CHEMICAL ECONOMICS - LITHIUM

At this time there is considerable enthusiasm for innovative battery technology for both electric vehicles and for domestic solar power back-up. Central to this new technology are developments in rechargeable batteries using lithium of which there are many types and variants. Of particular interest are developments of the lithium/air battery which has as its basis the oxidation of lithium metal:

$$4Li^+ + 4e \text{ and } O_2 + 4e = 2O^{2-}$$

$$4Li + O_2 = 2Li_2O$$

The interest in batteries based on this reaction is because the theoretical energy density of the battery approaches that for conventional transport fuels (40.6MJ/kg compared to diesel at about 44MJ/kg) and the alibility of the battery to recovery full efficiency following deep discharge. The latter is problem for many other lithium based batteries and major issue with lead-acid batteries.

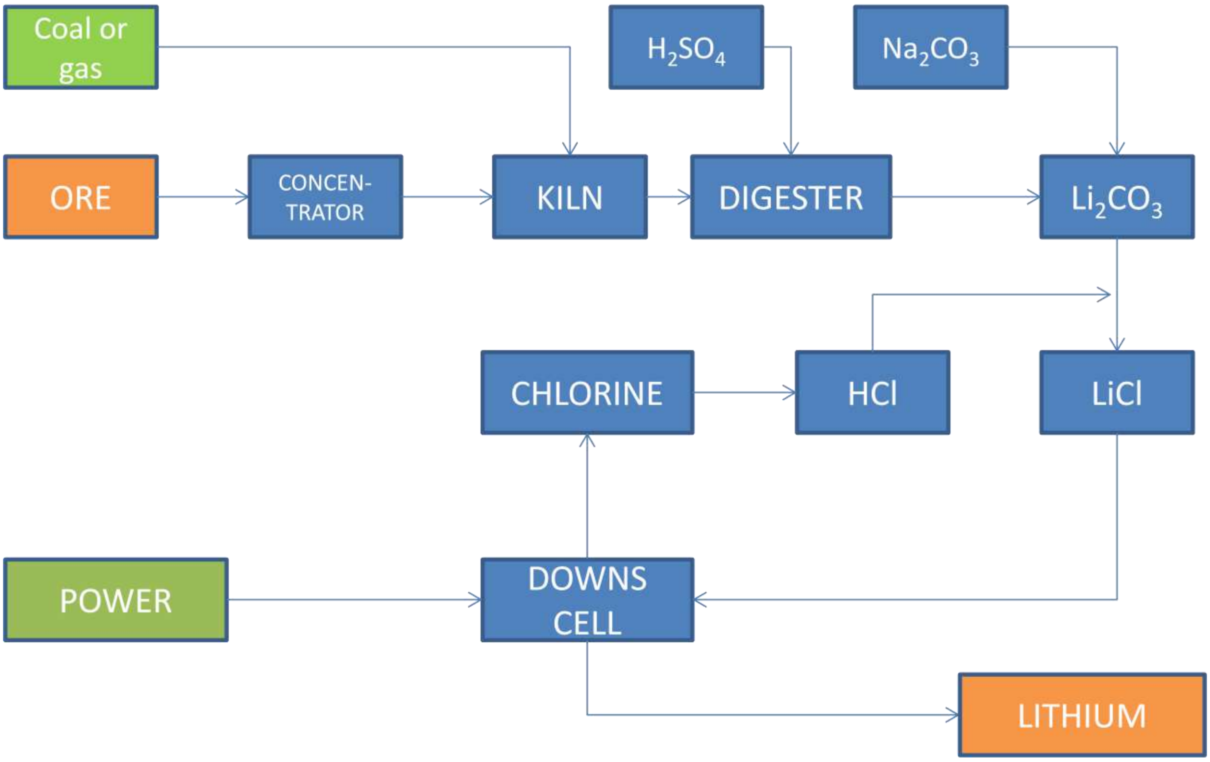
In practice the energy density will be less and current practice is far from this ideal, for example the battery pack in the Tesla car (which is a complex lithium ion battery) weighs approximately 400kg compared to a tank of conventional fuel at about 50kg.

Simply the lithium/air battery comprise a lithium metal anode and a graphene cathode. The cathode absorbs oxygen from the atmosphere which is converted into O^{2-} ions which diffuse through to a conductive layer separating the cathode and anode. Recharge is the reverse of the process. Of particular concern is that on re-charge build up of metallic bridges of lithium from the anode through the conducting layer can occur. This ultimately leads to an internal short circuit which can cause the battery to catch fire.

If solar power back-up is to take-off as is widely predicted by proponents of this technology, there will be a major demand for lithium batteries and hence lithium metal. Australia is a significant producer of lithium ores from the Talison Lithium mine at Greenbushes in WA and there are several prospects for new lithium mining ventures. These projects are in competition to extraction of lithium from brine lakes mainly in South America.

The steps in the production of lithium from ore is shown in Figure 1:

Figure 1: Process flow for production of lithium metal from spodumene ore



The principal ore for lithium production is *alpha*-spodumene which is a lithium aluminosilicate of empirical formula $LiAlSi_2O_6$; in its pure form it contains 8% lithium (as Li_2O) but most productive ore contains much less, typically 1.5 to 4.5% Li_2O. The first step is to concentrate the ore to about 90% spodumene by floation and gravity separation. Australian processing operations generally end here and the concentrate is exported.

Alpha-spodumene is very refractory and cannot be processed to extract the lithium. The *alpha*-spodumene is converted into the *beta* form which is less dense and from which the lithium can be extracted by sulphuric acid digestion. The transformation requires the *alpha*-spodumene to be heated to over 1100°C and is typically performed in a rotary kiln using coal or gas. The product is crushed in a ball-mill and after extraction with sulphuric acid the excess acid is neutralised with limestone. Then sodium carbonate (soda ash) is added to produce a lithium carbonate solution which is evaporated prior to the addition of more soda ash which precipitates the carbonate. This material is widely traded and competes with lithium carbonate produced from brine lakes.

Lithium metal is produced by electrolysis of a lithium chloride/potassium chloride eutectic at about 450°C. To perform this operation the lithium carbonate is converted into lithium chloride by the addition of hydrochloric acid. The lithium chloride is charged to the electrolysis cell (Downs Cell) where by-product chlorine is also produced. The chlorine can be traded for or converted into hydrochloric acid. The molten metal is extracted and cast into ingots. This process is very power intensive, typically 35 kWh/kg. The outline economics are shown in Table 1.

Table 1: Outline economics for the production of lithium metal from spodumene ore

Lithium carbonate production		US$/unit	US$/t lithium
Ore (t)	3.0% Li2O	70	$ 5,023.05
Kiln heat (GJ)	80.2 GJ/tLi	5	$ 401.20
Kiln & ball mill power (MWh)	1.1 MWh/tLi	70	$ 76.99
Sulphuric acid (inc allowance) (t)	7.77t/t Li	120	$ 931.99
Limestone (t)	0.72 t/t Li	30	$ 21.64
Soda Ash (t)	7.64 t/t Li	250	$ 1,909.22
Sub Total			$ 8,364.09
Capital costs			$ 2,509.23
Other Costs (15% Capex)			$ 376.38
Total			**$ 11,249.71**
Lithium carbonate		$2,113.51	
Lithium metal production			
Lithium Carbonate + allowance (t)	0.9139t/t LiCl		
LiCl (with HCl allowance) (t) (assumes Cl_2 and HCl have equivalent value)	6.42 t LiCl/t Li		$ 15,030.38
Power demand (MWh)	35.11 MWh/t Li	50	$ 1,755.67
			$ 16,786.05
Capital costs			$ 5,035.81
Other (15% Capex)			$ 755.37
Lithium Metal			**$ 22,577.23**

Starting with ore at a notional 3% Li_2O content, the cost of production of lithium carbonate is over $2,000/t which is equivalent to a lithium value of over $11,000/t. This production cost of lithium carbonate compares favourably with recent prices for this material which stand at over $5,000/t but may require further purification for battery grade product. Of note is the very high energy demand for this part of the process (80 GJ/t Li and 1.1MWh/t Li). This is mainly associated with calcining the ore to produce the *beta*-spodumene.

Transforming the carbonate to lithium chloride and producing the metal doubles the production cost to around $22,000/t which is also well below recent traded prices. But again further purification and metal casting may be required for the battery grade material.

Clearly producing the high valued metal is very energy intensive and increased production of lithium will be favoured by low energy prices. Since energy prices in Australia are no longer competitive with other parts of the world it is highly likely that Australia's role will remain as a provider of ore and concentrate to industrialised nations with low energy costs such as the USA, China and India.

Another point to note is that If we assume theoretical efficiency of the battery then at a notional power requirement of 20kWh/d for an average home, the lithium required for 1 weeks power supply as back-up would be 12.5kg. Allowing for efficiency losses and non-ideal operation, in practice the lithium required may be many times this amount. This is a significant amount of lithium metal to be carried by an ordinary household. As those of us who have experienced small laboratory fires involving a few grams of alkali or alkaline earth metals, the thought of a fire involving more than 12kg of metal is somewhat alarming. It should be noted that international airlines prohibit the transport of lithium batteries except under strict conditions because of the tendency to spontaneously ignite (due to internal shorting within the battery). Safety concerns about the widespread use of large lithium batteries in the household are largely ignored by the proponents of lithium battery technology and safety issues could become a major hurdle for the widespread up-take of solar/battery storage.

There are many challenging problems to be solved in the development of lithium battery technology which will require innovative chemical solutions. Large electronics conglomerates (mainly Japanese and Korean) are becoming dominant in the development of new battery chemistry and battery manufacture and many of the vehicle manufacturers are in joint venture with them (Tesla is reported to have an agreement with Panasonic). Of relevance to Australia would be new technology to extract the lithium from *alpha*-spodumene at lower energy cost that the current practice.

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