

LITHIUM METAL FOR THE BATTERY INDUSTRY

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Summary

The sources of lithium are detailed. Proven reserves indicate that the lithium industry can accommodate anticipated growth in demand for many years to come. The methods of lithium recovery leading to the production of a variety of chemical compounds and metal are described, as are metal forming operations. Processing of lithium metal in dry rooms, its packaging and shipping, and general safety considerations are included.

1. Introduction

The next major application for lithium metal and some lithium compounds is expected to be in batteries. There has been more promise than realization of this new market through 1978. However, the lithium producing industry does give serious consideration to the requirements of the battery industry in the approaching decade and later.

The overall demand for lithium in all its forms is not large, approximately 4000 tonnes, expressed as lithium metal, having been consumed in the non-Communist world in 1978. It has been speculated that some time after the turn of the century there will be an enormous upsurge in the demand for lithium. Such a prediction is based on its large-scale use in secondary batteries for load levelling and electric vehicles, and in nuclear fusion reactors. Until then, a more realistic growth rate of 5 to 10% annually would seem to be reasonable.

Most battery companies throughout the world are involved in the development of cells with a lithium negative electrode or are carefully following the literature on the subject. It is the intent of this article to provide background information about lithium that may be useful to the battery industry.

2. Occurrence

Trace quantities of lithium are found in rocks, clays, and waters throughout the world. Pegmatites and brines are the commercial sources of lithium now, and will probably remain so in the future.

Granitic pegmatites normally contain feldspars, quartz, and mica in addition to lithium minerals. Spodumene, petalite, and lepidolite are lithium aluminosilicate minerals that most often have provided the source of lithium for chemical operations. Spodumene from Kings Mountain, North Carolina has been the principal mineral source for lithium in the United States, especially since sanctions were imposed on Rhodesia in 1967. It is mined and processed by both Foote Mineral Company and Lithium Corporation of America in the tin-spodumene belt near Charlotte, North Carolina.

Complex lithium-containing brines in Clayton Valley, Nevada are concentrated by solar evaporation and processed to yield lithium on a commercial scale, also. The Foote Mineral Company facility at Silver Peak, Nevada is the third source of lithium in the United States.

These sources in the continental United States supply most of the lithium to the non-Communist countries of the world. Other potential sources in the Americas are being evaluated with regard to commercial exploitation. By far the largest is the brine region of the Salar de Atacama, Chile. A feasibility study by Foote Mineral Company is in progress. The spodumene pegmatites at Bernic Lake, Manitoba are also a potential commercial source of lithium. The Tantalum Mining Corporation now mines tantalite ore at this property and it is expected that a decision will be made in the future concerning the mining of the lithium resources. Economic recovery of lithium from brines of the Great Salt Lake, Utah will depend on the successful prior removal of magnesium.

3. Reserves and resources

Widely divergent opinions concerning lithium resources have surfaced recently. The opposite poles are represented by the U.S. Geological Survey and the lithium industry. Meanwhile, the Energy Research and Development Administration (now the Department of Energy) requested the National Academies of Sciences and Engineering to report on the role of nuclear power as an alternative energy source from 1985 to 2010. Availability of raw materials was one consideration and, accordingly, the Energy Resource Group formed a Lithium Sub-Panel including industry, government, and private consultant authorities to study the problem. The 1977 estimates of the Lithium Sub-Panel included the principal districts in the non-Communist world that have produced lithium in the past, are currently in production, or are presently being evaluated as potential lithium sources. The Sub-Panel's conclusions, reported by Evans [1], appear in Table 1.

The Lithium Sub-Panel also considered the future demand for lithium in "conventional" applications, that is, excluding secondary batteries and fusion reactors. Evans' [1] numbers show the actual usage in 1975 of 3156 tonnes growing to 5630 tonnes in 1985 and approximately 10000 tonnes in the year 2000.

TABLE 1

District	Location	Deposit	Feed to beneficiation and process (% Li)	Tonnes Li*	Inferred resources	
					Proved and indicated reserves	Inferred resources
Tin-Spodumene Belt	North Carolina	Pegmatite	0.68	376400		2773000
Clayton Valley	Nevada	Brine	0.02	40500		77300
Bikita Minerals	Rhodesia	Pegmatite	1.4	56800		56700
Preissac-Lacorne	Quebec	Pegmatite	0.58	63100		46400
Bernic Lake	Manitoba	Pegmatite	1.38	46600		-
Great Salt Lake	Utah	Brine	0.0035	260000**		-
Searles Lake	California	Brine	0.005	23700**		
Salar de Atacama	Chile	Brine	0.135	1290000		3000000
Manono-Kitolo	Zaire	Pegmatite	0.6	540000		1800000
Government stockpile	U.S.			6100		

*This is feed to beneficiation and process. Recovery figures downstream are proprietary.

**Economic lithium extraction is dependent on marketing of co-products.

4. Beneficiation and chemical processing

(A) The selectively mined *North Carolina pegmatites* have the average composition given in Table 2 according to Kesler [2].

TABLE 2

Mineral	%
Feldspar	41
Quartz	32
Spodumene	20
Muscovite	6
Other	1

After crushing and grinding the pegmatite, the mineral spodumene, $\text{Li}_2\text{O} \cdot \text{Al}_2\text{O}_3 \cdot 4\text{SiO}_2$, is separated with reasonable efficiency by froth flotation. This increases the lithium content from 0.65 - 0.70% to 2.7 - 3.2% in the spodumene concentrate, and yields "Sandspar"[®] (feldspars and quartz) and mica as co-products.

Naturally occurring monoclinic α -spodumene undergoes an irreversible lattice expansion to tetragonal β -spodumene when roasted to approximately 1100 °C. β -spodumene is susceptible to either acid or base attack whereby lithium values are made water soluble. α -Spodumene is quite refractory to chemical attack.

Both lithium producers roast β -spodumene with excess sulfuric acid. The calcine is leached with water, giving a solution of lithium sulfate. After pH adjustment, purification, and evaporation, the slightly soluble lithium carbonate is precipitated by addition of sodium carbonate. Some spodumene concentrates are sold directly to the ceramics, porcelain, and glass industries; but lithium carbonate is the first chemical compound produced. Sodium sulfate is a co-product.

(B) The *Clayton Valley brines* at Silver Peak, Nevada are pumped from wells 250 - 500 feet deep and subsequently concentrated by solar evaporation. Some 40 - 50 wells are employed. More than 3000 acres of ponds are required to produce a headfeed of suitable strength and purity for the subsequent chemical plant and recovery operation.

The brine is essentially a sodium chloride system with minor amounts of other elements present, as shown in Table 3 [3]. Salts composed of sodium, potassium, chloride, and sulfate ions reach saturation in sequence in the ponds as evaporation continues. Net evaporation amounts to 30 - 37 inches per year. A typical analysis of the final rich brine also appears in Table 3. The rich brine is precipitated with sodium carbonate to yield lithium carbonate.

(C) *Chemical processing and commercial utilization*

Lithium carbonate in addition to being the first out product manufactured from pegmatites and brines is the dominant item of lithium sales. The

TABLE 3

	Well brine	Rich brine
	(wt.%)	(wt.%)
Na	6.2	7.8
K	0.8	4.8
Mg	0.04	0.007
Li	0.04	0.50
Ca	0.05	0.004
SO ₄	0.71	2.9
Cl	10.1	16.1

biggest market is to the aluminum industry where its use in electrolysis cells lowers the temperature of the bath. This, in turn, improves operating efficiency and reduces fluoride emissions. It is also used extensively in ceramics, glasses, glazes, and enamels, because of its near zero coefficient of thermal expansion. A higher purity grade of lithium carbonate is increasingly prescribed in the treatment of manic-depressive psychosis [4].

Lithium hydroxide solution results from the reaction of aqueous calcium hydroxide with lithium carbonate. Crystallization of the solution gives lithium hydroxide monohydrate which is the starting material for many other lithium compounds. There are also major sales to the grease industry where its reaction with fatty acids produces a water insoluble lithium soap. Mixed with mineral oil, the resulting lithium-based greases have the advantage of retaining viscosity at both high and low temperatures and being water resistant. The great capacity for absorbing carbon dioxide shown by anhydrous and monohydrate lithium hydroxide is used on a small scale in a variety of life support situations.

Butyllithium is produced by the reaction of lithium metal dispersion with butyl chloride in an organic solvent. It is used to initiate anionic polymerization of butadiene, isoprene, and butadiene-styrene mixtures.

Lithium bromide results from the reaction of lithium carbonate with bromine in the presence of a reducing agent. Most bromide is sold as a strong brine for use in absorption type air conditioners.

The reaction of lithium carbonate or hydroxide with hydrochloric acid yields a solution of lithium chloride. Some chloride brine is used by the air conditioning industry, but the anhydrous salt is sold in much larger quantities. In a mixture with other salts, it is used as a brazing flux and as the head feed for lithium metal production.

5. Metal production

Lithium metal is produced by the electrolysis of the fused salt eutectic of lithium chloride and potassium chloride, approximately 55% LiCl and

45% KCl. The eutectic melts at 352 °C, lithium chloride melts at 613 °C; therefore, a considerable operating advantage is gained by the use of the eutectic. In the eutectic electrolyte, the electrode potential for the reduction of potassium is greater than for lithium; thus, the potassium content of lithium metal is low, less than 100 ppm. On the other hand, sodium in lithium chloride electrodeposits quantitatively into lithium metal during electrolysis.

Two basic types of electrolysis cells are used for lithium reduction: modified Down cells similar to those used in the manufacture of sodium metal, and open, air-swept cells. In the former, bottom return graphite anodes are separated from steel cathodes by a diaphragm in cells lined with ceramic bricks. The low density of molten lithium metal formed at the cathode permits its removal through riser pipes to a holding tank. Chlorine gas formed at the anode is collected and compressed.

Molten lithium rises to the surface of the electrolyte bath in air-swept cells. It is removed by ladling to holding tanks for cooling and cell salt separation. Chlorine gas swept from the cell can be scrubbed from its mixture with air by caustic lithia solutions to generate lithium hypochlorite, a commercial product. Air-swept cells employ several steel cathodes surrounding a graphite anode. No separator is used. Ignition of metal, especially if sodium content and humidity are high, can occur on the surface of air-swept cells. Recombination of lithium and chlorine is significantly greater in air-swept cells, also. These factors result in lower net current efficiencies than for the Downs-type cell.

Anhydrous lithium chloride is added periodically to both types of cells to maintain the approximate composition of the eutectic. Little makeup of potassium chloride is required. Water and other oxygen-containing compounds present in lithium chloride are harmful because oxygen released at the anode reacts with the graphite. This results in increased electrode separation and associated increase in cell voltage and decrease in current efficiency. Heavy metals are generally not contaminants in significant quantities in lithium chloride and, therefore, create few problems.

Stoichiometrically, more than six pounds of lithium chloride are required to produce one pound of metal. This 6 to 1 ratio of lithium chloride to lithium metal, and the quantitative recovery of sodium during electrolysis, means that the sodium content of lithium chloride is important. Thus, 50 ppm of sodium in lithium chloride yields metal with more than 300 ppm sodium.

Two grades of metal are produced commercially. The Standard Grade contains 1 200 - 8 000 ppm sodium, and the Battery Grade contains less than 500 ppm sodium. The reactivity of the Standard Grade with gases of the atmosphere is noticeably greater than that of the Battery Grade metal, presumably because of the greater sodium content.

6. Metal forming

Lithium metal at room temperature is very ductile and malleable. It is harder than the other alkali metals, but softer than lead. In principle, it is

easy to form into shapes by extrusion, rolling or punching. Many sizes of lithium foil, rod, billet, cylinders, and wire have been produced, as well as anodes of regular and complex shape. Forming of this soft metal is complicated by its tendency to stick to itself and other materials under relatively slight pressure.

Initial experience in forming lithium in air showed the need for maintaining humidity at a low level. Commercially available dry rooms that do not exceed 2% relative humidity at 21 °C are recommended. Lithium processed in such an atmosphere shows no visible tarnishing for a number of hours.

Dehumidification of dry rooms is accomplished with alumina, silica gel, lithium chloride, or molecular sieves. The latter probably has the capability of providing the lowest absolute humidity in commercially available dry rooms, but it is the most costly. An attractive feature of one of the systems based on lithium chloride is the relatively flat humidity profile that is obtained because of continuous regeneration of this dehumidifying agent.

Careful attention must be given to the design of the air handling systems in dry rooms in order to achieve uniform circulation of air and the avoidance of drafts. This is necessary for personnel comfort and because of the low density of thin lithium pieces. It is also suggested that dry rooms be designed to include windows to avoid claustrophobic effects.

There are no apparent long-term detrimental effects associated with continual working in a dry room. In one case, an employee did suffer from irritation of the eyes because of the dry conditions. Administering of eye drops, a commercial product, twice daily solved this problem. No other incident involving personal discomfort is known, although it is possible that personnel with a very dry skin condition might be adversely affected.

Forming of lithium by extrusion is conventionally achieved with a horizontal press. Assuming appropriate die design, the principal problems encountered in extrusion relate to the presence of lithium nitride and the extremely low strength of lithium metal. The tensile strength of lithium is in the range of 0.41 - 0.55 MPa (60 - 80 p.s.i.). Care must be taken to avoid tearing thin lithium foil during processing. The thinnest lithium foil produced is made by rolling techniques. The percentage reduction per pass through the rolling mill is limited by the stickiness of lithium.

The characteristic of lithium to self-weld and to stick to other materials at ambient temperature under slight pressure complicates rolling, punching, and slicing operations. Generally, the tendency for lithium to stick to synthetic plastic materials is less than it is to metals, even when the metal has been given an ultra-smooth surface finish.

The width tolerance of lithium foil is ± 0.5 mm (± 0.020 in.) of nominal. Thickness tolerances vary with the nominal thickness. Rolled foil, 0.13 mm (0.005 in.) thick, is generally guaranteed to $\pm 15\%$ of nominal, while a tolerance of ± 0.025 mm (± 0.001 in.) is guaranteed for foil in the range of 0.2 to 0.48 mm (0.008 - 0.019 in.) thick. With thicker foil, wider variation from nominal is permitted, reaching ± 0.05 mm (± 0.002 in.) for foil in the range of 1.27 to 3.05 mm (0.050 - 0.120 in.) thick. A weight specification is often

imposed on punched anodes; thus, anodes weighing approximately 0.5 g have a tolerance of ± 0.01 g.

It is difficult to quantify surface quality of lithium shapes. Many users state that "the lithium must be bright and shiny". However, rolled lithium has much more of a gloss than extruded lithium. Whether slight surface oxidation is harmful is a moot point. Occasionally, heat temper marks appear as a light pastel patina of various colors but cells made from such lithium have shown no difference in initial performance or after prolonged storage. Because of the relatively high price of lithium, the user in large-scale production will eventually have to determine the extent to which minor surface oxidation is detrimental to cell quality, if at all.

7. Packaging and shipping

Most lithium foil is packaged under dried argon in hermetically sealed cans, although some users prefer a coating of white mineral oil in addition. The degree of hermeticity of the cans is a variable, and efforts continue in an attempt to improve can hermeticity. Bulk shipments of lithium ingot coated with light mineral oil or kerosene are packed in 30-gallon steel drums approved by the Department of Transportation (DOT). Ingots shipped under argon usually arrive with surface conditions that are less satisfactory than those with the hydrocarbon coating. Lithium packaged as above in approved DOT containers may be shipped by common carrier, air freight (cargo planes only), or as deck cargo. A further limitation of 25 pounds of lithium per package in air freight shipments is imposed. Placards noting that the cargo is a flammable metal that reacts violently with water are required.

8. Safety considerations

Lithium is a reactive metal that deserves treatment with respect; however, its use in the dry rooms of the battery industry for many man years, with adherence to minimal precautions, has shown that it can be handled safely.

Water as liquid or vapor creates the majority of safety incidents with lithium. Generation of hydrogen with the possibility of its subsequent explosive ignition when lithium floats on water is well known. Under these conditions, lithium is much less reactive than sodium. Its higher melting point, 180.6 °C, lessens the tendency to form molten lithium with greater reactivity. In fact, disposal of small quantities of compacted lithium by keeping it submerged well below the surface of water is feasible. This technique has the added advantage of dissolving the decomposition product, lithium hydroxide, before it can become an air-borne aerosol.

Water vapor catalyzes the exothermic reaction of lithium with atmospheric gases. It can be shown that a bundle of lithium trimmings with large

surface area can undergo spontaneous combustion under conditions of high humidity if the heat of reaction is not dissipated.

Lithium metal in the dry room should be stored over-night or over weekends in sealed containers or under oil. This precaution is taken against the event of failure of the dehumidification equipment due to power outages, etc. It is recommended that dry rooms be provided with a thermal alarm system activated by a rapid rise in temperature.

Lithium fires are difficult to extinguish. Proprietary fire extinguishers based on graphite powder treated with surfactant offer the best chance of smothering such fires. Conventional fire extinguishers that contain reducible materials should not be used.

Severe caustic burns can result from particles of lithium metal on human skin. First aid treatment should include immediate removal of the particle followed by flooding the affected area with water for approximately 10 minutes. The lithium ion is not particularly toxic, as evidenced by its use in the form of lithium carbonate for the treatment of manic depression.

Conclusions

Known lithium reserves currently being exploited or being developed assure the battery industry of a continuing supply of lithium products for many years. Techniques for forming the metal into a variety of shapes have been developed to satisfy a multitude of anode requirements. Fabrication of lithium metal in controlled humidity rooms is a necessity to assure quality. Several years of experience with dry room operations and with attention to reasonable precautions have shown that lithium can be processed safely.

References

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