

Lithium and the Implications from the Commercial Introduction of Electric Vehicles

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Much excitement in the motor industry is being generated about electric cars reaching the marketplace by the third quarter of 2010. The Chevy Volt with a travel distance of 40 miles per battery charge will be the first of these commercially successful models. The vehicle will come with an on board gas generator to recharge the battery. The Volt's charger has 2 modes: 6.5 hours at 110 volts, and 3.2 hours at 220 volts. Similar even further range vehicles from Nissan, Mercedes and Volvo will be offered for sale during the coming year. However, the Department of Transportation has performed research indicating that 78% of all trips are less than 40 miles, 85% are less than 50 miles, and 93% are less than 70 miles.

This transformation from fuel driven vehicles to battery power may meaningfully alter the way that we lead our lives, reduce our carbon burden and place additional demands upon the electrical power grid. According to Austin Energy, there is enough total combined electrical capacity currently within the grid to allow overnight charging for 160 million electric vehicles such as the Volt. Of our entire oil consumption, some 2/3 of it is for transportation and 44% of this oil consumption can be replaced by battery generated power. Our other transportation needs include airplanes, trains, ships, and large trucks, none of which will make the transition to battery power. However for the passenger car the future seems to afford a battery future.

The breakdown in our use of petroleum for transportation needs is:

Gasoline for passenger vehicles	44%
Diesel	17%
Jet Fuel	5%
Fuel oil for home and industrial	15%
Petrochemical, plastics and fertilizer products	19%

Lithium which will power our battery needs is the 33rd most common mineral of the earth's crust and it is plentiful in nature as hard rock ore and as brine. It has a density which is half that of water, and is the least dense of all solids, being a mere 0.53 grams/cm³ at a temperature of 20 C. Unlike the heavier alkalis, lithium does not react violently with oxygen and is stable in dry air. Cost efficient methods are being explored for best extraction of this extraordinary mineral. The richest lithium source currently being harvested is the Salar de Atacama basin located in the Atacama desert in Chile. Brine extraction has become the preferred method of lithium extraction.

Lithium carbonate is produced commercially from one of three sources:

1. Extraction from mineral sources such as spodumene
2. Lithium containing brines – commercially available lithium brines in the United States are found in Silver Peak, Nevada and Searles Lake, California.
3. Sea water extraction

The methods for large scale lithium purification were developed by the Chemetalle Foote Corporation of King Mountain, North Carolina. Their strategy for reducing natural resources to useful metal involves conversion of the lithium salts to carbonate, then to chloride, followed by molten salt electrolysis. The first process used was obtaining pure lithium carbonate from spodumene, or lithium aluminum silicate ore (LiAlSi₂O₆). The ore is usually recovered from open pit mines, and this process was exploited commercially because of its relatively high lithium content and ease of processing. Alpha spodumene, with has a lithium oxide concentration of 5-7%

is able to be transformed to beta spodumene by heating to over 1100 C, and then is extracted with sulfuric acid to form lithium sulfate, treated with sodium hydroxide and sodium carbonate to form sodium sulfate (Glauber salt) and lithium carbonate. To manufacture lithium chloride of high purity the lithium carbonate is first transformed into lithium hydroxide before chlorination to give battery grade lithium chloride. This process is both time consuming and is costly in large scale application.

Lithium brine is dried in a series of solar evaporation ponds, and then removed by precipitation using soda ash, which then is transformed to lithium carbonate. The lithium rich brine deposits such as the Salar de Atacama are located in closed basins in high evaporation environments where lithium is present as a chloride or carbonate along with potassium and boron. Current technology transforms impure lithium carbonate into lithium hydroxide and the precipitation of calcium carbonate by treatment with soda ash. The key to obtaining high grade lithium is to use purified lithium chloride and carrying out electrolysis in the virtual absence of air and humidity to minimize lithium's rapid reactions. Impurities must be removed, which may include sodium, calcium, magnesium, as well as carbonate, sulfate and borate. The process concentrates brines, either natural or otherwise, containing lithium and other alkali and alkaline metal halides to 2-7% of lithium content. Most of the alkali or alkaline earth compounds are removed by precipitation at a pH between 10.5 and 11.5. The pH is modified with recycled lithium hydroxide, with removal of remaining magnesium and by lithium carbonate and/or carbon dioxide which produces calcium carbonate as a precipitate.

The concentration of lithium in seawater is only 0.2 parts per million, making the extraction of lithium from seawater impractical. Although the total amount of lithium found in seawater has been calculated as 2.5×10^{14} kg it would be difficult to extract given the low concentration. Rather, geothermal sources of lithium extraction are proving much more practical. The only efficient method for precipitating lithium from geothermal salts is through the use of aluminum salts. Of greatest interest is that the highest recovery of lithium occurs at a pH greater than 11. No product other than activated alumina is able to perform consistently at this high pH. In the presence of activated alumina the pure lithium salts get bound through adsorption, and are then released with greater than 99% purity.

Given the transition to lithium as a vehicle power source there is a major emphasis to improve battery performance and reduce weight. The battery in the Chevy Volt weighs 288 pounds. Dr. Gerbrand Ceder and colleagues at MIT have demonstrated that lithium iron phosphate can be manipulated to allow for extremely rapid cathode charging. Their work was sponsored by the National Science Foundation through the Materials Research Science and Engineering Centers program and the Batteries for Advanced Transportation Program of the US Department of Energy. This technology has already been licensed to manufacturers such as A123 Systems of Watertown, MA. When current is applied to charge a cell, lithium ions are trapped at the anode storage medium and move away from the cathode. When the battery discharges and produces current the ions then travel back to the cathode and produce current. The time that it takes the lithium to move on and off the cathode material is a rate limiting step. Lithium ion phosphate forms a lattice that creates small tunnels through which the lithium ions flow. Ceder and colleagues created a lithium phosphate glassy surface to coat these tunnels, which appear to speed the transport time for the lithium ions to move on and off the cathode. They published in Nature that this method allows for discharge rates which are two orders of magnitude greater than those used in today's lithium ion batteries. They go on to state that if the electric power grid were available an electric car with a 15kWh battery could be charged in 5 minutes (180kWh). This would allow a lithium ion battery to behave like an ultracapacitor. Charging of electric batteries would need to be done at specialized public filling recharge stations, as the charging of the lithium battery would require the delivery of 750 amps using 240 volts of alternating current (240 VAC). As a point of reference, the standard household electrical service for most entire homes is only 150-200 amps. However, these quick charge stations will only be possible if they can store energy the same way that an electrical vehicle (EV) will, but with more powerful batteries.

While this technology has been discredited by Zaghbi et al: Unsupported claims of ultrafast charging of LiFePO₄ Li-ion batteries, Journal of Power Sources, Vol 194: 2, December 2009, it is clear that the race is on for finding superior lithium extrusion and purification technologies.

The implication is that battery powered vehicles appear here to stay. There is going to be a requirement for superior methods to purify high grade lithium from geothermal and brine sources, and activated alumina by working at pH levels in excess of 11 appear to best fit the bill.