infrared spectra [6] showed that the concentration of sulfur dioxide in the electrolyte lagged behind the expected amount as a function of the discharge capacity until near the end of ambient temperature tests

lasting about one week. A stainless steel pressure vessel containing fresh electrolyte saturated with sulfur and sulfur dioxide, in which either fresh or discharged cathode material was either present or absent, established that the missing sulfur dioxide was not being held by the carbon cathode during cycling between room temperature and 100 °C. Electrolyte taken from a partially discharged cell, whether in the presence of cathode material or not, showed irreversible increases in pressure when cycled between room temperature and 100 °C. Fresh electrolyte saturated with sulfur and sulfur dioxide showed no such irreversible increases in pressure. The discharged electrolyte therefore contained substances in addition to thionyl chloride, sulfur dioxide, sulfur, and lithium tetrachloroaluminate.

Dey [7] found that cathode limited D-size cells, when placed in a differential scanning calorimeter immediately after discharge, exhibited exothermic peaks at 101 and 110 °C when heated linearly with time, but they were absent during returns or during scans of fresh (undischarged) cells. The evidence therefore indicated that there were one or more metastable intermediates present in the electrolyte of a discharged cell, but the available information was insufficient to identify them.

The presence of intermediates in the electrolyte of discharging or discharged cells has raised the question as to whether the intermediates might contribute to safety problems. Violent venting has occasionally occurred, for example, when cells are discharged at reduced temperature and then allowed to warm, as reported by Hayes *et al.* [8]. During the warming, thermocouples attached to the cells showed that their temperature rose faster than the ambient temperature, eventually leading to a more rapid but measurable increase, finally resulting in explosion. The results were fairly reproducible. Dey did not report any cell venting or thermal runaway during differential thermal analyses between room temperature and 120 °C of cells discharged at ambient temperature, but some of the decomposition could have occurred during discharge at the higher temperature, thereby reducing the amount of heat generated during the thermal analyses. The problem has yet to be quantitatively defined, since cells partially, or completely, discharged at ambient temperature on resistive load, on rare occasions, have also exploded during casual storage at room temperature. The presence of hydrolysis products is thought to play the key role in the initiation of reactions leading to thermal runaway in lithium/thionyl chloride cells [1].

The identification of intermediates might, instead, have a greater impact in helping to determine where to look for better catalysts for practical power sources containing $\text{SOCl}_2/\text{LiAlCl}_4$.

Kinetic measurements and the determination of the discharge mechanism

Cyclic voltammetric and rotated disc studies

Examples where derivations and the discussion of basic principles of cyclic voltammetry appear are: Vetter [9], Adams [10], Albery [11], Fried

[12], and Delahay [13]. Nicholson and Shain [14] have given a systematic analysis beginning with a simple, reversible reaction, then considered irreversible reactions, homogeneous chemical reactions, and the formation of slightly soluble products. Recently, Bjoernbom [15] and Fedkiw [16] presented theoretical treatments of porous, unstirred electrodes, Albery and Hitchman published a monograph describing the basic principles of rotated disc electrodes [17]. Additional theoretical treatments are covered by Behl and Chin [18] and by Adanuvor *et al.* [19].

In 1976, Behl reported the results of cyclic voltammetric analysis of 1.5 molar LiAlCl_4 in thionyl chloride, using an unstirred glassy carbon working electrode [20]. The results were qualitative, but showed one major solvent reduction peak before the carbon became passivated by lithium chloride. The passivation could be removed either by rinsing the carbon electrode in $\text{AlCl}_3/\text{SOCl}_2$, or by oxidizing the electrolyte on the working electrode above 4 V. The chlorine produced was removed by bubbling argon through the electrolyte. He concluded that the reduction of thionyl chloride was irreversible, both because no corresponding oxidation wave appeared, and because the difference between the peak and half-peak potentials was considerably greater than expected for a reversible reaction causing passivation of the working electrode. Blomgren *et al.* carried out cyclic voltammetric analysis of 1 M $\text{LiAlCl}_4/\text{SOCl}_2$, using pyrolytic graphite and pressure-annealed pyrolytic graphite electrodes, either unstirred or rotated [21]. While the pyrolytic graphite electrodes showed just one peak, the pressure-annealed pyrolytic graphite electrodes gave two solvent reduction peaks, and as in Behl's study, electrolytic oxidation at the working electrode removed the passivating layer. Whether the electrodes were held stationary or rotated at 300 r.p.m., the results were qualitatively similar.

Behl presented the first quantitative cyclic voltammetric study with both stationary and rotated discs in 1979 using glassy carbon and thionyl chloride without additional solvents, but varying the LiAlCl_4 concentration [22]. He reported that the current maxima were the same linear function of the square root of the potential scan rate, whether or not the discs were rotated up to 5000 r.p.m., indicating that the reduction was diffusion controlled even when the solution was briskly stirred. When the potential scan rate was held constant, the current maxima were found also to be independent of the electrolyte salt concentration between 0.5 and 1.5 molar. The measured peak and half-peak potentials again differed much more than the theory predicted for a reversible reaction with passivation by an insoluble product.

Using a glassy carbon ring-disc electrode, Behl found that the species produced by the reduction of thionyl chloride at the disc could be reoxidized at the ring, but the collection efficiency was only 2.4% of that predicted at 3000 r.p.m. The reduction of thionyl chloride was therefore irreversible, and the cause was that the species produced by the electrochemical step was unstable, reacting, in solution, rapidly after it formed. However, the oxidation at the ring could not have been the reverse of the reduction reaction at

the disc, since the lithium chloride produced at the disc presumably remained there as an insoluble phase. The collection efficiency may therefore have been adversely affected. Freshly-prepared electrolytes saturated with both sulfur and sulfur dioxide behaved identically to fresh electrolyte without these additional solutes, indicating that neither of them was further reduced during discharge.

Philips *et al.* used solutions with excess aluminum chloride in an attempt to reduce, or eliminate, the passivation caused by the lithium chloride, but found instead that during cyclic voltammetric measurements, the glassy carbon electrode still became passivated [23]. Adding sulfur monochloride reduced the passivation. The passivating substance could have been sulfur, since sulfur is very soluble in sulfur monochloride, but neither chemical analysis nor speculation was offered.

In order to remove all interference from insoluble discharge products, Bowden and Dey, rather than use an excess of aluminum chloride, used a supporting electrolyte with a low electrochemical background over a wide potential range, and in which thionyl chloride, lithium chloride, sulfur, and possible intermediates such as sulfur monochloride, were all substantially soluble [24]. The solvents were *N,N*-dimethylformamide and methylene chloride. Other solvents used were dimethylsulfoxide and acetonitrile. The electrolyte salt was tetrabutylammonium hexafluorophosphate.

The sacrifice was that both the sulfur and the sulfur dioxide would now be subject to electrochemical reduction during cyclic voltammetry at stationary plane platinum electrodes, and that the thionyl chloride and the products of discharge might be subject to complexation and redox reactions involving the organic solvents. It was for these reasons that they chose a number of solvents and investigated the qualitative electrochemical behavior of sulfur, sulfur dioxide, chloride, and sulfur monochloride, as well as thionyl chloride.

For each of dimethylformamide, acetonitrile, and methylene chloride, controlled potential electrolysis of solutions of thionyl chloride at a potential just cathodic of the first reduction wave removed this wave from the voltammetric scan, with a ratio of SOCl_2 to electrical equivalents less than 1 to 2. When the solution was warmed or allowed to stand, the first wave returned to the voltammetric scan. An example of this behavior is shown in Fig. 1, where the solvent was dimethylformamide [24]. Eventually, the ratio of SOCl_2 to electrical equivalents reached 1 to 2, as predicted by eqn. (1). Thionyl chloride was not only being reduced to a metastable intermediate, the decomposition of this intermediate was producing thionyl chloride again.

Bowden and Dey varied the sweep rate and the concentration of thionyl chloride in dimethylformamide. The current maxima were a linear function of the square root of the potential scan rate, again indicating that the reaction was diffusion controlled. They made no attempt to produce kinetically limited conditions by using rotated electrodes. The behavior of u.v.-vis spectra taken of acetonitrile-based electrolytes as a function of the amount of charge passed indicated that there were at least two intermediates

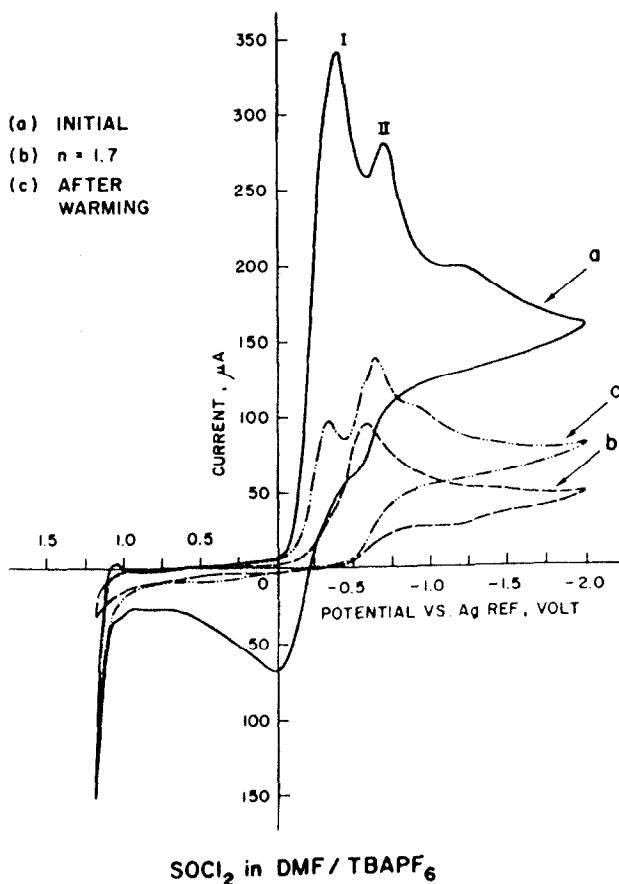


Fig. 1. Cyclic voltammograms of SOCl_2 in dimethylformamide/tetrabutylammonium hexafluorophosphate. Scan rate, 0.2 V s^{-1} (taken from ref. 24. Reprinted by permission of the publisher, The Electrochemical Society, Inc.). (a) Before controlled potential electrolysis at -0.25 V with respect to a silver/silver chloride reference electrode; (b) after exhaustive electrolysis; (c) after warming the solution.

in solution. Studies using supporting electrolytes with solutions of thionyl chloride or $\text{LiAlCl}_4/\text{SOCl}_2$ and glassy carbon electrodes were also carried out by Abraham and Mank [25], Venkatasetty and Saathof [26], and Dampier and Cole [27].

Doddapaneni [28] studied platinum electrodes, and pressure-annealed and glassy carbon electrodes in $1 \text{ M LiAlCl}_4/\text{SOCl}_2$, using both stationary and rotated discs. The pressure-annealed graphite electrodes were run both with, and without, iron and cobalt phthalocyanine catalysts. Without catalyst, the electrodes behaved similarly to those of Blomgren *et al.* [21] in that two reducing current maxima were observed on the unstirred electrodes. With catalyst, the current maxima merged together, shifted to a more positive potential, and increased threefold. Yet, the linear dependence of the current

maxima on the square root of the potential scan rate for unstirred electrodes showed that with, or without, catalyst, the reaction was still diffusion controlled.

At constant potential sweep rate, the logarithm of the current maxima was a linear function of the reciprocal of the absolute temperature, allowing Doddapaneni to estimate the activation energies both without (1.83 kcal/equiv.), and with, iron phthalocyanine (1.65 kcal/equiv.) [28]. He claimed to have been able to obtain kinetically controlled conditions both without, and with, catalyst, and that the reciprocal of the current maxima was a linear function of the reciprocal of the rotation rate from about 260 to 1200 r.p.m., thus indicating first order kinetics with, or without, catalyst. Doddapaneni's conclusions therefore differed sharply from Behl's [22].

Madou and Szpak [29], using glassy carbon and 1 M $\text{LiAlCl}_4/\text{SOCl}_2$, also found that the reduction of thionyl chloride was diffusion controlled and unaffected by stirring. They explained this as being caused not by concentration polarization in the liquid phase, but by the result of the restriction of transport into the pores of the lithium chloride film present on the carbon surface. They measured the impedance of carbon electrodes, presenting the data in Nyquist plots (real part of the impedance *versus* the imaginary part) for frequencies from 2×10^{-2} to 1000 Hz, and Bode plots (log frequency *versus* log of the magnitude of the impedance). They concluded that there was more than one electron transfer process occurring. Povarov and Chakhov [30] also explained similar results in terms of diffusion limited transport through a passivating layer and first order kinetics. Chiu *et al.* [31] concluded, as had Phillips *et al.* [23], that passive films persisted even when the solutions were made acidic by the addition of aluminum chloride.

Mozalevskaya *et al.* [32], using glassy carbon electrodes, studied solutions of LiAlCl_4 and tetra n-butylammonium perchlorate in SOCl_2 using cyclic voltammetry, again finding diffusion control of reductions in thionyl chloride solutions of lithium tetrachloroaluminate. They suggested that the contact between the carbon and the lithium chloride might have been acting as a p-n semiconductor junction, with the lithium chloride acting as the positive carrier. The reoxidation of any reduced species would therefore be inhibited by the junction.

In thionyl chloride solutions of tetraalkylammonium perchlorate where there was no passivating film on the cathode surface, Mozalevskaya *et al.* claim not only to have found no limiting cathodic current, but also an anodic current representing the reoxidation of reduced species if a sufficient amount of cathodic charge had passed. This behavior is shown in Fig. 2 [32]. From the Tafel slope, they found the apparent exchange current density (0.115 mA cm^{-2}), the thionyl chloride redox potential (3.31 V *versus* lithium), the intermediate resistances, and the number of equivalents of charge participating in the initial electron transfer reaction (close to unity). The results were compared with solutions also containing tetraalkylammonium chloride salts at three levels of concentration. The orders of both the

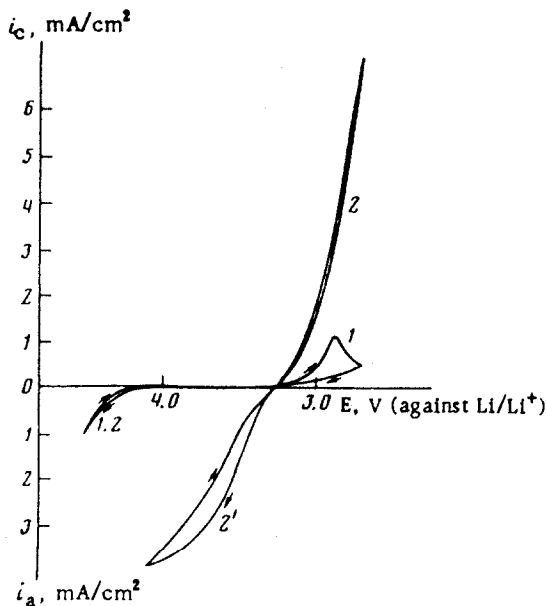
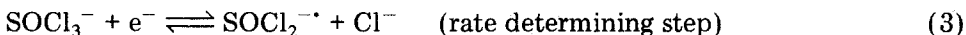


Fig. 2. Cyclic voltammetric curves obtained on a glassy carbon electrode in solutions of thionyl chloride (taken from ref. 32). (1) 0.5 M LiAlCl_4 ; (2) 0.5 M $(\text{C}_4\text{H}_9)_4\text{NClO}_4$, first anodic wave, followed by first cathodic wave; (2') as (2), second anodic wave.

cathodic and anodic reactions were found to be close to unity in the presence of chloride ion. The apparent exchange current increased markedly with the increase in chloride ion concentration. They concluded that in these electrolytes, the electrochemical stage consisted of a reversible one electron transition involving chloride ions, which stabilized the reduction product. They suggested that the following reactions were occurring in solutions containing chloride ions:



They ruled out the possibility that the reduction could proceed according to eqn. (4), a mechanism which had been suggested for solutions such as $\text{LiAlCl}_4/\text{SOCl}_2$, where the chloride ion concentration was very low [24]:



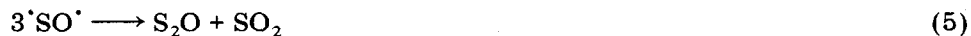
In perchlorate solutions without added tetraalkylammonium chloride, Mozalevskaya *et al.* found that the number of electrons involved in the electrochemical step increased to about 1.2. They postulated that an additional, or alternative, reaction was occurring which increased the number of electrons taking part in the electrochemical step. They did not attempt to use supporting electrolytes with anions alternative to perchlorate, likely to

be stable in thionyl chloride, such as tetraalkylammonium salts of hexafluoroarsenate, sulfate, or even tetrachloroaluminate, to confirm that perchlorate did not participate in any way.

Spectroscopic approaches

The use of quantitative infrared spectroscopy to follow the concentration of sulfur dioxide as a function of discharge depth for lithium/thionyl chloride cells has been mentioned above [6]. Dampier and Cole [33] also measured the concentration of sulfur dioxide in thionyl chloride-based electrolytes, using the absorption at 1330 cm^{-1} . They disagreed with the earlier work, concluding from their studies that the cathode carbon did preferentially absorb sulfur dioxide from the electrolyte during discharge, that this absorption accounted for the delay in the appearance of sulfur dioxide in the electrolyte, and that the electrochemical reduction of thionyl chloride produced no discharge intermediates with significantly long lifetimes. However, their measurements may have been affected by the large vapor volume left in the vessel they used to equilibrate the samples.

Another example where infrared spectroscopy was used to identify and follow the concentration of intermediate species is the work of Istone and Brodd [34]. Absorptions assigned to SO_2 (1335 cm^{-1}) and S_2O (689 cm^{-1}) were observed to change during the discharge of electrochemical devices to which infrared cells were attached by way of fine diameter Teflon tubing. The absorption maxima were observed qualitatively, and relative to the first overtone band, for thionyl chloride near 2400 cm^{-1} . Electrolyte samples were drawn into the infrared cell, then returned to the electrochemical cell by means of a syringe which was attached to the other end of the infrared cell through tubing. During discharge, the concentration of both species increased, consistent with the formation of both SO_2 and S_2O during discharge. During standing, the band at 689 cm^{-1} decreased, while the band at 1335 cm^{-1} increased. It was therefore proposed that S_2O was one of the metastable intermediates and, by implication, SO^{\cdot} as well, which decomposed to sulfur and sulfur dioxide:



The half-life of S_2O in the electrolyte was estimated to be about 20 min at ambient temperature. The presence of S_2O was not actually confirmed by any independent chemical or physical technique.

Brodd, initially proposing that S_2Cl_2 was an intermediate [21], noted that the infrared absorption at 438 cm^{-1} for S_2Cl_2 did not change during the discharge of a lithium/thionyl chloride cell [34]. More recently, Blomgren [35] maintains that sulfur monochloride is present at a level of 1 - 2% in discharging cells, not present in fresh electrolyte, and that the gas chromatographic analyses were performed under conditions which prevented the

reduction of thionyl chloride by sulfur to sulfur monochloride during the G.C. test runs.

Raman spectroscopic analyses of complexes formed between lithium tetrachloroaluminate and thionyl chloride or sulfur dioxide were reported by Bedfer *et al.* [36], and by Dhameincourt *et al.* [37].

Carter *et al.* [38] examined discharged electrolyte using ESR spectroscopy, and proposed that one of the intermediates was the dimer $(\text{OCIS})_2$, in which the chlorine atoms faced each other, as shown in Fig. 3. They proposed a very complicated mechanism with no fewer than five electrochemical steps, drawing on the results of gas chromatographic analysis to claim that sulfur monochloride was also an intermediate. Chlorine was present as well.

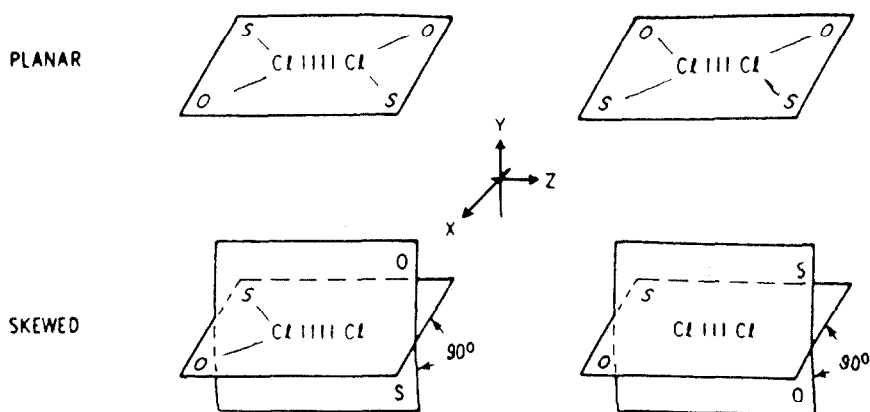


Fig. 3. Proposed structures for $(\text{OCIS})_2$ (taken from ref. 38(a). Reprinted by permission of the publisher, The Electrochemical Society, Inc.).

Catalysis in thionyl chloride cells

The number and variety of heterogeneous catalysts added to the cathodes of lithium/thionyl chloride power sources has grown steadily since 1980. With a few exceptions such as the cyclic voltammetric analyses by Doddapaneni noted above [28], most of the tests reported in the literature were carried out in experimental cells with the intent of improving the performance of cathodes for practical devices. It is not known how the catalytic materials function, or whether they even function by the same mechanism. Just a few examples are discussed here.

Without adding anything to the carbon, the capacity and running potential of cathodes in thionyl chloride cells can be significantly affected by the physical properties of the carbon and the treatment used to prepare the cathodes. Klinedinst showed that high surface area carbons with high oil absorption capacities would outperform carbons with lower surface areas [39]. A particularly striking example is shown in Fig. 4 where two otherwise

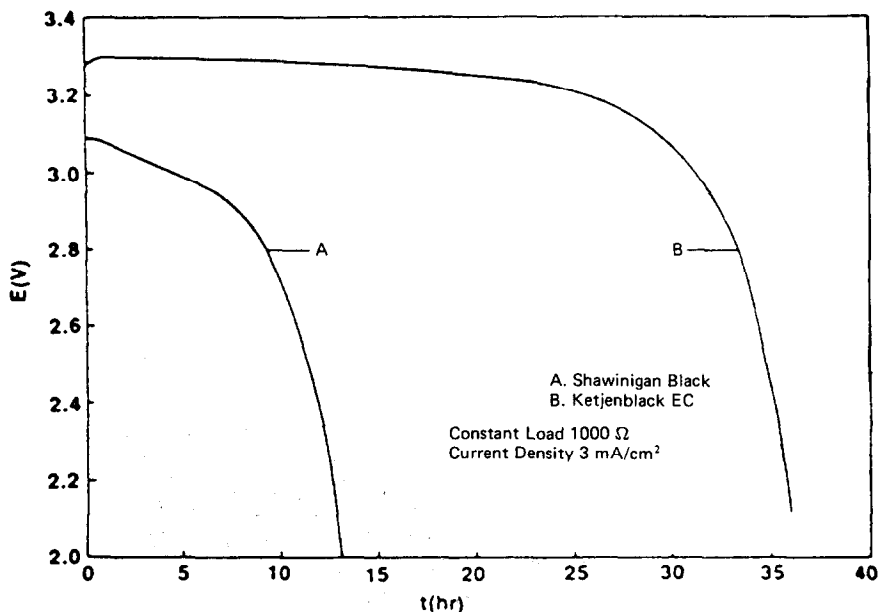


Fig. 4. Li/SOCl₂ cell discharge curves at -20°C . With 3 mA cm^{-2} current density (taken from ref. 39. Reprinted by permission of the publisher, The Electrochemical Society, Inc.).

identical cells were discharged at -20°C at 3 mA cm^{-2} . A cell with a Ketjenblack EC cathode ran 200 mV higher and realized nearly three times the capacity of a cell with an acetylene black cathode. Varying the porosity also significantly affected the rate capability. Walker *et al.* showed that the running potential of calcium/thionyl chloride cells could be improved by nearly 500 mV at 20 mA cm^{-2} over pure acetylene black cathodes by mixing 25% Ketjenblack with 75% acetylene black [60]. The performance of the Ketjenblack was improved by leaching first with acetone, then water. Analysis of the carbon failed to show how the leached Ketjenblack differed in any significant way from the original material.

Compared with carbon electrodes discharged at low current densities, those discharged at high current densities deliver less capacity per unit area before they passivate, because the lithium chloride tends to accumulate in the pores closest to the anode surface [40, 41]. We would expect that the resistivity of the electrolyte would be responsible: at higher currents causing an “*ir*” potential drop which would prevent carbon deeper within the cathode from reaching the overpotential required to allow reduction of the thionyl chloride. Yet, the capacity can be improved by increasing the surface area of the carbon and choosing the correct pore size and size distribution.

Hagan *et al.* [42] claimed that for their porous carbon electrodes, the reduction of thionyl chloride was substantially diffusion controlled only above about 20 mA cm^{-2} , and that the capacity was dependent upon the

concentration of the lithium tetrachloroaluminate. Sand's equation predicts that for an electrode being passivated by an insoluble discharge product, the reciprocal of the square root of the time required to passivate the electrode will be a linear function of the current density. For concentrations of LiAlCl_4 between 0.45 M and 3.0 M, Hagan *et al.* found the predicted linearity, and that 1.8 M LiAlCl_4 produced the maximum capacity (Fig. 5). They explained the result by saying that the solubility of LiCl reached a maximum of 0.16 M at 1.8 M LiAlCl_4 , and that the increased solubility of LiCl helped extend the capacity of the cathode.

The processes used to apply catalytic materials to carbon electrodes may themselves alter the carbon enough to realize some improvement in performance. However, tests against controls offer evidence that certain materials have catalytic activity towards the reduction of thionyl chloride when supported on cathodes prepared from acetylene black or other carbon. General classes include finely-divided metallic powders, transition metal compounds, transition metal/aromatic nitrogen complex salts, and halogens (chlorine or bromine) [39]. Examples include cupric chloride [43], finely-divided metallic platinum [39], iron and cobalt phthalocyanine [44], the polymer derived from the reaction of tetracyanoethylene with ferric or cobaltic acetylacetonate [45], cobalt dibenzotetraazaannulene [46, 47], silver, copper, and palladium [48], cupric sulfide [49], and vanadyl or manganese phthalocyanine [50].

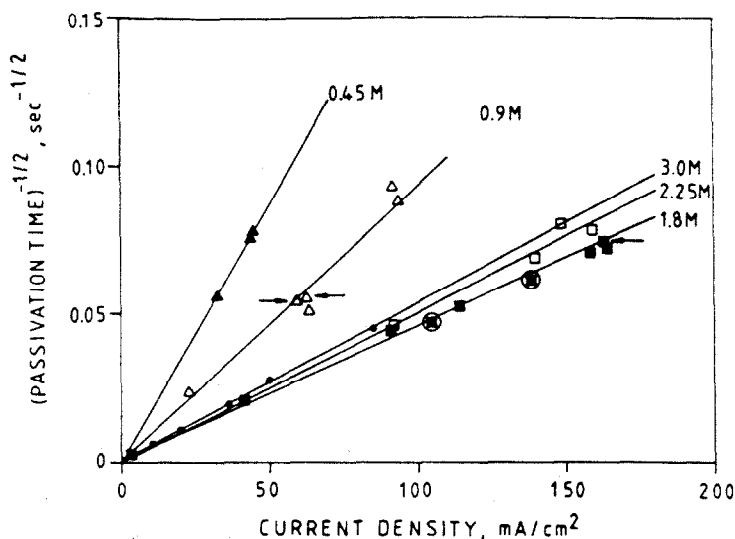


Fig. 5. $(\text{Passivation time})^{-1/2}$ vs. current density for various LiAlCl_4 concentrations. The arrowed points on the 0.9 M and the 1.8 M lines are the results of discontinuous passivation experiments. The circled datum points on the 1.8 M line are for 0.38 mm and 0.13 mm thick cathodes. The temperature was 20 °C (taken from ref. 42. Reprinted with permission from *Electrochim. Acta*, vol. 31, W. P. Hagan, N. A. Hampson, and R. K. Packer, the electrochemistry of the Li/SOCl_2 cell — I. the passivation of the cathode, copyright 1987, Pergamon Press publications).

Walsh and Yaniv reported that the electrochemical reduction of thionyl chloride on carbon (either Vulcan XC-72R or Shawinigan black), when catalyzed by cobalt dibenzotetraazaannulene, produced only 41% of the insoluble chloride expected in the carbon electrode per Faraday according to eqn. (1), when discharged at a current density of 100 mA cm^{-2} . An equivalent amount of lithium was also found, indicating that there were no lithium salts other than LiCl formed in the cathodes. The experimental cells had 20 mil cathodes with a loading of 15 mg carbon per square centimeter. The rest of the discharged lithium would have to remain either in solution or as lithium chloride precipitated in the separator and on the cell surfaces. The analyses were not complete enough to establish the overall discharge reaction.

There have even been papers reporting that the rate of thionyl chloride reduction is increased by the illumination of a carbon cathode. Chakhov *et al.* [51] explained the phenomenon in terms of the behavior of the interface between the lithium chloride and the carbon as a semiconductor junction. Madou *et al.* [52] agreed, showing also that when *n* type silicon was illuminated, the oxidation reaction was enhanced, but that the reduction current was not affected.

The experiments with silicon may have clouded the issue. While electrical conduction in solid lithium chloride is partly electronic and can be affected by impurities and by stoichiometry, the majority of the conduction still occurs by the transfer of lithium ions. Ionic conduction in lithium chloride was discussed by Ginnings and Phipps [53], and electronic conduction by Dekker and by Heyne [54(a) and (b)]. Positive electronic carriers or "holes", possibly do not contribute substantially to conduction in lithium chloride. Chakhov's contention that positive (electronic) carrier conduction in solid lithium chloride prevents the reoxidation of species electrochemically reduced from $\text{LiAlCl}_4/\text{SOCl}_2$, is probably in error. What prevents the reoxidation is more likely the chemical decomposition of the species produced during the reduction by the first electrochemical step.

An alternative explanation is as follows. Thionyl chloride is known to decompose reversibly to chlorine, sulfur monochloride, and sulfur dioxide [ref. 1, p. 328], and this decomposition is known to be affected by light [55]. The enhanced cathodic current could have been due to the increased concentration of chlorine, particularly since the noted relaxation time was slower than expected [52]. The formation of sulfur monochloride by the reversible dissociation of thionyl chloride would also be a convenient way of explaining its presence in the electrolyte of a discharging cell [35].

The reversible reduction of chlorine to chloride likely takes place in cells discharging at low rates [1]. Open circuit and low rate measurements, which do, in fact, produce reversible electrochemical reactions, have been erroneously assumed to represent the direct reduction of thionyl chloride during attempts to measure the "thermoneutral potential" and the entropy change for the lithium/thionyl chloride cell [1, 56 - 59]. If one of the electrochemical steps occurring during discharge at higher rates is also the

reduction of chlorine, then a substance which speeds up the dissociation of SOCl_2 to chlorine, sulfur monochloride, and sulfur dioxide should increase electrochemical activity in $\text{SOCl}_2/\text{LiAlCl}_4$.

If chloride ion is needed for the first electrochemical step [32, 42], and it is in short supply because of the limited solubility of lithium chloride, a substance which increases the rate of chloride formation, such as by the dissociation of SOCl_2 to SOCl^+ and Cl^- , should also increase the rate of electrochemical activity.

The next steps

A summary of reasonably supported findings and conclusions follows:

(i) The first step in the reduction of thionyl chloride on carbon involves the transfer of one electron, and is first order with respect to the concentration of chloride ion. The species produced is stabilized by chloride ion but decomposes rapidly in its absence or when the concentration is low. The reduction of $\text{SOCl}_2/\text{LiAlCl}_4$ is therefore irreversible. More than one electrochemical step occurs when the chloride concentration is low.

(ii) There are a number of unstable and metastable intermediates formed during the discharge of $\text{SOCl}_2/\text{LiAlCl}_4$, some of which persist in the electrolyte solution at ambient temperature for up to one week. One of these intermediates is $(\text{OClS})_2$. One re-forms SOCl_2 during its chemical decomposition.

(iii) The reduction of $\text{SOCl}_2/\text{LiAlCl}_4$ on carbon is diffusion controlled, because the reacting species must make their way through the porous film of discharge products. This diffusion control persists whether the solution is neutral or acidic, whether the carbon electrode does, or does not, contain a catalyst, or whether the solution is, or is not, stirred. Conflicting evidence also exists that kinetically controlled conditions can be obtained at moderate current densities.

Some of the most immediate remaining questions which come to mind are as follows:

(i) Catalysts located exclusively on the surface of carbon electrodes are able to influence what many workers have concluded to be a diffusion controlled reaction, not only by decreasing the overpotential, but by increasing the capacity of porous electrodes. Heterogeneous catalysis at the carbon surface should be capable of increasing the running potential during a kinetically controlled reaction, but not lower the "ir" potential drop within the electrolyte near the cathode, and therefore should not be capable of increasing either the capacity or the running potential of a diffusion controlled reaction.

The catalyst may not take part at all in the electrochemical step, but may act by increasing the rate of a chemical reaction required before the first electrochemical step. As examples, the catalyst may increase the rate of dissociation of thionyl chloride to chlorine, sulfur dioxide, and sulfur

monochloride, or dissociation to $\text{SOCl}^+ + \text{Cl}^-$. The first electrochemical reaction could then be either the reduction of chlorine or sulfur monochloride, or the reduction of SOCl_3^- [32].

(ii) Carbon electrodes quickly develop different passivating layers at the onset of discharge, depending upon whether the electrolytes are neutral ($\text{SOCl}_2/\text{LiAlCl}_4$ only) or acidic (excess AlCl_3) [31]. The addition of sulfur monochloride to acid electrolytes alleviates this passivation [23]. Since sulfur is very soluble in S_2Cl_2 , sulfur may be responsible for the passivation, forming immediately as soon as discharge begins. None of the currently proposed reduction mechanisms allows for this possibility. If the passivating layer is not sulfur, its identity should be determined.

(iii) If chloride ion is required for the reduction, as concluded by Mozalevskaya *et al.* [32], then there is no explanation for why the reduction is not inhibited by acidic electrolytes.

(iv) The sulfur monochloride present at a level of 1 - 2% could be a discharge intermediate. There are, however, at least two possible sources. If there is an equilibrium level of chlorine, then the S_2Cl_2 could also be produced by the dissociation of thionyl chloride. Whether it is an intermediate is therefore difficult to determine.

(v) For further studies, means of producing purely kinetically controlled reactions while varying the relative concentrations of relevant species, are required.

(vi) Carefully designed experiments, such as those of Bailey and Kohut [4], are needed to determine whether catalysts change the overall discharge reaction. Since different catalysts may not act in the same manner, the measurements of the product stoichiometries should be carried out for several catalysts. The results should be confirmed by using controlled potential electrolysis to determine the number of Faradays per mole of SOCl_2 reduced [24, 6].

References

- 1 C. R. Schlaikjer, in J. P. Gabano (ed.), *Lithium Batteries*, Academic Press, London, 1983, pp. 303 - 370.
- 2 J. J. Auburn and H. V. Venkatesetty, in H. V. Venkatesetty (ed.), *Lithium Battery Technology*, Wiley, New York, 1984, p. 133.
- 3 J. P. Gabano, *French Pat. 2,079,744* (October 18, 1971).
- 4 J. C. Bailey and J. P. Kohut, in J. Thompson (ed.), *Power Sources 8*, Academic Press, London, 1981, p. 17.
- 5 D. Vallin and Ph. Chenebault, *J. Power Sources*, 17 (1986) 353.
- 6 C. R. Schlaikjer, F. Goebel and N. Marincic, *J. Electrochem. Soc.*, 126 (1979) 513.
- 7 A. N. Dey, in *Proc. 28th Power Sources Symp.*, The Electrochemical Society, Pennington, NJ, June, 1978; *J. Power Sources*, 5 (1980) 57 - 72.
- 8 C. A. Hayes, S. L. Gust, M. D. Farrington and J. A. Lockwood, *Abstract #30, Electrochemical Society Fall Meeting*, 1986.
- 9 K. J. Vetter, *Electrochemical Kinetics*, Academic Press, New York, 1967.
- 10 R. N. Adams, *Electrochemistry at Solid Electrodes*, M. Dekker, New York, 1969.

- 11 J. Albery, *Electrode Kinetics*, Clarendon Press, Oxford, 1975.
- 12 I. Fried, *Chemistry of Electrode Processes*, Academic Press, New York, 1973.
- 13 P. Delahay, *New Instrumental Methods in Electrochemistry*, Interscience, New York, 1953.
- 14 R. S. Nicholson and I. Shain, *J. Anal. Chem.*, **36** (1964) 706.
- 15 P. Bjoernbom, *J. Electrochem. Soc.*, **134** (1987) 1600.
- 16 P. S. Fedkiw, *J. Electrochem. Soc.*, *Spring Meeting, 1988, Abstract #494*.
- 17 W. J. Albery and M. L. Hitchman, *Ring-Disc Electrodes*, Clarendon Press, Oxford, 1971.
- 18 W. K. Behl and D. T. Chin, *J. Electrochem. Soc.*, **135** (1988) 16.
- 19 P. K. Adanuvor, R. E. White and S. E. Lorimer, *J. Electrochem. Soc.*, **134** (1987) 625.
- 20 W. K. Behl, in *Power Sources Symposium, Atlantic City, NJ, June, 1976*, The Electrochemical Society, Pennington, NJ, p. 30.
- 21 G. E. Blomgren, V. Z. Leger, T. Kalnoki-Kis, M. L. Kronenberg and R. J. Brodd, in J. Thompson (ed.), *Power Sources 7*, Academic Press, London, 1979, pp. 583 - 593.
- 22 W. K. Behl, *J. Electroanal. Chem.*, **101** (1979) 367.
- 23 J. Phillips, J. C. Hall and H. F. Gibbard, in H. V. Venkatesetti (ed.), *Proc. Electrochem. Soc.*, Vol. 81-4, The Electrochemical Society, Pennington, NJ, 1981, pp. 41 - 53.
- 24 W. L. Bowden and A. N. Dey, *J. Electrochem. Soc.*, **127** (1980) 1419; **126** (1979) 2035.
- 25 K. M. Abraham and R. M. Mank, *J. Electrochem. Soc.*, **127** (1980) 2091.
- 26 H. V. Venkatesetti and D. J. Saathof, *J. Electrochem. Soc.*, **128** (1981) 773.
- 27 F. W. Dampier and T. A. Cole, *J. Electrochem. Soc.*, **133** (1986) 938.
- 28 N. Doddapaneni, *Abstract #735, Electrochem. Soc. Spring Meeting, 1983*.
- 29 M. J. Madou and S. Szpak, *J. Electrochem. Soc.*, **131** (1984) 2471.
- 30 Yu. M. Povarov and N. I. Chakhov, *Elektrokhimiya*, **16** (1980) 977.
- 31 J. G. Chiu, Y. Y. Wang and C. C. Wan, *J. Power Sources*, **21** (1987) 119.
- 32 V. A. Mozalevskaya, V. P. Ponkratov, N. V. Shavrin and V. N. Dam'e, *Elektrokhimiya*, **21** (1985) 359.
- 33 F. W. Dampier and T. A. Cole, *J. Electrochem. Soc.*, **134** (1987) 2383.
- 34 W. K. Istone and R. J. Brodd, *J. Electrochem. Soc.*, **129** (1982) 1853; **131** (1984) 2467.
- 35 G. E. Blomgren, *Pure Appl. Chem.*, **57** (1985) 383.
- 36 Y. Bedfer, J. Corset, M. C. Dhamelincourt, F. Wallart and P. Barbier, *J. Power Sources*, **9** (1983) 267.
- 37 M. C. Dhamelincourt, F. Wallart, P. Barbier, G. Mairesse and P. Descroix, *J. Power Sources*, **14** (1985) 77.
- 38 (a) B. J. Carter, R. N. Williams, F. D. Tsay, A. Rodriguez, S. Kim, M. M. Evans and H. Frank, *J. Electrochem. Soc.*, **132** (1985) 525; (b) S. S. Kim, B. J. Carter and F. T. Tsay, *J. Electrochem. Soc.*, **132** (1985) 335.
- 39 K. A. Klinedinst, *J. Electrochem. Soc.*, **132** (1985) 2044.
- 40 A. N. Dey and P. Bro, in D. H. Collins (ed.), *Power Sources 6*, Academic Press, London, 1977, pp. 493 - 510.
- 41 L. A. Beketaeva, Yu. M. Povarov and Yu. M. Vol'fkovich, *Elektrokhimiya* (1980) 863 - 867.
- 42 W. P. Hagan, N. A. Hampson and R. K. Packer, *Electrochim. Acta*, **31** (1986) 699 - 704; **32** (1987) 1787 - 1788.
- 43 W. K. Behl, *J. Electrochem. Soc.*, **128** (1981) 939.
- 44 N. Doddapaneni, *Proc. Power Sources Symp., 1982*, The Electrochemical Society, Pennington, NJ, pp. 169 - 171.
- 45 K. A. Klinedinst and R. A. Gary, *U.S. Pat. 4,452,872* (June 5, 1984).
- 46 F. Walsh and R. S. Morris, *U.S. Pat. 4,469,763* (Sept. 4, 1984).
- 47 F. Walsh and M. Yaniv, in A. N. Dey (ed.), *Proc., Vol. 84-1*, The Electrochemical Society, Pennington, NJ, 1984, pp. 103 - 110.

- 48 C. Y. Oh, Y. Y. Wang and C. C. Wan, *J. Power Sources*, 16 (1985) 233 - 239.
- 49 K. A. Klinedinst and C. R. Schlaikjer, *U.S. Pat. 4,495,266* (Jan. 22, 1985).
- 50 W. P. Kilroy and K. M. Abraham, *Rep. NSWC TR 87-104*, October 1, 1987.
- 51 N. I. Chakhov, Yu. M. Povarov and Yu. V. Pleskov, *Elektrokhimiya*, 16 (1980) 1445.
- 52 M. Madou, T. Otagawa, S. Gaisford, J. J. Smith and S. Szpak, *J. Electrochem. Soc.*, 135 (1988) 262.
- 53 D. C. Ginnings and T. E. Phipps, *J. Am. Chem. Soc.*, 52 (1930) 1340.
- 54 (a) A. J. Dekker, *Solid State Physics*, Prentice-Hall, Englewood Cliffs, NJ, 1957, p. 145; (b) L. Heyne, *Electrochim. Acta*, 15 (1970) 1251.
- 55 P. Pascal, *Nouveau Traité de Chimie Minérale*, Vol. 13, Masson, Paris, 1960, p. 1525.
- 56 H. F. Gibbard, in B. B. Owens and N. Margalit (eds.), *Proc.*, Vol. 80-4, The Electrochemical Society, Inc., Pennington, NJ, 1980, p. 510.
- 57 N. A. Godshall and J. R. Driscoll, in A. N. Dey (ed.), *Proc.*, Vol. 84-1, The Electrochemical Society, Inc., Pennington, NJ, 1984, p. 171; *J. Electrochem. Soc.*, 131 (1984) 2221.
- 58 L. D. Hansen and H. Frank, *J. Electrochem. Soc.*, 134 (1987) 1.
- 59 H. F. Bittner, B. J. Carter, W. S. Donely and M. V. Quinzio, *Abstract #22, Electrochem. Soc. Spring Meeting, 1988*.
- 60 C. W. Walker, Jr., W. L. Wade, Jr., M. Binder and S. Gilman, *J. Electrochem. Soc.*, 133 (1986) 1555.