

Analytical problem solving in lithium battery technology

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Abstract - While a great many cathodes have been studied in electrochemical couples with lithium, among the most successful have been the liquid oxidants, thionyl chloride and sulfuryl chloride, and this paper deals with analytical methods applied to these systems. The first section deals with the products and mechanisms of cell reactions. Wet chemical, chromatographic and gravimetric methods have been applied to reaction product analysis. Electrochemical methods have mainly been used for mechanism studies, although important intermediates have been identified by chromatographic and spectroscopic methods. Problems related to impurities have been studied most successfully by infrared spectroscopy and these applications are discussed in the second section. Although there are still a number of problems worthy of further study particularly related to mechanisms, great strides have been made through analytical problem solving towards understanding these complex systems.

INTRODUCTION

Lithium batteries are among the prime applications of nonaqueous solutions. Because of the low equivalent weight and high negative potential of lithium, these cells offer a high energy density and specific energy if a good positive electrode material is chosen. Liquid thionyl chloride and sulfuryl chloride are among the most important positive electrode materials known today for lithium batteries (Ref. 1,2). This may at first seem surprising to nonbattery chemists, since the direct contact of such a good oxidant with an excellent reductant would be expected to give off a great deal of energy, but almost all of it in the form of heat and little as recoverable electrical energy. However, because of the presence of an electronically insulating film on the lithium metal, the rate of the redox reaction is remarkably slowed to the extent that very long shelf lives are obtainable from such batteries. The film on the lithium electrode is thin enough, however, that lithium ions can be conducted with relatively low resistance and thus lithium functions as a metal/metal ion electrode.

The thionyl chloride or sulfuryl chloride serves as solvent for the electrolyte salt in addition to its role as oxidant at the positive electrode. Thus, the properties of these liquids as solvents for electrolyte salts are of interest as well as their electrochemical properties as cathodic materials. Furthermore, as the cell reaction proceeds and the thionyl or sulfuryl chloride is consumed, the composition of the electrolyte solution will change. In order to understand the effect of these changes on physical and electrochemical properties it is necessary to know in detail the cell reaction products under various conditions. Finally, the role of impurities on cell properties is important and therefore the level and source of any impurity should be ascertainable. All of these properties are subject to determination by analytical chemistry. Our laboratory as well as others have spent considerable effort to develop the methods used in these determinations and the results of those efforts will be discussed in this article.

CELL REACTION PRODUCTS

The products for the cell reaction for $\text{Li/SO}_2\text{Cl}_2$ cells will be discussed first. Chemical analyses were carried out by Blomgren et al. (3) on cells which were cathode limited and had been taken into deep discharge, with a cell cutoff of 0 volts. These were small cells which were later described in detail by Zupancic et al. (4). LiCl was

found as a product in the cathode by x-ray diffraction of the cathode residue after thorough washing with pure sulfuryl chloride. The sulfur containing species were identified as sulfur dioxide as the major component and lithium dithionite and lithium thiosulfate as minor components with 95 to 98% of the total sulfur accounted for. Sulfur dioxide was determined by absorption into iodine solution and titration with thiosulfate. Dithionite and thiosulfate were determined colorimetrically with naphthol yellow S and ferric thiocyanate methods, respectively.

Gilman and Wade (5) also did chemical analysis of the cell reaction products for Li/LiAlCl₄,SO₂Cl₂ cells. These were laboratory experimental cells which from their description seemed to be limited by the pore volume available for insoluble products in the cathode. The insoluble cathode products were determined by removing the porous carbon cathodes after discharge and washing thoroughly with sulfuryl chloride. X-ray diffraction of one of the cathodes showed only the diffraction lines of LiCl. Other cathodes were extracted with water and total chloride determined by potentiometric titration with standard silver nitrate solution. Aluminum was determined quantitatively to correct for any occluded lithium tetrachloroaluminate salt by the aurintricarboxylate colorimetric method. The result of the chloride analysis corrected for aluminum was that the number of equivalents of chloride determined as LiCl agreed with the number of equivalents of electricity consumed in the discharge to within the experimental error. It was thus concluded that LiCl was the only ionic product from the discharge. An attempt to extract a cathode with carbon disulfide did not yield any sulfur. It was then postulated that the only sulfur containing product was sulfur dioxide. A rather complicated pressure measurement gave reasonable agreement with this hypothesis although sulfur dioxide was not specifically analyzed.

While there appears to be a discrepancy between the results of the two studies discussed above, it is most likely that the different cell types which were used were responsible for the differences. The cell of Gilman and Wade had a large amount of sulfuryl chloride still present when the cell cutoff occurred ensuring that sulfuryl chloride was the cathode reactant up to that point. In the cells of Blomgren et al., however, the sulfuryl chloride was nearly exhausted before the cutoff so that sulfur dioxide could be reduced prior to the cell cutoff giving the dithionite as a product of that reduction, but at a lower potential than the sulfuryl chloride reduction. Thus, it is concluded that the final products for the lithium/sulfuryl chloride battery are sulfur dioxide and lithium chloride according to the reaction:



If however, the cell is designed with excess lithium, then the further reaction:



can occur at a lower potential if there is sufficient room in the porous cathode structure to accommodate the lithium dithionite product at reasonable levels of polarization. The presence of lithium thiosulfate may have been due to a disproportionation reaction of dithionite under the discharge conditions or to an artifact of the analysis. A definite correlation between the dithionite and thiosulfate levels was observed which suggests a close relationship between the two products.

Auborn et al. (6) examined discharged lithium/sulfuryl chloride cells and stated that sulfur was a major discharge product. Razzini et al. (7) also examined discharged cells and observed yellow crystals on the cathodes which they took to be sulfur without analysis. Unfortunately the lack of analysis in these works and the inability of Gilman and Wade (5) to detect sulfur makes this a questionable product for these cells.

Cyclic voltammetry has been employed along with chemical analysis to assist in understanding the discharge mechanism for sulfuryl chloride. Blomgren et al. (3) investigated several electrodes and found that compression annealed pyrolytic graphite electrodes gave the most detailed voltammograms of any material investigated. It was believed that the cause was the relative perfection of the surface compared to other electrodes and the tendency to hold intermediates on the surface for a long enough time to undergo further reactions. Behl (8) carried out similar studies on glassy carbon electrodes and found comparable but less detailed results. Schlaikjer (2) summarized the results of the two studies and the different interpretations advanced for similar peaks in the two papers. The essential difference in the interpretations is that Blomgren et al. interpret the first and second peaks as being due to the reduction of sulfuryl and thionyl chloride, respectively, where thionyl chloride is postulated as an intermediate. Behl, on the other hand, interprets the two peaks as being due to the

reduction of chlorine and sulfuryl chloride, respectively. Both mechanisms lead to sulfur dioxide and lithium chloride as the major products and both agree that a lower voltage reduction of sulfur dioxide can lead to dithionite product. Clearly, more work is required to fully understand the discharge mechanism of sulfuryl chloride.

Numerous workers have carried out analytical studies on thionyl chloride and its reduction products. Schlaikjer (2) reviews the methods and results and points out that several methods have given misleading results. This is particularly true for methods involving elevated temperatures such as gas chromatography. We have also found this to be the case and have developed methods to use GC without allowing the sample to see high temperatures. Thus, using chemically inert columns such as Kel-F wax on Chromosorb-T, the sample (solvent or electrolyte solution) is given on-column injection with the injection port maintained no higher than 35 degrees C. The column is held at a low temperature (-10 to -50 degrees C) until a substantial fraction of the eluent has passed through the column at which point a temperature rise may be programmed to elute higher boiling components. The method gives clean GC curves for thionyl chloride which has been freshly distilled. Using this methodology, Blomgren et al. (3) found sulfur monochloride present at a level of about 1 to 2% in the electrolyte from a partially discharged cell. About the same level of sulfur monochloride was found from a cell taken to deeper discharge while no detectable amount of this material was found in the initial electrolyte. These results led to the postulation of sulfur monochloride as an intermediate in the discharge of thionyl chloride cells. While we recommend using a subambient temperature column for GC work it may not be strictly necessary for accurate work. Carter et al. (9) have used GC with QF-1 liquid phase on Chromosorb G. They maintained the column and injector port below 130 degrees C in order to prevent reaction of sulfur and thionyl chloride and observed the presence of sulfur monochloride in partially discharged Li/SOCl₂ cells. These workers also found chlorine present in electrolyte from partially discharged cells by the GC method.

Because of the discrepancies of earlier work mentioned above, Bailey and Kohut (10) of our laboratory developed a special method to determine the reaction products within the cell. The method involved room temperature evacuation and trapping of all volatile material from the cell after various levels of discharge. This was followed by analysis of total sulfur and total chlorine after alkaline hydrolysis of volatile and nonvolatile portions in sealed systems. The sulfur was determined by permanganate oxidation to sulfate and gravimetric determination as barium sulfate. Total chloride was determined by oxidation of an aliquot with hydrogen peroxide, acidification and potentiometric titration with silver nitrate. By comparing weights and sulfur and chloride analysis of the the two cell portions with the electrochemical equivalents, the authors deduced the reaction stoichiometry to be:



The discharges were carried out at various temperatures (-50 to +71 degrees C.), at various depths of discharge and at various rates of discharge, always with the same result. They also determined elemental sulfur in the nonvolatile portion by carbon disulfide extraction and consistently found one mole per four equivalents of charge. This work has proved to be definitive and the reaction (3) is widely accepted as the overall reaction for Li/SOCl₂ cells.

While the overall reaction for thionyl chloride cells is well established now, there continues to be controversy regarding the mechanism and the chemical nature of intermediates for the reaction (Ref. 2,3,11-14). Cyclic voltammetry has been used for thionyl chloride cells to help explain the mechanism. Blomgren et al. (3) used pressure annealed pyrolytic graphite electrodes on their studies of thionyl chloride. As for sulfuryl chloride, a number of reduction peaks were seen. The peaks assigned to sulfur dioxide reduction occurred at similar potentials although other methods and cell analyses fail to show reduction of sulfur dioxide. A peak was not seen for sulfur monochloride, which was advanced as a key intermediate as discussed above. But experiments done with sulfur monochloride solutions showed that this material is reduced at more positive potentials than thionyl chloride and would be expected to react as it is formed. Thus, sulfur monochloride could build up to a small steady state concentration, but would not show a peak in cyclic voltammetry in agreement with the observation.

Behl (15) also did cyclic voltammetry on lithium tetrachloroaluminate thionyl chloride solutions, but on a glassy carbon electrode. His results showed one major peak which was assigned to the reduction of thionyl chloride and two weak peaks which were assigned to the reduction of ferric ion to ferrous and ferrous ion to iron metal respectively. It was believed that the iron impurity was brought in by way of the salt. Behl also

found with ring-disc experiments that the reduction of thionyl chloride produces an intermediate which could be oxidized at the ring electrode at more positive potentials than the reduction. He suggested that this intermediate may be the unstable molecule SO . He could not relate this species to the observed potential because it is so unstable it can not be studied separately. Dey (16) had previously postulated the presence of SO as an intermediate with the assumption that the reduction of thionyl chloride proceeded with a two electron process:



followed by a disproportionation reaction of SO :



Bowden and Dey (12) studied the reduction of thionyl chloride in organic solutions with cyclic voltammetry and coulometry. They also concluded that the SO intermediate could explain their results, particularly the reappearance of the reduction peak ascribed to thionyl chloride after exhaustive electrolysis and a waiting period. It was argued that the reappearance was possibly due to a complex of SO with thionyl chloride which decomposed to give more thionyl chloride after the waiting period. This explanation, however, requires considerable stability for SO , which is known as a very unstable molecule (Ref. 17). The work of Bowden and Dey (12) was criticized by Young (18), who pointed out that there are known reactions of thionyl chloride with the organic solvents used by those workers and, thus the results cannot be considered definitive without taking into account these reaction possibilities. The more recent work of Carter et al. (9), in addition to finding sulfur monochloride as an intermediate, also found a very short lived free radical intermediate by an ESR technique on frozen samples. This species was believed to be OCIS , resulting from rearrangement of the one electron reduction product of thionyl chloride, SOCl . While the mechanism of thionyl chloride reduction can not be said to be fully understood, there is certainly a much better understanding today as a result of continuing work.

IMPURITY CONSIDERATIONS - SPECTROSCOPIC METHODS

French and his coworkers (19) recognized in an early study that infrared spectroscopy was a convenient, useful method for studying thionyl chloride solutions. For example, the sulfur-oxygen stretching region is useful because the frequency of this band is very sensitive to its chemical environment, and the region contains few other bands. Thus, Schlaikjer et al. (21) measured the concentration of sulfur dioxide in thionyl chloride by the intensity of the 1333 cm^{-1} band. Abraham and Mank (21) determined sulfur dioxide in thionyl chloride and sulfuryl chloride in thionyl chloride by the band at 1415 cm^{-1} . These authors also assigned a band at 1110 cm^{-1} to the ionic complex, $\text{SOCl}^+\text{AlCl}_4^-$. This band, however, is better assigned to the neutral complex, $\text{AlCl}_3 \cdot \text{SOCl}_2$, which was studied with Raman spectroscopy by Long and Bailey (22).

Another region of interest is from 2800 to 3600 cm^{-1} . French et al. (19) were the first to make use of this spectral region when they studied the effect of water contamination on oxhyalides in one centimeter pathlength quartz cells. They observed a band at 2800 cm^{-1} when adding water to thionyl chloride and an additional band at about 3400 cm^{-1} when adding water to lithium tetrachloroaluminate solutions of thionyl chloride or sulfuryl chloride. These workers assigned the band at 2800 as due to chlorosulfurous acid (HSO_2Cl) and the band at about 3400 cm^{-1} as due to the OH stretching vibration of hydroxide ion coordinated to the aluminum ion. Later workers have agreed with the latter assignment, but have assigned the 2800 cm^{-1} band to hydrogen chloride (Ref. 20, 23, 24) and have shown that it can be used for quantitative determination of this very common contaminant of thionyl chloride.

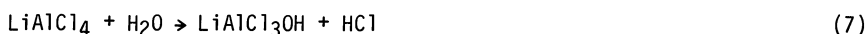
The band at about 3400 cm^{-1} has also received some discussion. Schlaikjer et al. (20) reported that position of the band was at 3300 cm^{-1} when a thionyl chloride solution was prepared with moist aluminum chloride, but shifted to about 3400 cm^{-1} when the same solution was saturated with lithium chloride. They thus assigned the bands to the species AlCl_2OH and AlCl_3OH^- respectively. Bailey and Blomgren (25) studied the spectrum of aluminum chloride in thionyl chloride solution with added anhydrous lithium hydroxide and observed strong bands at 3380 and 685 cm^{-1} . These bands correspond to the weak bands observed by them at 3380 and 675 cm^{-1} from solutions of slightly moist lithium tetrachloroaluminate in thionyl chloride. These were assigned as the OH stretching and AlO stretching vibrations for the AlCl_3OH^- ion. These spectra are similar to those observed by Tait and Osteryoung (26), who added water to an acidic melt of aluminum chloride and 1-methyl-3-ethylimidazolium chloride and observed three new

bands at 3323, 1119 and 703 cm^{-1} . These were assigned as OH stretching, A1OH bending and A1O stretching vibrations, respectively, of the AlCl_2OH molecule. These assignments were verified by additions of D_2O . From the evidence to date, it does not appear that the A1OH grouping interacts strongly with the rest of the molecule so that it is difficult to distinguish between the neutral, three coordinate species (AlCl_2OH) and the anionic, four coordinate species (AlCl_3OH^-). In thionyl chloride solutions, the A1OH bending vibration is undoubtedly masked by the strong SO bending region. These peaks are important for two reasons. The first is that the presence of OH ion in the system tends to increase corrosion of the lithium electrode (Ref. 25). Therefore, the quality of the electrolyte solution with regard to this source of corrosion may be tested by monitoring the infrared spectrum in the OH stretching region. The second is that the position of the A1O stretching peak is in a region in which several other species absorb. A number of these species are potentially harmful to the lithium batteries. Thus Istone and Brodd (13) observed a band at 689 cm^{-1} and assigned it to the unstable species disulfur monoxide on the basis of no other evidence and no discussion of the 3400 cm^{-1} region. Also, Salmon et al. (27) observed a band at about 690 cm^{-1} and assigned it to the highly unstable molecule, Cl_2O . In the absence of other information, it is difficult to accept either of these assignments. It is more likely that some moisture contaminated their systems in both cases and formed some of the AlCl_3OH^- species.

We can summarize the effects of moisture on lithium tetrachloroaluminate solutions as revealed by the infrared evidence by the following sequence of reactions. Water may react directly with thionyl chloride to form sulfur dioxide and hydrogen chloride:



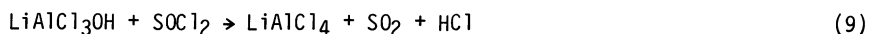
Water may also react in the neutral salt solution with the salt in a partial hydrolysis reaction:



or in the acidic solution with aluminum chloride:



The partially hydrolyzed aluminum species may then react with thionyl chloride as follows:



and



It isn't known if only hydrogen chloride or if both this material and the hydrolyzed aluminum salts react with lithium, but either case will ultimately result in lithium corrosion to form hydrogen gas. Since hydrogen is a noncondensable gas this is a particularly bad result for sealed cells. In other infrared studies the addition of lithium carbonate to solutions of aluminum chloride in thionyl chloride gave rise to interesting spectra (Ref. 25). Two pairs of CO stretching bands were observed indicating the presence of two species for which the degeneracy was removed. The two splittings observed were assigned as arising from carbonate ions coordinated to aluminum ion in both a monodentate (1540 and 1490 cm^{-1}) and a bidentate (1608 and 1445 cm^{-1}) configuration. On heating these solutions, bands attributable to carbon dioxide and sulfur dioxide as well as two new bands at 800 and 674 cm^{-1} appeared, while the carbonate bands disappeared. The new bands are in about the same positions as those seen by Abraham and Mank (21) in the solution from overdischarged lithium-thionyl chloride batteries and assigned to the AlSCl_2 ion. Bailey and Blomgren (25) assigned the peaks to lithium aluminum oxide chloride species on a tentative basis because of the unlikelihood of sulfide ion being present in that system and the comparison of other aluminum oxygen vibrations with the 800 cm^{-1} position. One other infrared band has been observed at about 1070 cm^{-1} in electrolyte from overdischarged anode limited cells (ref. 21, 27). No satisfactory assignment is available for this band. It was suggested (29) that the thionyl ion (SO^{2+}) was responsible, but one would expect this species to absorb at higher frequencies than the SO vibration in thionyl chloride.

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