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THE LITHIUM–THIONYL CHLORIDE BATTERY — A REVIEW

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Summary

The lithium–thionyl chloride nonaqueous cell system is a recent development. Low atomic weight and high electrode potential make lithium unique as an anode in energy devices. Preparation of the anode, cathode, and the electrolyte is reviewed. The construction of the cell, its performance characteristics, uses, etc., are also surveyed.

Introduction

In the area of power sources, the lithium–thionyl chloride battery system is one of the major research developments in recent years [1 - 6]. This battery has evoked considerable interest because of its ability to operate at extremes of temperature. The lithium–thionyl chloride battery system has the advantage of long shelf life and possesses high energy density, power density, and cell voltage.

In the initial stages of development, lithium–thionyl chloride battery research suffered because of the battery's inability to discharge at high rates. However, this difficulty was overcome by suitable modifications to the design of the battery and by using better conducting electrolytes. These results have been achieved after more than a decade of research work in the area of high-energy density nonaqueous battery technology.

Lithium metal has certain unique properties. Of these, two important physical properties are made use of for constructing the lithium–thionyl chloride cell. They are the atomic weight and the single electrode potential. The former is the lowest among the known metals, and the latter is the highest. However, lithium metal reacts vigorously with water, as do other alkali metals, and therefore new problems and challenges have to be faced when this metal is used in the fabrication of a battery.

In order to overcome the problem of the high reactivity of lithium with water, anhydrous solvents are used. Typical organic and inorganic solvents have some additional special advantages; their freezing points are much lower

than that of water, and often their boiling points are higher. Hence, batteries with solvents other than water will have low-temperature operational capabilities. However, these advantages are offset by the inability of the nonaqueous solvents to conduct ions in a manner similar to water even when salts are dissolved in them. The dielectric constants of the nonaqueous solvents are, typically, much lower than water, and the conductivity of nonaqueous solutions is much less than aqueous solutions.

Despite the reactivity of lithium and water, lithium batteries have been constructed to operate in aqueous solutions [3]. However, for long term use, nonaqueous batteries are much preferred and this review will be restricted to that field of endeavour.

Thionyl chloride has been used as both a solvent and as an oxidant (depolariser) in the lithium−thionyl chloride battery. Compatibility studies with lithium metal reveal that the solvent, when pure, does not undergo any change and is reasonably inert. Some of the properties of thionyl chloride are compared with other inorganic solvents such as sulfuryl chloride and phosphorus oxychloride in Table 1.

Anode

According to the available literature [7], the anode is prepared by pressing lithium ribbon of the desired size on to an expanded nickel grid which acts as a current collector. For the well known commercial D size cell, the dimensions of the anode are reported as 20 × 1.5 × 0.015 in. Dey [7] has reported that the size of the anode has a great influence on the performance of the cell.

TABLE 1

Physical properties of inorganic solvents

Properties	Solvents			
	$SOCl_2$	SO_2Cl_2	$POCl_3$	Water
1. Physical nature	Liquid	Liquid	Liquid	Liquid
2. Density (g/cm^3)	1.655	1.667	1.675	1.0
3. Boiling point (°C)	76.1	78.0	105.3	100
4. Melting point (°C)	−104.4	−53.8	1.5	0
5. Viscosity (cP)	0.6	0.92	1.11	1.0
6. Dielectric constant	9.05	10.0	13.9	80.0
7. Conductivity (ohm^{-1} cm^{-1})	2×10^{-6}	3×10^{-6}	2×10^{-8}	0.8×10^{-6}
8. Li−Depolariser (cell voltage) V	3.65	3.90	3.10	2.20
9. Theoretical energy density (W h/kg)	1 540	−	1 540	2 200

Cathode

Different varieties of carbon [8] are used to construct the cathode on a nickel matrix which acts as the current collector. According to the literature [7, 9] colloidal Teflon is used as the binding material for fabricating the carbon electrode. The composition of the paste is given as: carbon; 81% by weight; Teflon binder; 19% by weight.

The paste is spread over an expanded nickel grid. It is then pressed against two stainless steel plates. The pressed electrode is dried under vacuum at a temperature of 110 °C. Reported literature reveals that the cathode of the commercial D size cell has dimensions of 20 × 1.5 × 0.19 in., and that of the AA size cell 2 × 1 × 0.03 in. [10]. Although Teflon is commonly used as a binder for the cathode construction, polyethylene, paper pulp, etc., are also used as binding materials [7 - 9]. The performance of the battery is significantly affected by the quantity and the nature of the binder [11].

Separators

Different types of separator are made use of in the construction of the lithium–thionyl chloride battery. They are generally of nonwoven glass sheet [10, 11], nonwoven rayon [9], glass filter paper [9] or porous polyethylene sheet [2].

Electrolyte

The complex electrolyte, lithium chloroaluminate, or lithium aluminium chloride, is used in the lithium–thionyl chloride battery. The preparation of this compound was first reported by Kendall [12] in 1923. It is prepared by mixing equimolecular proportions of anhydrous lithium chloride and aluminium chloride in a mortar and the pulverised sample is kept at a temperature of 180 °C, under a helium [13] argon [14] or nitrogen [15] atmosphere. During the preparation of this compound, a small quantity of aluminium metal is formed as an impurity [16]. This can be removed from the electrolyte by skimming, since aluminium is insoluble in molten lithium aluminium chloride.

Lithium aluminium chloride can also be prepared by other methods. In one of these [9], dry lithium chloride and aluminium chloride are mixed together in equimolecular quantities and the mixture is heated at 100 °C for 4 - 5 h under dry hydrogen chloride gas. In order to overcome the tedious methods of preparation of lithium aluminium chloride, Auborn *et al.* [17] used equimolecular quantities of anhydrous lithium chloride and aluminium chloride dissolved in distilled thionyl chloride under a nitrogen atmosphere. Lithium aluminium chloride solution can be prepared by reacting aluminium chloride and lithium chloride in thionyl chloride solution, the excess of alu-

minium chloride is precipitated with a quaternary ammonium salt and the precipitate is filtered from the solution [18].

Recent X-ray examinations have not revealed the structure of the compound [13], and a comparison of the crystal structure of lithium aluminium chloride shows that it is not isomorphous with other known alkali aluminium chlorides [7, 19]. Weppner *et al.* [13] studied the conductivity of lithium aluminium chloride over a temperature range of 25 - 200 °C. Its conductivity at 25 °C was found to be 1×10^{-6} ohm^{-1} cm^{-1} [17], and at 174 °C, 0.35×10^{-6} ohm^{-1} cm^{-1} [20]. The phase diagram of this compound has been studied in detail [12, 19, 21], and it was shown that lithium aluminium chloride is in the ternary phase of lithium chloride and aluminium chloride.

Campanella *et al.* [22] have reported on the method of preparation of anhydrous electrolytes in anhydrous solvents. Lithium aluminium chloride solution can be prepared by dissolving known quantities of the electrolyte in anhydrous thionyl chloride under an inert, dry atmosphere using nitrogen gas. The conductivity of this compound in thionyl chloride is reported as [11, 23]:

σ LiAlCl$_4$ = 2.04×10^{-2} ohm^{-1} cm^{-1} at 1.73M;

σ LiAlCl$_4$ = 7.8×10^{-3} ohm^{-1} cm^{-1} at 0.9M.

The highest solubility of lithium aluminium chloride in thionyl chloride is 4.5M at 25 °C. Traces of water in the solution can be revealed using infrared spectra [24]. The conductivity of lithium chloroaluminate is reasonably satisfactory for a practicable battery. In nonaqueous solutions, the solubility of inorganic electrolytes largely depends on the size of the anion. The larger the size of the anion the greater will be the solubility of the electrolyte. The reason for the conductivity of lithium aluminium chloride in thionyl chloride is attributed to the reaction between thionyl chloride and aluminium chloride and, thereby, the formation of associate pairs. These associated pairs dissociate and the process of dissociation is accelerated in the presence of lithium chloride.

Cell

Three sizes of lithium–thionyl chloride batteries, *viz.*, AA, C, and D sizes, are being commercialised. These cells are designed to discharge at low- and high rates. The "bobbin" type [17] cells are designed to discharge at low rates and the "spiral" or "wound" or "jelly roll" type [17] at high rates. The spiral type is a high-power-density battery, and the bobbin type is a high-energy-density battery. The lithium anode is separated from the cathode by a suitable separator and the insulation of the electrodes is provided by Teflon. The electrolyte is carefully introduced into a nickel-coated iron can under a dry, inert atmosphere and the can is then sealed under vacuum using glass as a sealing material. In order to reduce the explosion hazards, specially designed vents are used. The performance characteristics of these cells are given in

TABLE 2

Discharge characteristics of C [28] and D [7] size cells

Temperature (°C)	C cell			D cell		
	Energy density (W h/kg)			Energy density (W h/kg)		
	100 mA	1 A	3 A	100 mA	1 A	3 A
25	356.4	316.8	262.2	387.2	308.0	220.0
−30	299.2	233.2	–	220.0	88.0	–
−55	–	–	–	187.0	–	–

Table 2. Designs for the lithium–thionyl chloride batteries are discussed by Marincic [25 - 27].

Commercial AA, C, and D size batteries [7, 17, 28 - 30] were discharged at different rates and temperatures. Typical discharge characteristics of C [28] and D [7] size cells at various discharge rates and temperatures are given in Tables 2 and 3.

Comparison of the lithium–thionyl chloride cell with other primary cells

It is worthwhile to compare the lithium–thionyl chloride cell with other well known primary cells such as the zinc–carbon cell, the Mallory cell, etc. Table 3 gives the available data from the literature [31, 32] and from these, it is clear that the lithium–thionyl chloride battery is superior to many of the existing aqueous primary cells, especially from the point of view of energy density, shelf life, and low-temperature performance.

Explosion hazard

Dey [7, 33] discovered that the lithium–thionyl chloride cell tended to explode on accidental short circuiting, heating or over-discharge. It was observed that after 28.5 min of discharge at the 10 A rate the cell voltage dipped to a very low level. At that point the current was turned off and, after a lapse of 1.5 min, the cell exploded. It was also noted that when the cells were shorted, explosion occurred, in spite of the operational vents which were designed to open at 500 - 550 psig (3·4 - 3·8 MP). In order to understand and avoid the cause of this phenomenon, two possibilities were explored.

The first approach was to use a vent which opened at very low pressures and allowed the electrolyte to escape prior to thermal runaway. When the cells containing electrolyte were shorted, the temperature of the cells initially increased and consequently the electrolyte began to escape from the cells. No explosions were noticed. The pressures developed inside the cells were between 100 and 130 psig (0·7 - 0·9 MP).

TABLE 3

Comparison of the lithium–thionyl chloride cell with other (aqueous) primary cells [31, 32]

Properties	Lithium–thionyl chloride	Zinc–carbon	Mallory Zn–HgO	Alkaline Zn–MnO$_2$	Magnesium cell	Silver oxide–zinc
O.C.V.	3.65 V	1.5 V	1.35 V	1.5 V	1.8 V	1.85 V
Efficiency at −28.5 °C	85%	0%	0%	3%	23%	50%
Efficiency at −6.6 °C	96%	5%	3%	15%	58%	70%
Energy density (W h/kg)	209.0	42.9	88.0	57.2	58.0	110.0
Shelf life (Years)	10	1 - 2	3 - 4	2 - 3	5 - 7	1 approx.

However, when the cells with low pressure vents were discharged at low rates, explosion occurred. It was also noted that the low pressure vents did not prevent the explosion of the cells on over discharge.

The second approach to alleviate the explosion hazard was to reduce the rate capability of the cell by reducing the size of the electrode. It was expected that this method of approach would reduce the heating effect of the cell when shorted. With the D size cell, evaluation was made with 7 and 11.5 in. long lithium anodes. The cells were fabricated with vents to withstand 500 psig (3·4 MP) pressure. It was noted that the cell with the 11.5 in. lithium anode exploded when short-circuited at room temperature. The cell with the 7 in. lithium anode did not explode at room temperature. However, at the storage temperature of 72 °C, the 7 in. lithium electrode cell exploded when short-circuited. Hence, from these experiments, it was concluded that cell explosions could not be prevented under all circumstances by decreasing the rate capabilities.

Cost comparison

Since lithium cells are a new addition to the available energy sources, it is of interest to know their cost. It is difficult to compare the cost of the lithium cells with existing alkaline cells because of the differences in cell manufacture processes. We can, however, compare to some extent the cost of the active materials for each type of cell. Table 4 [34] gives an approximate comparison between three alkaline cells and lithium cells.

It can be seen from the Table that the cost per ampere hour is less for the lithium cell than for the alkaline cells, except for the zinc−manganese dioxide cell. Even though the cost of the materials is less for lithium cells, the sophistication of the manufacturing technology may result in a higher cost. Here, one should note the following advantages of the lithium cells [35] : (a) more payload may be possible with lithium cells due to their smaller size and light weight; (b) greater shelf life; (c) good sub-zero temperature performance; (d) lower maintenance cost associated with battery replacements, especially in remote areas or in applications where replacement of the cell is a laborious process. Considering the above advantages, we may conclude that the cost of the cells may be comparable with other alkaline cells.

Uses

Future prospects for lithium batteries are exceedingly bright. Lithium batteries find applications in military and civilian equipment [31, 36, 37].

TABLE 4

Comparison of the cost of the lithium–thionyl chloride cell with other primary cells component-wise [34]

Components used	Cell system			
	Zinc–manganese dioxide cost (cents/A h)	Zinc–mercuric oxide cost (cents/A h)	Zinc–silver oxide cost (cents/A h)	Lithium–thionyl chloride cost (cents/A h)
Zinc	0.113	0.113	0.113	–
Mercury	0.128	0.128	0.128	–
Potassium hydroxide	0.085	0.060	0.060	–
Carbon	0.042	0.053	–	0.043
Zinc oxide	0.008	0.006	0.006	–
Manganese dioxide	0.177	–	–	–
Mercuric oxide	–	9.548	–	–
Silver oxide	–	–	45.23	–
Lithium	–	–	–	0.583
Thionyl chloride	–	–	–	0.118
Aluminium chloride	–	–	–	0.023
Lithium chloride	–	–	–	0.047
Total components cost	0.553	9.908	45.537	0.814
Total cost of the components per W h	0.369	7.339	30.358	0.226

Acknowledgement

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