Lithium

Overview

Toward New Technologies for the Production of Lithium

Georges J. Kipouros and Donald R. Sadoway

The lightest of all metals, lithium is used in a variety of applications, including the production of organolithium compounds, as an alloying addition to aluminum and magnesium, and as the anode in rechargeable lithium ion batteries. All of the world's primary lithium is produced by molten salt electrolysis. This article reviews the current technology for lithium extraction and assesses the prospects for change.

INTRODUCTION

With a density about half that of water, lithium (from the Greek "lithos," which means "stone") boasts the lowest density of all solids, a mere 0.53 g/cm^3 at 20°C. Its electronic configuration is $1s^2 2s^1$; its atomic number is 3; and its atomic mass is 6.941 g/mol. Typical of alkali metals, lithium's crystal structure is body-centered cubic. The element reacts with water (and moisture in the air) to produce the hydroxide, LiOH, and hydrogen gas. Unlike the heavier alkalis, lithium does not react violently with oxygen; indeed, the metal is stable in dry air when the dew point is maintained below -38°C.

Lithium is not a structural metal; in the majority of its applications, it functions as a chemical reagent. Table I compares the properties of lithium with those of steel and aluminum, the dominant structural metals, and with those of magnesium and titanium, both considered too pricey for mainstream structural applications.1 Table II reports world production figures for these five metals.2-4 Even though the world production of lithium amounts to only 12,500 tonnes per year, the high unit price of the metal translates into annual sales of approximately \$1 billion and, thus, puts the value of the world lithium industry at par with that of titanium and magnesium. Harben and Edwards have reported upon trends in the global lithium industry, which they characterize as being in a state of rapid flux.5 Lithium shares with magne-

Table II. Metals Production and Pricing Statistics						
	Fe	Al	Mg	Ti	Li	
Production (t/y, 10 ⁶)	752	21	0.35	0.0525	0.0125	
Price (\$/kg)	0.45	1.50	3.96	19.82	89.43	
Sales (\$, 109)	338	31.5	1.39	1.04	1.12	

sium the imminent possibility that its market distribution may be radically altered by rapid growth in one application: automotive die casting in the case of magnesium and anodes for rechargeable batteries in the case of lithium. It is curious that in the present lithium-ion

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battery,⁶ we find compounds of lithium and cobalt, two of the four metals (the other two are gold and magnesium) for which prices have risen over the past 30 years (after adjustments for inflation).⁷ In response, considerable effort is being directed at displacing cobalt-bearing compounds.⁸

Is there a scientific basis for metal

	Table I. Properties of Selected Metals					
	Fe	Al	Mg	Ti	Li	
Melting Point (°C)	1,535	660	650	1,660	180	
Boiling Point (°C)	2,860	2,518	1,093	3,287	1,347	
Density (g/cm ³)	7.87	2.70	1.74	4.54	0.53	
E (GPa)	211	71	45	120	5	

prices? Table III shows that aluminum is more abundant in the earth's crust than either iron or magnesium, yet steel is, by far, the cheapest metal.9 So relative abundance does not explain pricing. However, there is some correspondence between the prices of steel and aluminum and the free energies of formation of their oxides.¹⁰ Magnesium, titanium, and lithium do not fit this pattern, largely due to the much smaller tonnages involved. As tonnages rise, making more efficient use of capital, prices of these latter three metals can be expected to fall. Nicholson's review of the pricing history of lithium shows that from 1964 to 1996, the price of this metal rose 23 percent in constant dollars.7 However, the effects of the drop in price of lithium carbonate in South America and the growing demand for lithium in rechargeable batteries have yet to be felt by the market.

LITHIUM METALLURGY

With regard to the metallurgy of lithium,^{11–14} the metal is found in nature as hard rock ore and as brine. The strategy for reducing these resources to metal involves conversion to carbonate, then to chloride, followed by molten salt electrolysis. Spodumene (LiAlSi₂O₆) is one example of a hard rock resource. Conversion to carbonate involves either alkaline fusion and carbonation or acid roasting, calcination, and carbonation. The double salt KLiSO₄ is one example of a brine resource. Conversion to carbonate involves purification (removal of potassium) and precipitation. Potential methods to win lithium from pegmatites, natural brines, and clays have been discussed.15-17 The carbonate is then converted to the chloride with the action of a chlorinating agent such as hydrogen chloride. Table IV gives the salient features of the electrolytic reduction process. The cell has a central cathode of mild steel on which lithium is produced in liquid form. Opposing graphite plates

serve as the anodes on which chlorine evolves. A bell-shaped structure positioned above the cathode collects the rising liquid metal and prevents it from reacting with the chlorine gas which also rises. Anhydrous lithium chloride is the cell feed. Potassium chloride is the solvent and supporting electrolyte because it alone, among the common alkali and alkaline-earth chlorides, has a decomposition potential that is more extreme than that of lithium chloride. Put another way, electrolysis of a melt comprising LiCl-NaCl will produce lithium metal containing a substantial amount of sodium, which is highly undesirable if lithium is to be used in battery applications. The electrolysis temperature is governed by the physical chemistry of the molten salt. The eutectic point of LiCl-KCl is 350°C and 42 mole percent KCl.¹⁸At 400°C, the liquid range extends from about 35-45 mole percent KCl. At this temperature lithium metal is molten, but its vapor pressure is acceptably low. Operational data for the electrolysis cells may be found elsewhere in the literature.14

What are the challenges and opportunities for lithium extraction? Certainly, there is the need for new electrode materials. Avoiding the use of carbon would make the process environmentally friendlier and might even enable the design of a long-lived bipolar cell. One of the authors has enunciated criteria for the selection of materials that can serve as inert anodes in Hall-Héroult cells producing aluminum.19 Metal alloys consisting of a base metal (or metals) plus aluminum have been identified as the most promising materials.20 Perhaps it is time to apply these concepts to lithium electrolysis. Installing cathodes made of a material that is wetted by molten lithium would afford new opportunities in cell design. In aluminum reduction cells, the material showing the most promise is titanium diboride, which has graduated from laboratory testing to installation in industrial cells for long-term performance assessment.²¹ There is also a need for a new process for preparing anhydrous lithium chloride in a manner that is energy efficient and gives a product of high purity. Alternatively, new electrolyte chemistries that do not require conversion to chloride might prove to be attractive. For example, lithium metal has reportedly been produced as

Table IV. The Electrolytic Production of Lithium				
Electrolyte	LiCl-KCl eutectic			
Feed	LiCl			
Femperature	400-460°C			
Anode	Carbon			
Cathode	Mild Steel			
Overall Cell Reaction	LiCl (l) \rightarrow Li (l) + 1/2 Cl ₂ (g) for which $E^{\circ}_{427^{\circ}C} = 3.6 \text{ V}$			
Anode	$\text{Cl}^- \rightarrow 1/2 \text{Cl}_2(\text{g}) + \text{e}^-$			
Cathode	$Li^+ + e^- \rightarrow Li(l)$			
Current Density	2 A/cm^2			
Energy Consumption	35 kWh/kg			

Table V. Reactions for the Production of Lithium by Thermochemical Reduction

Carbothermic Reduction $\text{Li}_2\text{O} + \text{C} \rightarrow 2 \text{ Li} (g) + \text{CO} (\text{lithia feed, carbon reductant})$ 6 LiOH + 2 C \rightarrow 2 Li (g) + 2 Li₂CO₃ + 3 H₂ (LiOH feed, carbon reductant) 3 LiOH + FeC₂ \rightarrow 3 Li (g) + Fe + 3/2 H₂ + CO + CO₂ (LiOH feed, iron carbide reductant) Metallothermic Reduction of the Oxide $2 \text{ Li}_2\text{O} + 2 \text{ CaO} + \text{Si} \rightarrow 4 \text{ Li}(g) + \text{Ca}_2\text{SiO}_4 \text{ (c.f., Pidgeon process)}$ $3 \text{Li}_{2}\text{O} + 2 \text{Al} \rightarrow 6 \text{Li}(g) + \text{Al}_{2}\text{O}_{3}$ Metallothermic Reduction of the Hydroxide $2 \operatorname{LiOH} + 2 \operatorname{Mg} \rightarrow 2 \operatorname{Li}(g) + 2 \operatorname{MgO} + H_2$ 2 LiOH + Al \rightarrow Li (g) + $\overline{LiAlO_2}$ Electrolytic-Calciothermic Reduction of the Oxide Cathode $Ca^{\scriptscriptstyle 2+}+2 \; e^{\scriptscriptstyle -} \to Ca$ $Ca + Li_{2}O \rightarrow CaO + 2Li$ Anode $O^{2-} + 1/2 C \rightarrow 1/2 CO_2 + 2 e^{-1}$ or $O^{2-} \rightarrow 1/2 O_2 + 2 e^{-}$

an amalgam intermediate by the electrolysis of an aqueous solution of lithium hydroxide. Lithium metal is then produced by electrorefining the amalgam at 225°C in a cell containing an electrolyte of molten LiI-CsI eutectic.²²

PARADIGM SHIFTS

What about radical innovation (i.e., totally different reduction chemistry)? Here is a short list of candidates, none of which is in commercial use: electrolysis of carbonate feed, carbothermic reduction, metallothermic reduction, electrolytic-calciothermic reduction, and electrolysis of lithia from an oxide melt. Electrolysis of carbonate feed would eliminate the chlorination step. There are reports of laboratory-scale tests,23,24 and a patent has been granted.²⁵ Carbothermic reduction has been studied many times in the past with other metals such as aluminum and magnesium, but has never been shown to be a commercial success.^{26,27} However, in view of the much higher price of lithium, it may be possible to make carbothermic reduction economically viable. Table V shows three candidate reactions involving a variety

Table III. Properties of Selected Metals						
	Fe	Al	Mg	Ti	Li	
Price (\$/kg)	0.45	1.50	3.96	19.82	89.43	
Abundance						
Percent	4.1	8.2	2.3	0.56	0.002	
Rank	4	3	7	9	31	
Free Energies of Formation of the Oxides, M _x O _y						
kJ/mol O ₂	503	1,055	1,138	899	1,124	
kJ/g M	6.7	29	23	18	40	

of feedstocks and carbothermic reductants. Metallothermic reduction is also a possible route to metal. Also shown are reactions for the reduction of lithium oxide by silicon and aluminum. Some experimental data taken under Pidgeonlike conditions have been reported.28 Table V continues with reactions for the reduction of lithium hydroxide by magnesium and aluminum. Calcium can also reduce lithium oxide to metal. A novel concept that combines electrolysis and metallothermic reduction is given in the table as well. The process involves insitu generation of calcium from a bath of calcium oxide and calcium chloride into which one adds lithium oxide. At the cathode, the product of electrolysis is calcium metal, which chemically reduces lithia added to the bath. At the anode, one has the choice of either a consumable anode producing CO/CO₂ or a nonconsumable anode producing oxygen. The process can be viewed as calciothermic reduction of lithium oxide combined with the in-situ generation of the calcium reductant. Lastly, there is electrolysis of lithium oxide from an alloxide electrolyte. The concept is complete aversion of carbon and chlorine chemistries. Lithium oxide is broken directly into its constituent lithium and oxygen. Obviously, there are major technical obstacles to overcome. However, if it can be shown to be viable, the process would be environmentally sound and long-term sustainable.29 Ironically, electrolysis of the oxide was the method by which Davy and Brandé in 1818 produced the first lithium metal.

CONCLUSIONS

The demand for lithium metal and for new lithium compounds will continue to grow. Environmental concerns coupled with the shift in resource chemistries will provide incentives for the search for new extraction technology, which will predictably involve a new application of molten salt chemistry.

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