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A review of lithium supply and demand and a preliminary investigation of a room temperature method to recycle lithium ion batteries to recover lithium and other materials

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Abstract

Recent publications have discussed the potential for scarcity of materials needed for future engineering designs and manufacture [1, 2, 3]. In the case of a recent DOE report [1], materials needed for the production of green energy technologies were deemed as those needing study.

A major conclusion of these papers is that there is a need for recycling of materials that are designated as strategic or have a potential of becoming scarce. Lithium is one such material. It is critical to the battery industry, especially in compact consumer electronics (e.g. mobile phones and tablets) and in hybrid electrical and fully electrical vehicles. In this paper the role of lithium in electronics and vehicles is reviewed. Also reviewed are the reserves, projected mining capacity, and forecasted demand for lithium. Based on these three, it is predicted that there will be a shortage of lithium between 2021 and 2023 if lithium is not recycled [4].

Current lithium ion battery technologies recover little if any lithium and are energy intensive since they incinerate or shred batteries after they have been cooled in liquid nitrogen. This paper showcases a preliminary experiment where a battery was discharged by immersion in brine and safely opened manually. Pristine copped and the external protection circuit were easily recovered intact. Future experiments will attempt to recover lithium, aluminium, and the electrolyte with the aim of developing a method of recycling at room temperature that recovers all valuable materials, especially lithium.

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Keywords: lithium supply and demand; lithium ion batteries; recycling

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1. Introduction

The adoption of electric motors in vehicles at the expense of internal combustion engines is desirable in order to achieve reductions in tailpipe emissions of green-house gases and air quality pollutants (NOx, VOCs, PM), as well as a reduction in noise pollution. The replacement of fossil fuel power plants with generating stations for solar, wind, and other renewables is desirable in order to achieve stack emission reductions of the same gases and pollutants. Electricity generation from renewable energy sources is, unfortunately, generally intermittent and grid storage is necessary in order for its wide-spread adoption to be realized. Electrification of vehicles and massive expansion of grid storage capacity are both greatly aided by the development of a high energy density, reliable and affordable energy storage technology. A very promising current energy storage technology for both applications, especially vehicles, is the common lithium ion rechargeable battery.

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2. Lithium ion batteries

Lithium ion batteries were first introduced in 1976 by Whitingham [5] and the original design has since been refined. Modern lithium ion batteries use transition metal oxides with lithium in their lattice structure (e.g. $LiCoO_2$ and $LiMnO_2$) as the active cathode materials, lithium salts dissolved in an organic solvent or gel (e.g. $LiPF_6$ in ethylene carbonate) as the electrolyte, and typically graphite as the active anode material. During discharge, lithium atoms ionize and deintercalate from the anode, diffuse through the electrolyte, and intercalate in the lattice structure of the transition metal oxides in the cathode; electrons flow through an external circuit from anode to cathode. During recharging, the reverse process occurs. Compared to other battery chemistries lithium ion batteries have a much higher voltage (3.7 V for $LiCoO_2$ vs. 1.2 V for NiMH), have at least twice the energy density (volumetric and per mass), and have a relatively low rate of self-discharge (half that of NIMH or NiCd batteries). Lithium ion batteries can also be recharged at any remaining capacity with no need for periodic full discharges without affecting the number of full cycles the battery will function (i.e. if over its lifetime the battery can discharge x Joules the charging regime will not affect the value of x). It is these advantages that make lithium ion batteries the superior technology to electrify vehicles and a good contender for grid storage. [6,7]

3. Electric Vehicles

Electric vehicles (hybrid, plug in hybrid, or fully electric) are in the early part of market introduction: between 2000 and 2010, 1.5 million electric cars were sold – a small figure compared to the total of 60 million cars of all types sold in just 2011 [4]. The International Energy Agency (IEA) has outlined a roadmap for how the electrification of the transportation sector can be achieved by the market through the concerted effort of governments, intergovernmental agencies, automobile manufacturers, universities and research institutions, utilities companies, and non-governmental organizations. Briefly, the roadmap calls for the annual production of – and predicts the sale of – at least 5 million electric vehicles (plug-in hybrids and electric vehicles) by 2020. It further predicts that 50% of the cars that will be manufactured and sold in 2050 will be electric vehicles [8]. 95% of the electric vehicles sold in the first decade of the 2000s had NiMH batteries. However, lithium ion batteries are set to displace NiMH ones due to the advantages mentioned in section 2 [4]. Current vehicles require circa 4 kg of lithium [4] for a battery pack with 20 kWh capacity at a battery cost of 6,000 to 12,000 $US [8]. The IEA roadmap expects that optimised versions of current lithium ion batteries will be used in electric vehicles in the near future and that further improvements will require new battery chemistries, which should be developed before the end of the decade to ensure improvements do not stall [8]. Critically, the new chemistries anticipated (for example lithium alloy anodes) are still lithium based. It took 20 years since the first commercialisation of lithium ion batteries (1991 [7]) for them to develop to the level that they can be used in marketable electric vehicles. There are no known materials in industry that can replace lithium, nor are there other non-lithium battery systems being developed that can compete with lithium ion systems in terms of cost or performance [6]. It is reasonable to conclude therefore that, for the near and mid future, the successful commercialisation of electric vehicles depends upon an ample supply of lithium at a price not much higher than that which it is today (in 2012 the price for battery grade lithium carbonate was $6,000 per ton [9]).

4. Lithium Supply and Demand

Vikström et al. (2013) have conducted a detailed study of the world's reserves of lithium, production capacity, and compared these with the anticipated lithium demand from electric vehicles sales predicted by the IEA roadmap. Vikström et al. (2013) quantified lithium resources and reserve[1] from 112 sites: more sites than were analysed in any of the studies referenced. The sites included both rock deposits and brines. Also examined was the possibility of extracting lithium from oceans; this possibility was discounted since 5 million m^3 of seawater were required to produce one tonne of lithium. The study concluded a reasonable estimate of global lithium reserves accessible in the near to mid future would be of 15 million tonnes, with 30 million tonnes being a best case estimate. World resources of lithium were estimated to be 65 million tonnes. [4]

Vikström et al. (2013) predicted future production rates of lithium by modeling historical rates using three models, which are commonly used to forecast production rates of minerals and energy resources (see Table 1). The ultimate recoverable reserves (URR) of lithium used in these calculations were 15.5 and 30.0 million tonnes. The fitted parameters were t_0 (peak year), k (a growth factor), and M (an exponent in the Richards curve). [4]

Table 1: Lithium production rate forecasting models [4]

Logistic	$q(t) = \frac{URR}{1 + e^{-k(t-t_0)}}$
Richards	$q(t) = URR\left(1 \pm e^{\mp k(t-t_0)}\right)^M$
Gompertz	$q(t) = URR \cdot e^{\left(-e^{-k(t-t_0)}\right)}$

The logistic model describes a completely free market driven entirely by supply and demand. Out of all the three models, it predicted the fastest rising production rate of lithium and the earliest peak production rate. The models were restricted to a maximum annual depletion rate (extracted amount divided by remaining reserves) of 5% to prevent mathematically sound but impractical production rates; however the restriction proved unnecessary as none of the fitted models predicted a depletion rate greater than 5%. [4]

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[1] Resources are the geologically assumed amounts of lithium exploitable at a site; these values are largely academic and change only when new data are available for better estimates. Reserves are the amounts of lithium that are extractable with current technology, market conditions, and social conditions; reserves change as the technology and socioeconomic conditions change.

Critically, the production models assumed that lithium is not recycled. This was justified by the authors with the facts that: 3% of lithium ion batteries are collected for recycling; that recycling is usually designed to primarily recover other valuable components (e.g. cobalt), and; that there is currently no large scale industrial lithium recycling process which is economically viable . [4]

Vikström et al. (2013) compared the range of production rates forecasted by the above models (from lowest to highest prediction rate for all models, using both URRs) with anticipated lithium demand until 2050. The demand forecast assumes that demand for lithium for uses other than electric vehicle batteries will be constant – a very conservative assumption given that the consumer goods lithium battery market is expanding rapidly [9] – and that as many electric vehicles with lithium ion batteries will be built as is predicted by the IEA's roadmap. The comparison is illustrated in Figure 1. [4]

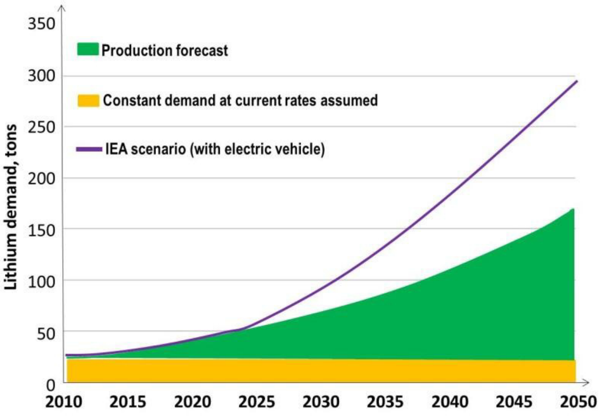

Figure 1: Lithium production rates range of forecasts (in green shading) compared with anticipated demand from current uses (yellow shading) added to anticipated electric vehicle battery demand (sum is in blue) [4]

5. Discussion

As it can be clearly seen in Figure 1, even with the most optimistic production scenario, demand from electric vehicles will outstrip supply between 2021 and 2023 [4]. It is important to note that lithium demand for grid storage is not included at all in these forecasts. A skeptic may rightly point out that the IEA roadmap predicts a very aggressive uptake rate of electric vehicles and that a lower rate of increase of demand may actually occur. However, the uptake rate is completely in line with electric vehicle sales targets announced by governments all over the world [8] and thus represents a level of market demand that governments are willing to stimulate. It would be unfortunate, considering the environmental benefits of driving electric vehicles rather than internal combustion engine vehicles, if that which limits adoption of electric vehicles is lithium supply rather than market demand. Furthermore, it would be similarly unfortunate if that which limits adoption of electricity generation from renewable sources is lack of supply of lithium for batteries to be used for grid storage rather than other market forces, such as the cost of the generating stations themselves. In order to avoid these potential bottlenecks in production (and associated environmental quality gains) it will be necessary by 2021 to 2023 to have an annual supply of lithium greater than the forecasted mining rates. A very good way to ensure such a supply would be to recycle lithium from products that have reached their end of life. This makes the prospective benefits from recycling automotive lithium ion batteries particularly attractive.

Gruber et al (2011) (a study similar to that conducted by Vikström et al. (2013)) found that recycling can indeed have a very significant impact. The study assumed a similar amount of lithium reserves and forecasted a similar rate of adoption of electric vehicles. The study found that ensuring an annual supply of lithium greater than what could be extracted through mining alone is indeed achievable by years 2021 to 2023, if at that time it were possible to recycle 100% of discarded lithium batteries at a lithium recovery rate of 90%. Consequently, 55 to 63% of lithium used would be recycled material (the rest would be virgin material) and world lithium reserves would last well into the 21st century. [10]

6. Supply and demand conclusions

Adoption of cars with electric motors rather than internal combustion engines and an expansion of grid storage capacity to accommodate intermittent renewable energy sources are ways that reductions in green-house gas emissions can be achieved. Lithium ion batteries are the best energy storage option for electric cars for the near and mid future and are a good option for grid storage. A comparison of anticipated lithium demand to forecasted lithium supply shows that in the early 2020s, without recycling, supply will not be able to keep up with demand and therefore adoption of electric vehicles will likely be stalled. In order to give widespread adoption of electric vehicles the best chance of occurring it is therefore necessary that methods of large scale recycling of lithium ion batteries, especially of automotive batteries, be developed.

7. Recycling and preliminary qualitative experiment

The literature shows that research is well underway into recycling lithium ion batteries; Xu et al. (2008) provide an excellent review [11]. The research focuses almost exclusively on batteries with $LiCoO_2$ cathodes [11], which are not favoured for use in cars since they are not robust enough [6]. Batteries with Li-nickel-manganese-cobalt, Li-iron phosphate, or Li-manganese spinel cathodes are favoured in automobiles instead (the notable exception being Tesla Motors which does use $LiCoO_2$ cathodes) [6]. The research also shows that typically batteries are shredded whole or incinerated and the metals contained therein are recovered by acid leaching followed by precipitation.

An added deficiency of the vast majority of recycling processes currently in use is that electrolyte is not recovered. This is unfortunate since the salvage value of electrolyte in a typical AA battery in 2001 was 0.23 $US while that of the whole battery was 0.49 $US, thus electrolyte represents nearly 50% of total salvage value [9]. Furthermore, the batteries' external protection circuits, which prevent over discharging and overcharging [6], are destroyed by the shredding or incineration processes, which is also unfortunate.

Our lab has begun research into the development of recycling method for automobile batteries that is as energy efficient as possible, recovers as many materials for reuse and recycling as possible, and that produces as few pollutants as possible. Though the research is in the very early stages and no lithium has been recovered so far, the results of a qualitative preliminary experiment are worth reporting. The experiment consisted of manually disassembling a 3.7V lithium ion camera battery, most likely with a $LiCoO_2$ cathode, comprised of one cell. The battery, was chosen since it was readily available.

Opening a lithium ion battery is potentially hazardous, which is one of the reasons why in industry they are incinerated or immersed in liquid nitrogen then shredded [11]. The hazard is primarily due to the presence of residual lithium atoms in the anode which may react violently with moisture. A secondary hazard is the lithium salts in the electrolyte which destabilise at high temperature and also react violently [6].

The first hazard was mitigated in our experiment in a novel way. The external protection circuit of the battery was removed so that the battery could be fully discharged. Fully discharging moves the majority of lithium atoms from the anode into the cathode, where they do not react with water. The battery was discharged by immersing it in a saturated NaCl solution. The initial voltage of the battery was 1.39V and it decreased to 0.60, 0.28, and 0.30 after 1, 3, and 22.5 hours respectively. After 22.5 hours the battery was short-circuited with a zinc plated copper wire and the current through the wire was measured. It was 160 µA, which signifies the battery had negligible capacity left. The battery was then opened in a ventilated area and unrolled. The organic solvent quickly evaporated. The inside of the battery consisted of a strip of copper coated with anode material, a strip of polymer lithium ion permeable separator, and a strip of aluminum coated with cathode material all rolled and stuffed into an aluminium casing. See Figures 2, 3, and 4 below.

Figure 2: Anode, separator, and cathode roll in aluminium casing.

Figure 3: Anode, separator, and cathode roll.

Figure 4: Unrolling of anode, separator, and cathode strips.

A section of the coated copper strip was cut and immersed in water. No reaction was seen or heard and the temperature of the water remained unchanged, indicating that indeed the anode was most likely devoid of lithium ions and that the safety precautions worked. It was however also observed that, immediately after immersing in water, the coating on the current collector was very easy to scrape off leaving behind a pristine copper strip. Prior to immersion it was very difficult to scrape off the coating. Pieces of a coated aluminium strip and electrode separator were also immersed. A reaction was neither seen or heard, nor had the temperature of the water changed. Unlike the anode (coated copper), immersing the cathode in water made it much more difficult to scrape coating off.

The results of this experiment show that discharging a cell in brine, after its protection circuit has been removed, is an adequate safety precaution to prevent lithium reacting with moisture. This option is much less energy intensive than incineration or immersion in liquid nitrogen. The experiment also shows that it is possible to recover pristine copper without shredding it, dissolving it, and precipitating it; thus pointing to further energy consumption reductions and process simplifications. Furthermore an external protection circuit was recovered intact and it may be reusable.

In the future Li-nickel-manganese-cobalt and Li-iron phosphate batteries will be disassembled using the same procedure and a method to also recover the lithium, aluminium, and electrolyte will be developed.

8. Conclusions

Lithium ion batteries are common today, and provide the highest energy density available for rechargeable devices. We believe they are set to become the battery of choice for many electrical energy storage systems, especially where portability is required.

Forecasts show that unless recycling of lithium ion batteries becomes viable on a mass production scale, there will be a shortage of lithium. Hence there is an urgent need to find viable recycling techniques.

To that end, a preliminary step in lithium ion battery recycling is reported here.

9. References

[1] Chu S. U.S. Department of Energy “Critical Materials Strategy”, December 2011.

[2] T. E. Graedel, Rachel Barr, Chelsea Chandler, Thomas Chase, Joanne Choi, Lee Christofferson, Elizabeth Friedlander, Claire Henly, Christine Jun, Nedal T. Nassar, Daniel Schechner, Simon Warren, Man-yu Yang, and Charles Zhu. “Methodology of Metal Criticality Determination”. Environmental Science and Technology. DOI: 10.1021/es203534z. 2012/01/08. ISSN: 1520-5851.

[3] T. E. Graedel, Julian Allwood, Jean-Pierre Birat, Matthias Buchert, Christian Hagelüken, Barbara K. Reck, Scott F. Sibley, and Guido Sonnemann. “What Do We Know About Metal Recycling Rates?” Journal of Industrial Ecology p 355.

[4] H. Vikström, S. Davidsson, and M. Höök, “Lithium availability and future production outlooks,” Appl. Energy, vol. 110, pp. 252–266, Oct. 2013.

[5] M. S. Whittingham, “Electrical energy storage and intercalation chemistry,” Science, vol. 192, no. 4244, pp. 1126–7, Jun. 1976.

[6] I. Buchmann, “Battery University.” [Online]. Available: http://batteryuniversity.com/learn/. [Accessed: 01-Nov-2013].

[7] J.-K. Park, Principles and Applications of Lithium Secondary Batteries. Weinheim, Germany: Wiley-VCH Verlag & Co. KGaA, 2012.

[8] L. Fulton, “Technology Roadmap Electric and plug-in hybrid electric vehicles,” Int. Energy Agency, no. June, 2011.

[9] Canada Lithium Corporation, “Canada Lithium Corporation Forward-looking Statement.” [Online]. Available: http://www.canadalithium.com/i/pdf/presentation.pdf. [Accessed: 01-Nov-2013].

[10] P. W. Gruber, P. a. Medina, G. a. Keoleian, S. E. Kesler, M. P. Everson, and T. J. Wallington, “Global Lithium Availability,” J. Ind. Ecol., vol. 15, no. 5, pp. 760–775, Oct. 2011.

[11] J. Xu, H. R. Thomas, R. W. Francis, K. R. Lum, J. Wang, and B. Liang, “A review of processes and technologies for the recycling of lithium-ion secondary batteries,” J. Power Sources, vol. 177, no. 2, pp. 512–527, Mar. 2008.