ADVANCES IN PRIMARY LITHIUM LIQUID CATHODE BATTERIES

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Summary

Recent work on cell development and various aspects of cell chemistry and cell development of lithium/thionyl chloride liquid cathode batteries is reviewed. As a result of safety studies, a number of cell sizes can now be considered satisfactory for many applications and the energy densities of these cells is higher than any other developed battery system. Primary batteries operate with low to moderate currents and the anode delay effect appears to be under reasonable control. Reserve cells are in the design stage and operate at high to very high power densities as well as very high energy densities. The nature of the anode film and the operation of the lithium anode has been studied with substantial success and understanding has grown accordingly. Also, studies of the structure of the electrolyte and the effects on the electrolyte of impurities and additives have led to improved understanding in this area as well. Work in progress on new electrolytes is reviewed. The state of the art of mathematical modeling is also discussed and it is expected that this work will continue to develop.

Introduction

The lithium/thionyl chloride liquid cathode battery with lithium tetrachloroaluminate electrolyte salt has the highest energy density and specific energy among the developed primary battery systems and is capable of high discharge rates. However, most of the active or non-reserve primary batteries based on this system have been designed for only moderate currents under continuous discharge conditions. Thus, the capability of high power density has been sacrificed for the sake of system safety with present designs. In earlier designs, the cell polarization was sometimes sufficiently high that internal heat generation led to runaway reactions when the melting point of lithium was exceeded. Reserve cells have often been designed for much higher rates of discharge, since energy density of the system is usually not as important as for active cells and better heat rejection methods may therefore be included. This paper reviews the state of the art of cell development as well as work on specific aspects of cell chemistry on this and related systems.

Only recent work (since 1985) is included because of earlier comprehensive reviews [1 - 3].

Active batteries

The state of the art of presently manufactured batteries of this type was given at the 32nd Meeting of the Power Sources Symposium. The paper of Kaduboski and Horvath [4] presented data from Eveready Battery on an "F" size jellyroll construction cell which had about 0.7 W h cm^{-3} energy density at 2 A current (4.2 mA cm^{-2}) on a room temperature discharge. The capacities exceeded military specifications at low and high temperatures as well as at room temperature, and the voltage delays (time to voltage recovery above 2.5 V) were below 1 s for all storage, current, and temperature conditions. While these capacity figures are not as high as could be obtained with other cell designs, a heavy premium was placed on safety. In fact, the cells performed very well under casual abuse conditions and did not present a safety hazard. It was only under severe abuse conditions such as crushing, flame or puncture that venting with lithium fires occurred, and only on heat tape heating to 500 °C did a loud bang occur with the lithium fire.

Results on multicell batteries utilizing the same size unit cell as the above were presented by Hall and DeBiccari [5]. The room temperature and high temperature tests gave somewhat higher capacities, while the low temperature test gave poorer capacity and longer delays. Also, the elevated temperature storage tests gave diminished capacities, even at room temperature discharge. The multicell battery behavior was studied on severe abuse testing and several explosions were reported. Milder abuse testing did not lead to violent incidents, however.

Staniewicz et al. [6] reported on progress with a different size unit cell and its incorporation in an 8 cell battery. Again, safety was the emphasis and the role of a properly operating vent in controlling violent incidents during severe abuse testing was studied. They found that 12 A h of capacity could be obtained from a fresh unit cell at room temperature with a 2 A drain giving 0.58 W h cm^{-3}. No violent incidents were observed under casual abuse conditions. The authors ascribe this fact to the reliable venting of the cell at pressures of between 150 and 200 p.s.i.

For a battery designed for pulse operation only, it is possible to construct high rate designs which appear to have adequate safety of operation. DeBiccari [7] describes two batteries of this type. Pulse currents as high as 26 mA cm^{-2} were found to be manageable in pulse modes of 20 ms to several minutes. One of the batteries is a stack of short, cylindrical unit cells while the other is a stack of square, prismatic cells. While the energy densities are much lower than the moderate rate batteries described above, they provide 10 times the energy of the nickel–cadmium batteries they are designed to replace.

Iwamaru and Uetani [8] describe the design and operation of a low rate R6 ("AA") size cell intended as a memory back-up source. The cell is hermetically sealed and has a central cathode bobbin of acetylene black with a Teflon binder. The energy density of this battery is higher than the above cells, giving about 0.82 W h cm^{-3}. An unspecified additive was found necessary to control the anode delay phenomenon. The cells operated very well over the temperature range of -40 to 60 °C, had very good shelf life, and were very resistant to damage during abuse conditions.

Watson *et al.* [9] took a novel approach to cell design for low rate cells when they utilized a catalyzed, very high porosity (95%), sintered nickel electrode as a cathode collector. They used a U-shaped cell typical of heart pacer design and had a single lithium anode between two porous nickel cathode collectors. The high porosity permitted high volumetric efficiency. Based on external dimensions, the energy density was about 1 W h cm^{-3} at low discharge rates and preliminary safety testing looked good, although severe abuse tests had not yet been carried out.

Reserve batteries

These batteries are reviewed only briefly here because the field is under rapid development and the types of cells which ultimately succeed may depend on how many applications are found for the system. The essential aspect of the reserve cell is that combinations of components which are mildly unstable together, most importantly the electrolyte phase and the lithium anode, can be kept separate until activation of the cell. The method of activation depends, in part, on the time available for activation. Some methods are to fracture a glass container, to puncture a diaphragm covering part of the container or to open a valve to the container holding the electrolyte, followed by fluid flow driven by absorption of electrolyte into the separator and cathode structure [10 - 15]. This process requires time to reach an equilibrium where most, if not all, of the electrolyte is present inside the electrode stack. An important aspect of this approach is that chloroacidic electrolytes (those with excess aluminum chloride) can be used in order to permit very high rates of discharge. Chloroacidic electrolytes cause anode corrosion, but high rate reserve cells can tolerate the low corrosion rate [14]. Sulfuryl chloride electrolytes have also been found to be useful in reserve cells [14]. These cells can operate at high discharge rates, typically in the range 20 - 100 mA cm^{-2} [10 - 15].

Another activation concept which can be applied is to pump the electrolyte into the interelectrode space. The presence of a pump would increase the weight and volume on the battery substantially, but in one design, the cell could be made in a configuration to permit the electrolyte to flow during operation [16]. Test fixtures have shown that cell operation in this mode is possible at rates of up to 500 mA cm^{-2}. It appears that high capacities would be possible at these high rates because the product, lithium chloride, would be swept away from the electrodes. Also, heat could be efficiently dissipated to the surroundings by the flowing electrolyte [16].

Lithium anodes

The most important aspect of the lithium anode chemistry is the nature of the anode film. It is the presence of this film which permits the possibility of making an electrochemical cell. Furthermore, it is the tightness and repairability of the film which allow active cells with long shelf lives to be constructed. This results, however, in an anode delay phenomenon. Studies of the nature of this film have continued through the years, *e.g.*, see Peled [17], but information and new perspectives are still being uncovered. Mogensen has reported fundamental data on film growth as measured by impedance techniques [18]. He shows that impedance growth is most rapid with neutral electrolyte, less rapid with chloroacidic electrolyte, less with chloroacidic electrolyte–sulfur dioxide mixtures, and least rapid when the latter electrolyte has lithium coupled to stainless steel. The impedance was thought to be directly related to the film thickness. The impedance growth rate for the neutral electrolyte was found to be approximately parabolic, which suggests a film growth rate limited by electronic conductance of the film. Measurements of the film by SEM observations showed the thickness to be at least an order of magnitude thicker than that predicted by the impedance model. It should be noted that in many cases, especially for the types of electrolytes studied by Mogensen, a slow rate of film growth is accompanied by anode corrosion, which is very deleterious to active cells. The corrosion effect can be accelerated further by coupling the lithium to a more noble metal which can serve as a site for cathodic reduction.

Using a device developed by Bailey [19], Boyd was able to examine LiCl films on lithium which had been bent in the SEM so as to fracture the film and allow examination in cross section [20]. The work was done with neutral electrolyte (1.5 M $LiAlCl_4$ in $SOCl_2$) under the conditions of room temperature and 71 °C storage, with, and without, poly(vinyl chloride) (PVC) additive in the electrolyte and with, and without, iron contaminant in the electrolyte. The work clearly shows a duplex film — a dense, compact film adjacent to the lithium and a collection of well faceted, loosely connected crystals on the electrolyte side. The thicknesses of the two layers and the crystallite size in the porous layer depend on the storage conditions. Most importantly, the samples with PVC in the electrolyte gave the thinnest films by far, while those with iron contamination and no PVC were very thick. The film thicknesses were of the same order of magnitude as those of Mogensen [18], and thus, also larger than expected from impedance curves. The growth rates of the films without iron were found to be parabolic for the relatively short times of these experiments. Voltage delay curves measured on cells undergoing the same storage conditions with identical electrolytes agreed with the film thickness measurements at the extremes. The samples with intermediate thicknesses did not always follow the same order, but voltage delay is a difficult measurement to carry out reproducibly.

Independent experiments in cells have shown that the use of PVC does not cause accelerated anode corrosion or capacity loss.

Ohsaki [21] confirmed the reduction of voltage delay and impedance growth due to the presence of poly(vinyl chloride) in the electrolyte. He found that a copolymer (of unspecified type) of vinyl chloride–vinylidene chloride (VC–VDC) also had an excellent effect on reducing delay, while all other tested chlorinated polymers and poly(ethylene) had poorer results or had no effect on reducing delays. Delays were measured in bobbin type "AA" cells which had been stored under various conditions. A.C. impedance measurements were also made on these cells and the results correlated well with the delays. Interesting methods of studying the films were developed. Lithium strips were stored in polymer containing electrolyte for about 5 h, rinsed, and dried. Some of the strips were subjected to EDAX measurements which showed the presence of Cl, presumably due to LiCl. Those samples which had reduced voltage delay showed smaller chlorine peaks, which indicated thinner films. Other strips were carefully immersed in ethanol until all of the lithium dissolved. A free standing polymer film was recovered and studied in the SEM from solutions containing PVC, VC–VDC or a chlorinated PVC. None of the other solutions yielded a free standing film. It was concluded that only these three materials made coherent films which were strongly attached to the lithium, resulting in a change in LiCl morphology and reduced growth rates for LiCl crystallites. The thickness of the PVC film was estimated, from the depth of a pin hole in the film, to be 1.5 μm.

While the operation of PVC has been clearly demonstrated, the understanding of the use of cyanoacrylate films is in a more speculative situation. Fleischer and Ekern used SEM and ESCA to study the effects on lithium which had been treated with cyanoacrylates and then stored in thionyl chloride solutions [22]. The ESCA studies were definitive in showing that no substantial amount of unchanged polymer remained on the surface after storage in thionyl chloride electrolyte. This means that either a trace effect or an effect due to dissolved cyanoacrylate (probably as monomer) caused the changes in the morphology and growth kinetics of the LiCl film which were observed by the SEM studies. Cyanoacrylate coatings were also employed on lithium with sulfuryl chloride/LiGaCl$_4$ electrolyte cells [23]. Good capacities were obtained, but no information was given concerning delay times. Initial voltage data that were given indicated that there might be a problem in this area. More comprehensive studies of the LiCl film should be undertaken if better understanding of the cyanoacrylate effect is to be sought.

Another area requiring better understanding is in the use of BrCl and Br$_2$ additives to thionyl chloride electrolyte. Ponkratov and coworkers [24] have determined polarization resistances of lithium samples stored in these electrolytes. Large increases in this property and in the delay time were observed on increasing storage time compared with the neutral electrolyte without additives. Direct studies of the lithium film were not undertaken, however, so the chemical and physical natures of the films are not known.

Two other recent papers have studied the lithium anode under different preparation methods. Hedges *et al.* [25] studied lithium films which had been electrodeposited from neutral electrolyte onto nickel microdisk electrodes. The small electrodes permitted the elimination of solution ohmic drops and cyclic voltammetry measurements allowed determination of lithium dissolution kinetics. The freshly deposited lithium gave, on the return sweep, the nearest film-free lithium electrodes that it is possible to obtain. The overpotentials for dissolution were small and the activation energies, which were also small, indicated low lithium ion solvation energy by thionyl chloride. Plotting the data on Allen–Hickling plots showed a smooth transition with constant slope through zero overpotential, indicating simple Butler–Volmer kinetics on a film-free surface at all temperatures. By depositing lithium potentiostatically and waiting for various periods prior to potentiostatic stripping, the corrosion process could be studied. Delay effects and actual separation of lithium from nickel were observed after various times. The results clearly show that if a lithium deposit stands for only one hundred seconds on open circuit, a film forms which is sufficient to inhibit further corrosion and requires a nucleation step if further lithium is deposited. It appears that if the film on a battery anode is broken during discharge, the anode may act with very low overpotential on those areas of film-free lithium. The second study involving a different surface of lithium was carried out by Delnick [26]. The lithium in this case was prepared by dipping stainless steel screen flags into molten lithium in an oxygen- and nitrogen-free dry box. The electrodes, after solidification, were then placed in neutral electrolyte solutions. The surfaces of lithium had minimum oxide coverage at this point. d.c. impedances were obtained by extrapolating a.c. impedance curves measured at open circuit. Polarization resistances were then measured on the electrode by studying the time evolution of the current under low field potentiostatic conditions. This measurement is a better definition of the condition of the film than conventional delay measurements. It was found that 10 ms was fast enough to obtain consistent results (the current did not change for shorter times) under all film conditions. The two results gave a one to one correspondence. This work showed that with this improved understanding of delay, the d.c. impedance can be used as a measure of the condition of the lithium chloride film when carried out at open circuit. The presence of two semicircles in these impedance plots (as previously observed) indicated at least two limiting processes at OCV.

The calorimeter studies of Hansen and Frank also bear on this problem [27]. The heat evolution of cells was measured to very long times and it was found that at long times, the heat evolution followed an exponential growth rate rather than a parabolic one. Furthermore, the slopes of the log–log plots (the values of the exponent) were substantially different at the two temperatures studied. The results were rationalized on the basis that, at short times, the heat evolved was due to lithium corrosion, while at longer times a slow reaction of a long-lived intermediate in the electrolyte solution was

believed to contribute. Combining these results with heat measurements on closed circuit conditions led the authors to conclude that it was likely that sulfur monochloride was the intermediate that slowly degraded.

Mention should also be made of an inorganic coating which is put on lithium prior to battery manufacture. The work is described in general terms in a paper [28], and specifics are given in a U.S. patent [29]. These authors used cyanoacrylate in some parallel studies and found capacity losses after storage. The inorganic coating gave good delay and capacity performance. Several methods and compositions for putting these coatings on from the vapor phase are described in the patent, but it is not clear which will ultimately be preferred.

Recent work has advanced another additive to thionyl chloride batteries to minimize the voltage delay phenomenon [30]. Addition of sulfur trioxide to $LiAlCl_4$ in thionyl chloride allows the formation of a tetra(chlorosulfato) aluminate ion which improves the voltage delay properties. Again, only preliminary information is available and much study is required to fully establish the mechanism, preferred method, and composition of the additive.

Electrolyte solution studies

The electrolyte phase of liquid cathode batteries has many important requirements if a successful galvanic cell is to be constructed. The subtle nature of the reaction with lithium to form a film of reaction product of just the right properties has been discussed above, and obviously much remains to be learned of this requirement. The electrolyte must have a high electrical conductivity to minimize ohmic losses in the battery, must facilitate the anode reaction with low overpotentials, and must be capable of being reduced on the cathode collector material with low overpotentials. These requirements are also subtle as will become evident. In this section, the aspects of electrolyte structure, purity, and transport properties are discussed.

Spectroscopic studies have now been extensively applied to reveal the chemistry and structural factors involved in oxyhalide electrolyte solutions, mostly of the chloroaluminate electrolytes in thionyl chloride. The use of infrared spectroscopy to study various impurities in thionyl chloride solutions was reviewed recently [31]. Since that time, the fate of hydroxide ion in these solutions has been clarified [32] by isotopic substitution, infrared experiments, and ^{27}Al NMR measurements, while the origin of a previously unassigned band in the i.r. at 1070 cm^{-1} has been shown to be due to the chlorosulfate anion coordinated to aluminum ion [30]. One of the most interesting aspects of the chemistry of these solutions is the central role played by the aluminum cation, even though it is initially dissolved as either the tetrachloroaluminate ion in the neutral solution or as the $SOCl_2$ coordinated $AlCl_3$ species in the chloroacidic solution. Anions of higher

Lewis basicity than chloride, such as hydroxide, carbonate, oxide or chloro-sulfate, can displace the chloride ion in the first coordination shell of aluminum, which gives rise to the acid–base chemistry of the system. Oxide ion seems to be unique in the system, since it can bridge bond between two aluminum centers [32]. The oxide ion also appears to exchange readily in the system, which indicates a high degree of reactivity and mobility. This probably accounts for the facile conversion of the native oxide film to LiCl on lithium metal when it is introduced into neutral thionyl chloride electrolyte. The fact that this lithium chloride film forms almost immediately [25, 33] also indicates that the solubility of lithium chloride in the neutral electrolyte is very low, and that the recent measurement showing a solubility of a few tenths molar [34] is probably too high by several orders of magnitude.

Raman spectroscopy has shown that the lithium cation also has an interesting coordination chemistry in the neutral electrolyte [35]. This is particularly the case as the electrolyte undergoes changes during discharge of the cell. The lithium cation is solvated initially by two molecules of thionyl chloride. As sulfur dioxide builds up in the electrolyte due to the discharge reaction, lithium complexed by one molecule of thionyl chloride and one of sulfur dioxide becomes the dominant species. Finally, in a sulfur dioxide-rich solution, the lithium ion is complexed by three molecules of sulfur dioxide. There also appears to be another species present after deep discharge which has not yet been identified. The effect of the complexation by the solvent molecules is to suppress the vapor pressure of the solvent, particularly of the sulfur dioxide. This fact, along with the adsorption of SO_2 by carbon in the cathode collector, is sufficient to explain the difficulties several workers have had in obtaining the theoretical amount of sulfur dioxide on analysis of reaction products [36]. The low solvation number of the lithium cation, especially for pure thionyl chloride electrolytes may indicate the pre-dominance of solvated ion pair species in the electrolyte solution. The solvation number for lithium ions in the absence of ion pairs is usually four when steric hindrance is not a factor.

Utilizing a theory developed for low dielectric constant media, which is capable of describing solutions of high concentration [37], the author has computed values of the degree of dissociation of contact ion pairs of lithium tetrachloroaluminate in thionyl chloride. The association constant was varied around the measured value, while the distance of close approach of the solvated ions was varied around a calculated value [38]. An approxi-mate experimental value of the degree of dissociation can be obtained from the ratio of the conductivity–viscosity product at a given concentration to that at infinite dilution (the Walden Ratio). We have carried out measurements of conductivity and viscosity of lithium tetrachloroaluminate solutions of thionyl chloride to high concentrations and at various temperatures [39] in order to compute this quantity. Figure 1 compares calculated values with the Walden Ratio at room temperature. Redissociation of ion pairs at con-centrations above 10^{-2} M is verified by the experiments. Values at tem-
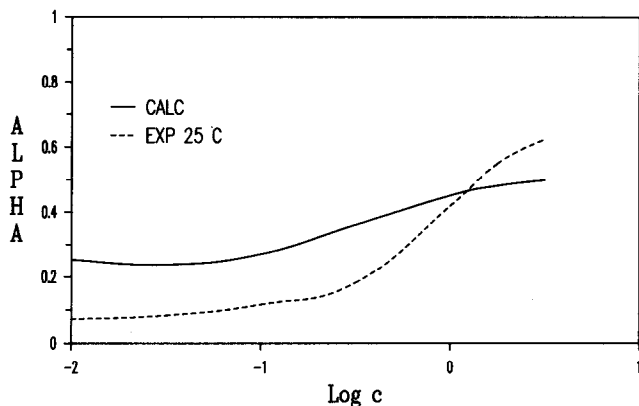
Fig. 1. Theoretical calculation (calc.) of degree of dissociation (ALPHA) and experimental evaluation of Walden Ratio ($\Lambda\eta/\Lambda_0\eta_0$) at 25 °C (EXP 25 °C) *vs.* logarithm of molar concentration.
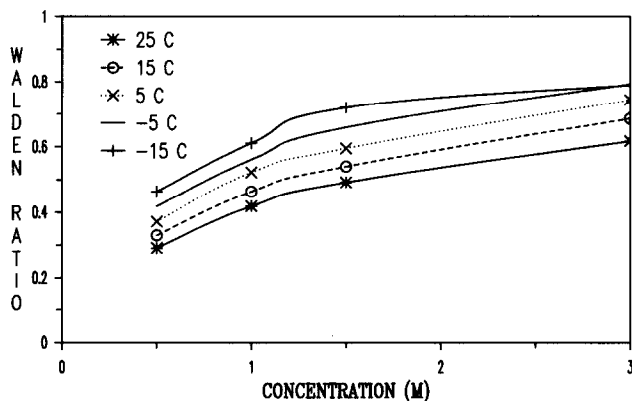

Fig. 2. Experimental values of the Walden Ratio as a function of concentration at various temperatures (−15 to 25 °C).

peratures other than room temperature were not calculated since the dielectric constant at other temperatures is not known. Figure 2 shows the experimental Walden Ratio, and the direction of change with temperature is exactly what would be expected. The dielectric constant is expected to increase with decreasing temperature, and this would change the degree of dissociation in the observed direction. The qualitative picture of the formation of ion pairs at low concentration, followed by the redissociation of these pairs at high concentration, is quite consistent with the experimental values.

We have also investigated new electrolytes to test hypotheses for performance improvements [39]. One electrolyte has sulfur monochloride additions to the 1.5 M LiAlCl$_4$ in thionyl chloride solution. Two levels, 5 and 18% of the additive, were investigated. The basis of the hypothesis was

that, if sulfur monochloride acts as an intermediate in the reduction of thionyl chloride, the presence of excess sulfur monochloride might enhance the kinetics of the reduction reaction and improve the reaction product distribution. We found that the conductivities of the electrolytes with added sulfur monochloride were lower than the control electrolyte (1.5 M LiAlCl$_4$ in SOCl$_2$) while the viscosities were almost identical for the three solutions, Table 1. The capacities were measured in small, cylindrical, bobbin-type cells (Eveready designation — L31) and it was found that at lower rates (6 mA cm^{-2}) the control and 5% solutions gave about the same energies, while at higher rates (10 mA cm^{-2}) the 5% solution gave slightly higher energy than control. The operating voltages of the 5% solution were also higher. The capacities of the 18% solution were, in all cases, lower, Table 2. Further evaluations of the effects are in progress.

A second set of electrolytes was investigated under the hypothesis that a purely chlorobasic electrolyte would change the entire cell chemistry, making it likely that the insoluble product of the cell reaction would now appear in the anode compartment rather than the cathode compartment and allow higher cell reaction rates. Most chlorides are, at best, sparingly soluble in thionyl chloride, but we found that 1-methyl-3-ethylimidazolium chloride (MEIC) is quite soluble. Also, the 1 M solution is more conductive than a 1 M LiAlCl$_4$ solution in thionyl chloride, while the viscosities are comparable, Table 1 [39]. In attempting to evaluate the electrochemistry of the electrolyte, it was found that stainless steel or nickel coupled to lithium or to carbon are subject to intense corrosion reactions. The lithium and the carbon remain essentially unaffected, but the carrier metals dissolve rapidly. We found that molybdenum collectors were stable in the electrolyte, but the lithium voltage was not stable, even at open circuit. We are at present investigating the MEIC electrolyte in mixtures with LiAlCl$_4$. We found that

TABLE 1

Physical properties of some thionyl chloride electrolytes at 25 °C

Electrolyte	Conductivity (mS cm^{-1})	Viscosity (cP)	Density (g cm^{-3})
1.0 M LiAlCl$_4$–SOCl$_2$	15.35	1.26	1.68
1.5 M LiAlCl$_4$–SOCl$_2$	19.49	1.75	1.69
1.5 M LiAlCl$_4$–SOCl$_2$ with 5% S$_2$Cl$_2$	18.57	1.78	1.69
1.5 M LiAlCl$_4$–SOCl$_2$ with 18% S$_2$Cl$_2$	15.20	1.82	1.70
1.0 M MEIC–SOCl$_2$	16.37	1.25	1.61
1.25 M LiAlCl$_4$–SOCl$_2$ +0.25 M MEIC +0.25 M AlCl$_3$	20.08	1.67	1.67

TABLE 2

Summary of capacity tests — EBC L31 cells — 2.7 V cut-off

Electrolyte	75 Ω discharge			40 Ω discharge		
	h	A h	W h in.$^{-3}$	h	A h	W h in.$^{-3}$
1.5 M LiAlCl$_4$–SOCl$_2$	19.7	0.85	10.3	8.1	0.66	7.36
1.5 M LiAlCl$_4$–SOCl$_2$ +5% S$_2$Cl$_2$	18.6	0.84	9.7	8.0	0.66	7.41
1.5 M LiAlCl$_4$–SOCl$_2$ +18% S$_2$Cl$_2$	16.8	0.76	8.8	6.3	0.51	5.73

mixing solutions of the two salts results in the formation of a precipitate, probably LiCl. Adding aluminum chloride in a stoichiometric amount to the MEIC, however, yields a stable solution. We still experience some corrosion in the cell environment and are trying to find a way to minimize the effect. The conductivity of the mixed electrolyte is higher than a solution of LiAlCl$_4$ of the same ionic strength and the viscosity is lower (Table 1). This work has made it clear that there is still much chemistry to be learned in these solutions.

Mathematical modeling

The evolution and dissipation of heat are extremely important aspects of the viability of liquid cathode batteries. Because the generation of heat is intimately connected with the generation of the electrical current and the local polarizations within the battery, a comprehensive model which couples the two types of flow, current, and heat, is required for a complete explanation of the situation. Unfortunately, this is a difficult and complicated undertaking, especially with the complex geometries of many battery designs. The result is that, up until now, mathematical models have usually dealt with one or the other of the two flows. A considerable amount of work has been done in this area, but only the recent studies will be discussed here. Reference is made to the papers discussed for further information in the field.

Current distribution studies are best represented by the elaborate studies done by Tsaur and Pollard [40 - 42]. This series of papers deals with the neutral electrolyte, the acid electrolyte, and finally the effects of nucleation and precipitation of lithium chloride in the cathode. There are several interesting results. The paper on precipitation shows that these effects will be present even when the solubility of LiCl is only 10^{-10} M, if the rate of nucleation and the rate of growth are slow enough. Considerable supersaturation occurs in the cathode in this case, and in the acid electrolyte an important interaction between the rate of diffusion of aluminum chloride

and the rate of LiCl growth occurs. Because of these factors, it was found that the cell voltage and capacity at a given rate are not sensitive to the magnitude of the solubility product for the precipitate. Another important finding in the neutral electrolyte is that for a fixed cathode geometry (no cathode swelling) the effect of improving the exchange current or the specific surface area is to improve the voltage, but lower the capacity of the electrode (Fig. 9 of ref. 40). The implication of this result is that the use of catalysts in the positive electrode may not be beneficial unless structural modifications are made as well. While the agreement with experiment is not quantitative, this work represents a milestone in modeling efforts.

Two papers are taken to represent the state of thermal modeling. The paper of Szpak *et al.* [43] deals with a model of thermal runaway generated by a single point heat source in a lithium–thionyl chloride battery. The model applies to the presence of a hot spot within the battery brought about, for example, by an internal short circuit. If a critical temperature is reached, a runaway situation is predicted, in agreement with observations. This kind of modeling can be valuable in battery design to prevent the occurrence of such events. The second thermal paper to be highlighted [44] deals with heat transfer paths in spirally wound "D" cells. It was found by this model that the radial direction is the most important for heat transfer, and if the battery is placed with its bottom on a thermally insulating material, the radial direction is the only important direction. Experimental verification of the results of both of the above papers could be important to design considerations. Also, it is important to consider the effects of current distribution on the thermal properties, and ultimately to couple the two types of flows. This is expected to be an active field in the future.

Cathode studies

The design of these highly porous bodies, and the materials of construction have occupied battery scientists since the first liquid cathode batteries were constructed. The most commonly used material in cathodes is one or more of the many types of carbon. In addition, many additives which are presumed to operate as catalysts for the electrochemical reduction have been added to the carbon. Since this field was recently reviewed [45], only a few comments will be made here. The reduction of thionyl chloride is a complex process and the final products are undoubtedly due to chemical processes following the electrochemical steps. As a result, the reaction is highly irreversible and effects are difficult to sort out, as even the voltage in the absence of external current is best defined as a rest potential rather than an e.m.f. [46]. Added to this is the fact that many of the additives either dissolve (phthalocyanines) or change chemical form (copper to copper chlorides) which complicates the interpretation drastically [45, 46]. Finally, effects in liquid cathode batteries are strongly interactive and what happens at one electrode almost always affects the other electrode. Therefore, work

which is devoted to study of just one electrode can yield interesting results [47], but these results do not always translate into finished cells because of the interactions. This area of work will undoubtedly be the focus of much effort in coming years.

Acknowledgement

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