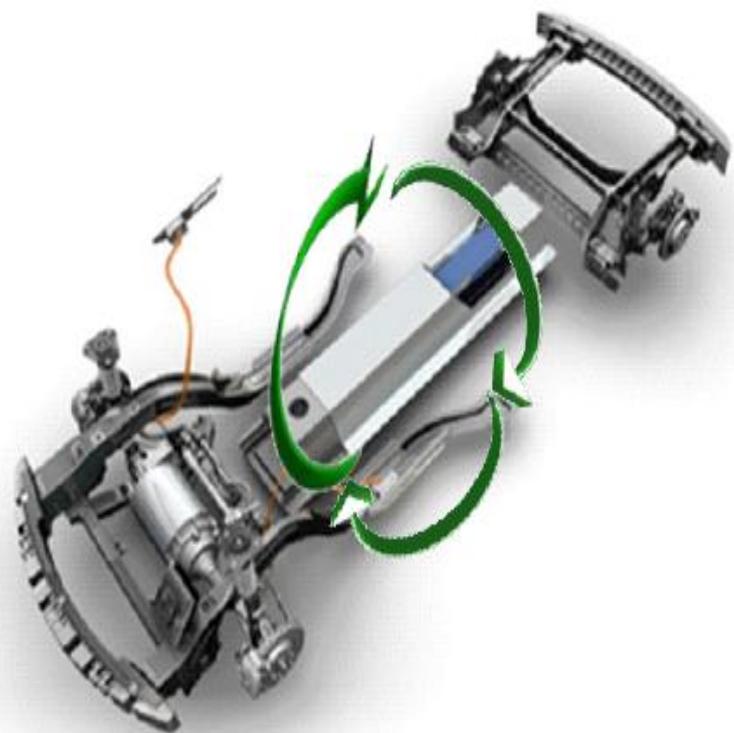


A REVIEW OF 'THE IMPORTANCE OF RECYCLING LITHIUM-ION BATTERIES FOR LITHIUM, IN VIEW OF IMPENDING ELECTRIC VEHICLE INDUSTRY'

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ABSTRACT

Automobile electrification is one of the technological developments, that will commence an earth friendly transport system, by mitigating emissions and hopefully lead to a less fossil fuel dependent society. With commercial success attained by models like Nissan's leaf and Chevy's Volt, the consumer market looks promising to assimilate vehicle electrification. At present these technologies include HEVs (hybrid electric vehicles), PHEVs (plug-in hybrid electric vehicles), EVs (complete electric vehicles).

A closer look at these technologies will lead us to one of the crucial components of electric vehicles, the "batteries". This component decides one of the key performance factors which is the energy storage and usage, which means it is the basis for public acceptability.

The lithium-ion battery chemistries are chosen to fulfill this requirement. Although lithium constitutes of a small fraction of the complete battery weight, still its continued availability in future is debated among many resource analysts.

INTRODUCTION

Batteries from the hybrid and electric vehicles should be treated both to guarantee safe disposal and recover elements of value. In the context, this report brings forth - present lithium resources and the requirement projections for future. To make sense of the projections, a brief about the battery technologies and a survey of batteries used in market is also put forth. In the context of resource availability a review of present lithium recovery methods, stressing on the need for developing better methods is presented.

Lithium ion batteries are popularly used batteries for powering device scale electronics. Over a span of a decade, they have now taken over what used to be a Ni battery market with stark growth rate and the predictions for future only seem to establish them furthermore in the battery industry, [Figure 1](#), (Pistoia 2009), [Figure 2](#) (Pillot 2010). The recent development of hybrid vehicle and electric vehicle technology, which find the Li-ion as a promising chemistry however made the resource analysts question the future availability and sustainability of this new vehicle battery product.

The analysis results were conflicting to the point of presenting totally opposite views on availability of lithium, [Table 1](#), (Paul Gruber 2010). From the selected predictions shown below (Tahil 2008), stressed that the produced amount of lithium is not enough to sustain the growth rate of the electric vehicle industry projected along with the growth rate of the other industries which use lithium as well.

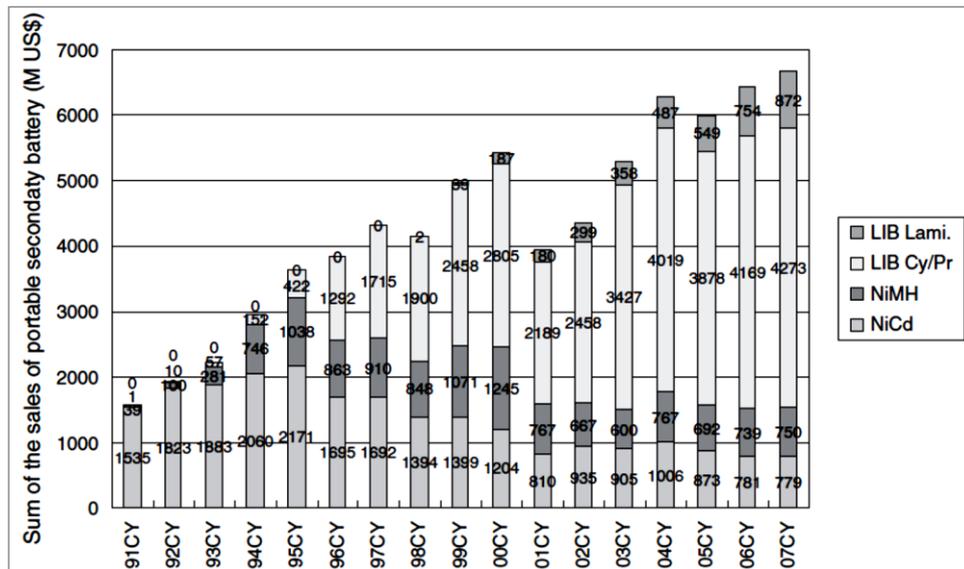


Figure 1: The increase in Li-ion batteries in portable devices from 2000-2007, CY- cumulative years (Pistoia 2009)

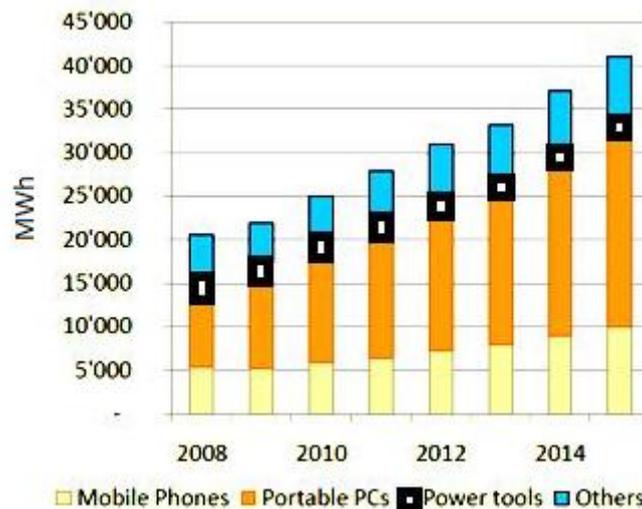


Figure 2: Portable rechargeable battery projections by application until 2014 based on current annual growth rate +10 %, (Pillot 2010)

Table 1: World total lithium resource and reserve estimates (Mt. Li), (Paul Gruber 2010).

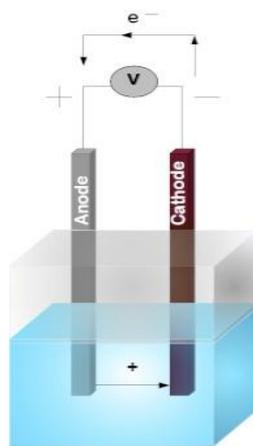
Li Resources	Deposits Included	Reference	Li Reserves	Deposits Included	Reference
19.2	15	Tahil (2008)	4.6	11	Tahil (2008)
25.5	8*	USGS (2010)	9.9	8*	USGS (2010)
29.9	24	Evans (2008)	29.4	40	Yaksic/Tilton (2009)
64.0	40	Yaksic/Tilton (2009)	39.4	61	Clarke/Harben (2009)**

Lithium is the lightest metal in the periodic table (Atomic weight: $6.941 \text{ g} \cdot \text{mol}^{-1}$). (Fenton Walter, Esmay Donald et al. 1957) It is silvery and soft to cut. It has a low thermal expansion coefficient, ($25 \text{ }^\circ\text{C}$). These properties make lithium covetable

in many industries such as grease, glass industries. It's high electro-chemical potential (3.7 V) and energy density of lithium, that gives Li -ion batteries an edge over other battery chemistries.

1. WHAT IS A BATTERY?

A battery is an electrochemical cell, [Figure 3](#), with an anode, a cathode, and an electrolyte. Batteries can be classified in to primary and secondary depending on their utility. Primary batteries cannot be recharged and secondary batteries are rechargeable. For any type of a battery, the materials are so chosen for all the main parts, such that all working parameters are optimized, mainly the cell potential. The cell potential is defined as the difference between the chemical potential of the anode and cathode (Pistoia and Gianfranco 2005).



Zinc – copper half-cell reactions (during discharge) are shown as an example of a working electrochemical cell below

At Cathode (negative)



At Anode (positive)



Net cell potential; E is the reduction potential

Figure 3: Schematic of an electrochemical cell

1.1 PRIMARY AND SECONDARY BATTERIES

The introduction of the 'dry cell' - a battery in which the electrolyte is a solid/paste, marked the beginning of 'primary batteries'. The batteries that could be used to store energy, fit into small electronic devices, were portable and could be replaced with ease with minimal cost (Scrosati 1994). With the requirement which carried over to the power storage components due to the development in electronics, that needed to function for long periods without having to replace the batteries, the secondary batteries were made. It is possible to recharge and re-use secondary batteries for many cycles because of their

reversible charged particle movement ([Figure4](#)) within the battery. In order to create such reversible cell chemistry with minimal structural disintegration, due to the cycle of charge and discharge, new materials had to be made. Electrodes that can undergo deep charge/discharge cycles, without any significant loss of capacity, were made possible by *intercalation*¹ chemistry. Many of these electrochemically active materials, which are able to resist shock failure due to intercalation, are however not good electronic conductors, so it is necessary to add an electrically conductive material. Hence the active material is deposited on to a conductive metal substrate such as Cu or Al. To physically hold the electrode together with the substrate, a binder /adhesive is also added. Thus, most electrodes of today are complex porous composites (Whittingham 2004). It is now well-established that a number of transition metal oxides or sulphides and other materials can reversibly incorporate or intercalate lithium into vacant sites in their lattice without substantially altering the host structure, for a number of cycles (Vincent 2000). Some of the more used secondary batteries are listed in Table2. A comparison of various primary batteries and secondary batteries with respect to their energy densities is shown in [Figure5](#).

It can be noted, [Figure 5](#), that nickel metal hydride and Li-ion battery are both at nearly equal levels in terms of their energy density per unit volume, but the Li-ion battery offers better energy density per unit weight. The specific energy varies from 100 Wh kg⁻¹ to 150 Wh kg⁻¹ (Scrosati and Garche 2009) depending on the compound. The newer thin film lithium-ion batteries have a range between 300-500 Wh kg⁻¹ (Patil, Patil et al. 2008). Because of these attributes lithium and its compounds possess, they have become a popular choice for battery materials.

Table 2: Comparison of different cell potentials for few popular secondary battery chemistries (Wakihara 2001)

Battery System	Cathode	Electrolyte	Anode	Voltage (V)
Lead Acid	PbO ₂	H ₂ SO ₄	Pb	2
Ni – Cd	NiOOH	KOH (aqueous)	Cd	1.2
Ni – MH	NiOOH	KOH (aqueous)	Hydrogen adsorbed alloy	1.2
Li – ion	CoO ₂	Organic Electrolyte - Carbon Lithium salts		3.7

¹ An intercalation process is defined as a reversible *topotactic* reaction in which the guest species occupy empty sites in a solid structure. A *topotactic* chemical reaction is one in which all chemical solid state reactions that lead to a material with crystal orientations which are correlated with crystal orientations in the initial product, so that the initial and final lattices are in coherence

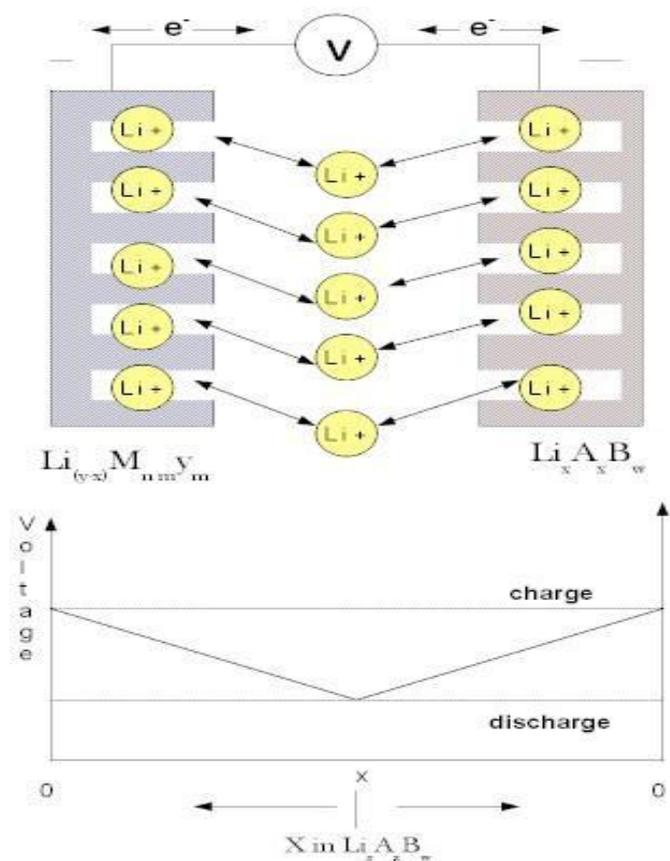


Figure 4: A Li-ion rechargeable battery showing 'to and fro' movement of Li-ion during charge and discharge cycles (Patil, Patil et al. 2008)

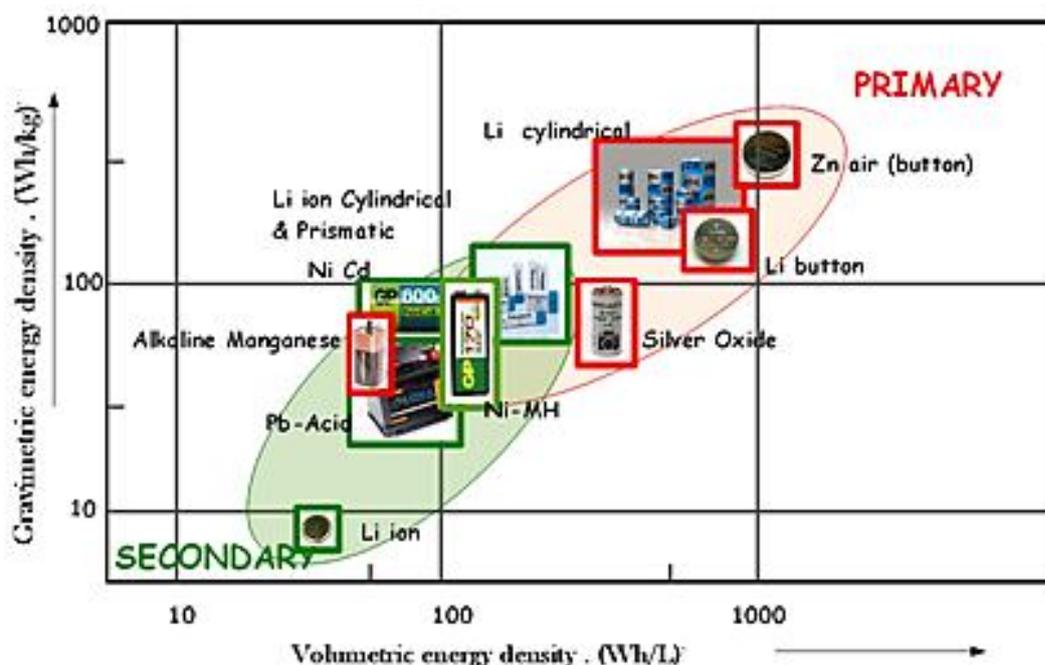


Figure 5: A ragone plot of primary batteries and secondary batteries of various chemistries (Pistoia and Gianfranco 2005)

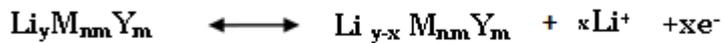
1.2 THE LI-ION RECHARGEABLE BATTERY

Li-ion batteries (as explained previously) have represented a turning point in the field of power sources for a variety of applications because of their desirable characteristics (Pistoia 2009), such as high specific energy and energy density, low self-discharge, long cycle life, almost no maintenance, negligible memory effect, higher capacity, possibility of miniaturization and very thin form factors. However there are some issues which need to be addressed before they are accepted as large (vehicle scale) batteries. Some of the issues are noted as (Pistoia 2009) relatively need for a protection circuit to avoid overcharge and discharge and excessive temperature rise, degradation at high temperatures, lower power than Ni–Cd or Ni–MH at low temperatures. However, it is to be stressed that some of the above drawbacks are being progressively reduced with continuous study (Tsang, Sun et al.; Endo, Kim et al. 2000; Sarre, Blanchard et al. 2004; Lestriez 2009) and enhanced battery engineering.

[Figure 4](#), demonstrates the working of a Li-ion battery.

The charge \longleftrightarrow discharge reactions half-cell reactions

At Cathode,



At Anode,



The complete cell reaction,



1.3 DESIGN ASPECTS OF A LI-ION CELL

The conventional designs of the battery are such as the ones shown in [Figure 6](#). Stacked cells are held together by pressure from the cell container. The lithium-ion gel polymer stacked cells are prepared by bonding/laminating layers of electrodes and separators together. The separator properties should not change significantly during the bonding process. In some cases, the separators are coated to help in bonding process, thus reducing the interfacial resistance. The spirally wound cells are made by winding two layers of separators tightly along with the cathode and anode layers, resulting in a cathode/ separator/ anode/separator configuration (also called jelly roll). Once wound, the jellyroll is inserted into a can, and filled with electrolyte. A header is then crimped in to the cell to cover the can from top. In some prismatic cells, the jel-

lyroll is pressed at high temperature and pressure and then inserted into thin prismatic (rectangular) mantels (Johnson and White 1998). It has been shown (Sit, Li et al. 2004) that the cell-specific energy and energy density are affected significantly by the cell geometric shape, the material of the can, the cell discharge voltage, the cell temperature, and the cycle number. The geometric difference between the cylindrical and prismatic cells has shown to have caused the prismatic cells to perform as much as 9% better in cycling tests and with a 12% difference in the cell energy density, even though the total volume of prismatic cell was 2% larger among the tested samples, [Figure 7](#).

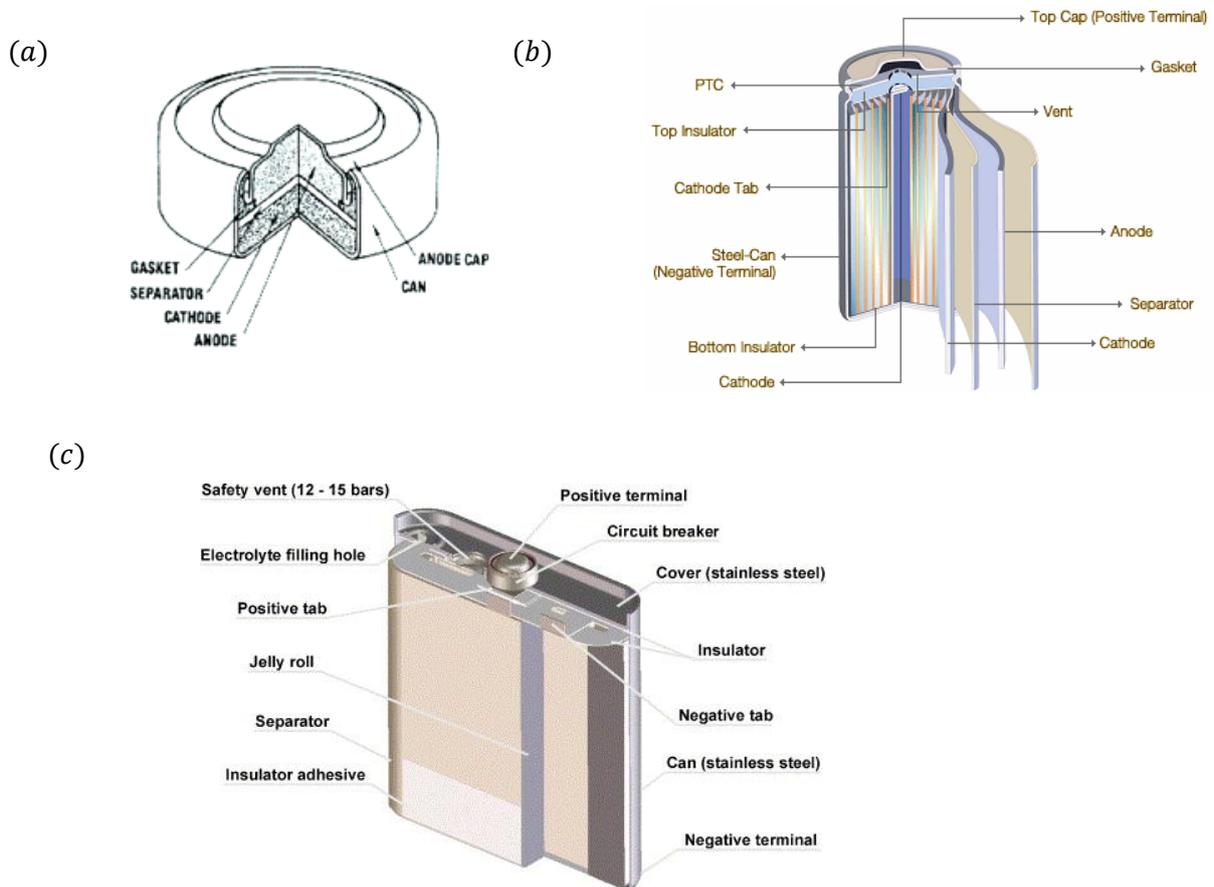


Figure 6 Schematic of typical: (a) button cell (primary); (b) spiral wound cylindrical lithium-ion; (c) spiral wound prismatic lithium-ion (Arora and Zhang 2004)

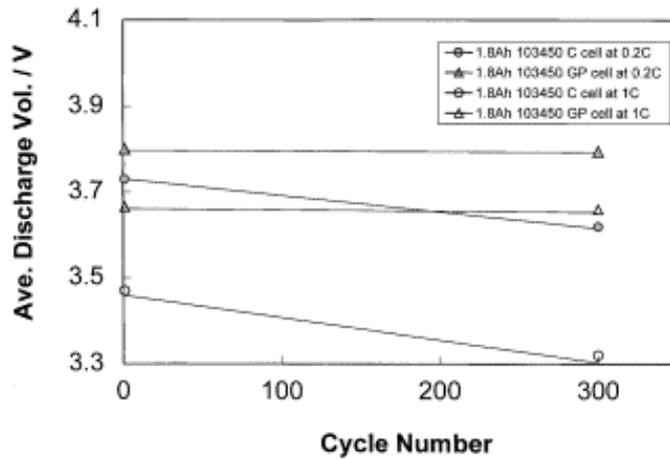


Figure 7 Average discharge voltages at 0.2 C vs. cycle number for cylindrical (C in graph) and prismatic cells(GC in the graph)

A more recent lithium-ion battery design is the thin film battery also called the li-polymer battery, [Figure8](#) (Patil, Patil et al. 2008). In order to construct a thin film battery, it is necessary to fabricate all the battery components (anode, electrolyte, cathode including the current leads) all into multi-layered thin films by suitable techniques. The active solid films are sequentially deposited on a substrate. Usually, the active lithium compound used for anode, is prepared by vacuum thermal vapour deposition (VD).

Solid electrolytes and cathode or sometimes even anode materials of oxides are prepared by various sputtering techniques such as radio frequency sputtering (RFS), RF magnetron sputtering (RFMS), chemical vapour deposition (CVD) and electrostatic spray deposition (ESD) are also other processes used(Bates, Dudney et al. 2000).

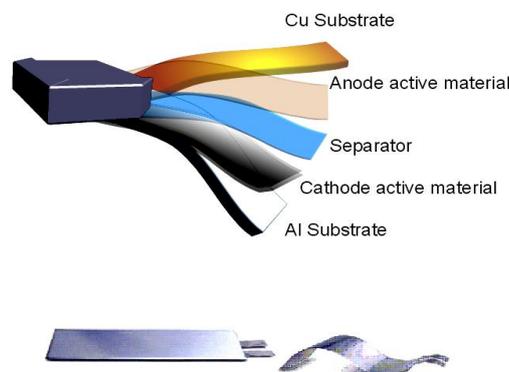


Figure 8 Schematic of layers with in a thin film Li-ion battery

1.4 CHEMICALLY ACTIVE COMPONENTS OF A LITHIUM-ION BATTERY

The chemically active parts within the lithium-ion cell; the anode, cathode, electrolyte, adhesive and additives are discussed briefly below.

1.4.1 ANODE

Though promising research is being reported on various lithium alloys, tin based composites, glasses, at present carbon in various forms (graphite, hard carbon and microspheres) is the most commonly used anode-active material.

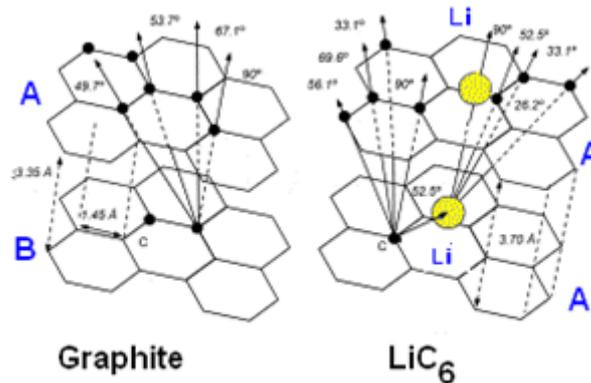


Figure 9 Structure of graphite and LiC₆ (Inaba, x00Fc et al. 2009)

Graphite, [Figure 9](#), is built of ABAB layers, which is held together by van der Waals forces. Each layer contains a conjugated sp² bond. When Li-ions move into these layers, this layer arrangement changes to AAA2– this arrangement is reversible, allowing to and fro movement of the lithium-ion(Shu, McMillan et al. 1993).

Thus, graphite serves as the host structure for lithium intercalation and the structure is studied to be resilient enough to provide reversibility by allowing easy insertion and de-insertion of lithium. In practice, at room temperature, graphite accepts sufficient lithium to form LiC₆ which on reversal of Li-ion movement can deliver 372 mAh.g⁻¹. Lithium charge capacity and cyclic efficiency depends strongly on the cross sectional structure of the fibres, such as onion, radial and random structures.

Thus the new generation anodes use carbon fibres subject to different heat treatment processes for better structural incorporations. In particular, mesophase pitch-based carbon fibres (MPCFs), [Figure 10](#), exhibit a high degree of anisotropy with regard to mechanical, electrical, magnetic, thermal as well as chemical properties. These anisotropies are directly related to the layered structure with strong interlayer interactions and very weak van der Waals interplanar interactions between adjacent graphene sheets aligned parallel to the fibre axis (Endo, Kim et al. 2000) .

A new electrolyte system has been developed, in which it is reported that the use of an anode has been avoided completely in the FORTU battery, which is a metal-free

system, in which lithium is produced within the battery on charging from the cathode system that uses lithium cobalt oxide (G. Hambitzer 2000). This uses the standard lithium cobalt oxide cathode material, but the electrolyte is liquid sulphur dioxide with lithium tetra-chloroaluminate (LiAlCl_4) as the electrolyte salt. This solution has a freezing point below -80°C and conductivity at room temperature of about 10 times that of organic electrolytes. Hence, this system has high power capability.

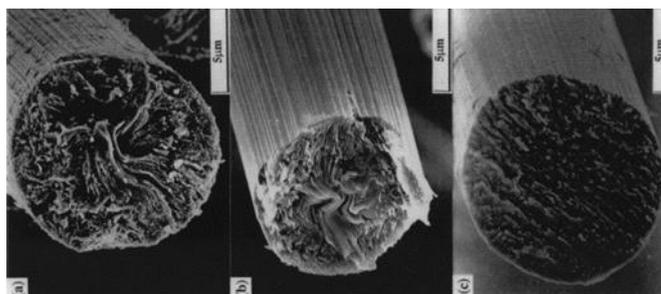


Figure 10 FE-SEM photographs of milled MPCFs with HTT (a) 1000°C , (b) 3000°C , and (c) high modulus mesophase pitch-based graphite fiber (P-100) (Endo, Kim et al. 2000)

1.4.2 CATHODE

As mentioned in (Whittingham 2004), the requirements for a material to be successfully used as a cathode in Li-ion batteries are: It should be readily reducible/oxidizable ion, for example a transition metal, should react with lithium in a reversible manner. This necessitates an intercalation-type reaction in which the host structure essentially does not change as lithium is added. It should have a high free energy of reaction with lithium, high capacity, voltage (around 4V). It should also be a good electronic conductor, hence generally a metal is preferred. Its toxicity should be fairly low and its cost should be low.

Almost all of the research and commercialization of cathode materials has centered on two classes of materials. The first contains layered compounds with an anion close-packed or almost close-packed lattice in which alternate layers between the anion sheets are occupied by a redox-active transition metal and lithium then inserts itself into the essentially empty remaining layers, [Figure 11.a](#).

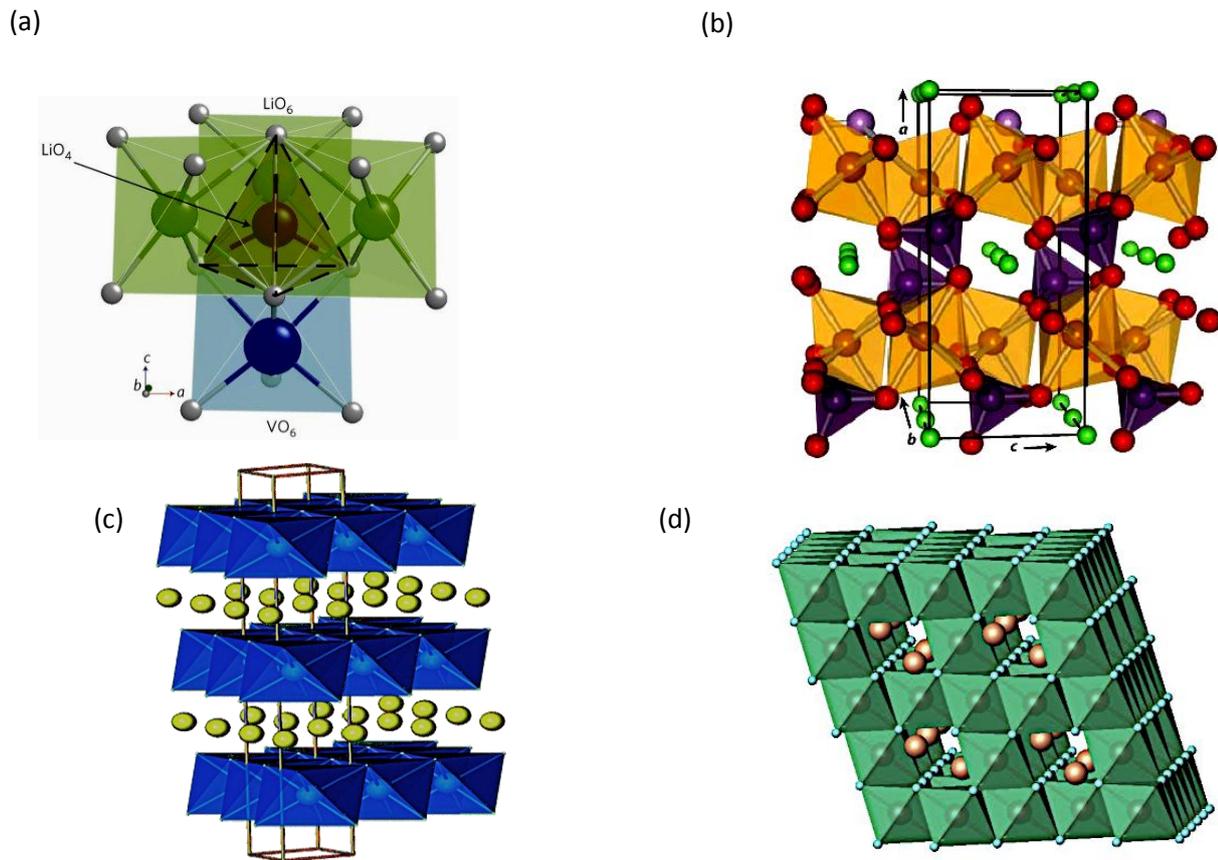


Figure 11: (Whittingham 2004) (a) Layered structure of (first kind of Lithium-compounds) for ex: LiTiS₂, LiVSe₂, LiCoO₂, LiNiO₂; (b) three dimensional spinel structure; (c) structure of V₂O₅ showing the square pyramids sharing edges of the basal planes; (d) Crystal structure of LiFePO₄ (Li, Yao et al. 2008)

The first kinds of Li-ion batteries were made used LiTiS₂ (Vincent 2000) as cathode material, followed by LiCoO₂, LiNi_{1-y}Co_yO₂, and LiNi_yMn_yCo_{1-2y}O₂. The spinels, [Figure 11.b](#), may be considered as a special case where the transition-metal cations are ordered in all the layers (Fergus 2009). The materials in the second group have more open structures, like many of the vanadium oxides, [Figure 11.c](#), the tunnel compounds of manganese dioxide, and most recently the transition-metal phosphates, such as the olivine LiFePO₄, [Figure 11.d](#). The first group, because of their more compact lattices, will have an advantage in energy stored per unit of volume, while the second group compounds such as LiFePO₄, are of much lower cost. Some of the preferred chemistries are discussed below.

LiCoO₂

One of the most popular cathode materials for lithium-ion batteries is lithium cobalt oxide. LiCoO₂ forms the α -NaFeO₂ structure, a distorted rock-salt structure where the cations order in alternating (1 1 1) planes. This ordering results in a trigonal structure, the planes through which lithiation (intercalation of Li-ion) and de-lithiation (de-intercalation) can occur, Figure 11.a.

One of the drawbacks however is that, Cobalt is more costly than other transition metals such as manganese, nickel and iron. Other problems with LiCoO₂; is that it is not as stable as other potential electrode materials and can undergo performance degradation or failure when overcharged. Several reasons have been given for the degradation during cycling. One is that cobalt is dissolved in the electrolyte when the electrode is delithiated during charging, such that less lithium can be intercalated during discharge. Another is that the CoO₂ layer formed after full delithiation shears from the electrode surface, which also results in less capacity for lithium intercalation. In addition, there is a sharp change in lattice parameter with change in lithium content, which can lead to stresses and micro-cracking of the cathode particles.

LiNiO₂

LiNiO₂ (Fergus 2009) has the same structure as of LiCoO₂, but is cheaper and has a higher energy density (15% higher by volume, 20% higher by weight), but is less stable and less ordered, as compared to LiCoO₂. The lower degree of ordering results in nickel ions occupying sites in the lithium plane, which impedes lithiation/delithiation and also creates challenges in obtaining the appropriate composition. Its structure is very unstable in the overcharge state and it is difficult to make a perfect structure at industrial scale. The addition of cobalt to LiNiO₂ increases the degree of ordering, which leads to nickel ions occupying sites in the nickel/cobalt plane rather than in the lithium plane. Thus, LiNi_{1-x}Co_xO₂, typically containing mainly nickel (x~0.8), has been used to take advantage of the low cost and higher capacity of nickel relative to cobalt.

Li₂Mn₂O₄

Manganese oxides are among the most popular cathode materials in primary lithium batteries due to abundance of manganese; low cost, favorable charge density, rather high electronic conductivity, better stability on overcharge and suitable electrode potential (Ohzuku and Brodd 2007). Three-dimensional framework structures of LiMn₂O₄ or the spinel structures have cross-linked channels allowing ion insertion, Figure 11.b. The size of the channels must be sufficiently large to accommodate the ions. The advantages of three-dimensional frameworks over two-dimensional layered structures like LiCoO₂ are: the possibility of avoiding the co-insertion of bulky species such as solvent molecules, the smaller degree of expansion/contraction of the

framework structure upon lithium insertion / de-insertion. The spinel structure is the reason this is a more commonly used chemistry for larger batteries. However, compared to the others it suffers from a smaller energy density and a lower chemical stability, inducing a shorter life especially at high temperature (Whittingham 2004).

LiFePO₄

The high cost, toxicity (LiCoO₂), safety hazards and chemical instability (LiNiO₂, and LiMn₂O₄) of the conventional cathode materials prohibits their use in biomedical applications. A promising class of cathode materials are lithium phosphates (LiMPO₄) with the olivine structure in which phosphorous occupies tetrahedral sites, the transition metal (M) occupies octahedral sites and lithium forms one-dimensional chains along the [0 1 0] direction. The phosphate most commonly used for the cathode is LiFePO₄, Figure 11.d, which delithiates to FePO₄ as the Fe²⁺ is oxidized to Fe³⁺. Some iron ions occupy lithium sites, which results in the formation of Li-ion vacancies to maintain charge. There is a miscibility gap between FePO₄ and LiFePO₄, so the delithiation occurs by growth of a two-phase material rather than a continuous change in lithium content (Fergus). The formation of a two-phase mixture establishes a fixed activity, which results in a relative flat discharge profile. This makes it a promising cathode material for lithium rechargeable batteries.

Table 3: Various lithium-ion cathode chemistries with their respective average voltage and energy densities [83]

Active Material (Cathode)	Average Voltage	Energy Density
LiCoO ₂	3.7 V	110-190 Wh/kg
LiMnO ₂	4.0 V	110-120 Wh/kg
LiFePO ₄	3.3 V	95-140 Wh/kg
Li ₂ FePO ₄ F	3.6V	70-105 Wh/kg
LiNi _{1/3} Co _{1/3} Mn _{1/3} O ₂	3.7 V	95-130 Wh/kg

1.4.3 ADHESIVES & POLYMERS

The electrodes of a lithium-ion battery (LIB) are composite active materials that need to be bound to the conductive substrates. Proper binding is necessary to efficiently move the charged particles to the surface of the electrochemically active material particles. The binder additive is a combination of several polymers and organic additives that perform critical multiple roles. Such a complex medium is generally obtained by mixing together the active material grains with non-electron-active additives such as a very fine powder of conductive carbon and a binder. The carbon additive helps electronic movement of the charged particles within the composite electrode improves electronic contacts between particles in the active layer (Lestriez 2009). Tape casting is popular in the electrode manufacturing processes. A slurry of active material, con-

ductive carbon and binder mixture is prepared through ball milling. This slurry is then cast in a slot-die or rolled.

After drying, composite electrodes are usually pressed down to about 30–40% porosity using a rolling machine or hydraulic press. This treatment is essential for obtaining simultaneously high energy, high rate and good cycling stability. The composite obtained films are porous and electronically conducting. They are then impregnated by the liquid electrolyte during the battery assembly. For long-lasting battery operation, the composite electrode needs to be chemically and electrochemically stable. It also needs to maintain a good mechanical cohesion in the presence of the liquid electrolyte and during the volume changes which occur when inserting and extracting Li^+ ions within the active material grains.

Polymers with higher electrochemical stability such as poly tetra-fluoroethylene (PTFE), or poly vinyl di-fluoride (PVdF) have been most widely adopted as the binder for composite electrodes in Li-ion battery (Babinec, Tang et al. 2007). A copolymer of vinylidene fluoride with hexafluoropropylene, (PVdF-HFP), is used in both polymeric electrolyte and composite electrode of the plastic lithium-ion battery technology (Tarascon, Gozdz et al. 1996). A significant amount of research has been conducted to replace the PVdF binder, because of its high cost, insufficient mechanical properties strong binding strength, low flexibility and stability aspects.

Also an attempt has been made to switch from the non-aqueous to the aqueous processing techniques, to reduce the cost, the safety and due environment concerns associated with the use of the organic solvents for PVdF, i.e., N-methyl-2-pyrrolidone, NMP. Aqueous binders will thus gradually replaced PVdF for the anodes binding. Similar work is being done for cathode as well.

Examples of other binders are poly ethyleneoxide (PEO), poly acrylonitrile-methyl methacrylate (PMMA), aromatic polyimides, and polypyrrole for non-aqueous processing; gelatin, poly acrylamide-co diallyldimethylammonium chloride (AMAC), and polyacrylic acid (PAA) for aqueous processing. Many Combinations of polymers have also been proposed for the aqueous processing such as: Carboxy methyl cellulose (CMC), styrene-butadiene rubber latex (SBR latex), and PAA; acrylonitrile-butadiene (NBR) rubber latex and CMC; poly acrylic rubber latex (LA132) and CMC, ammonium polyacrylic acid (PAA-NH_4) and LA132; NBR, CMC and the iso-octylphenylether of polyoxyethylene (Lestriez 2009).

1.4.4 ELECTROLYTE

Progress in lithium batteries relies as much on improvements in the electrolyte as it does on the electrodes. The electrolyte provides for the movement of ionic transport and electronic transport, and in a perfect battery the Li-ion transport number will be unity in the electrolyte. Solid polymer electrolytes are currently the most popular electrolytes for Li-ion batteries. It is because they can offer an all-solid-state construction, good mechanical and electrochemical properties, a wide variety of shapes and sizes

and a higher energy density, no corrosive or explosives can leak out, and lesser internal short-circuits (Dias, Plomp et al. 2000) In true solid electrolytes only Li^+ ions are mobile. Other much less mobile ions in a solid electrolyte are arranged in a crystalline or glassy matrix in which Li^+ ions move through vacant and/or interstitial sites. This type of Li^+ transport occurs in inorganic solid electrolytes. At ambient temperatures the ionic conductivity of solid electrolytes is poor. In true solid electrolytes the contribution of the counter anion to the ionic conductivity is considerable. The most desirable polymer electrolytes are those formed by solvent free membranes, for example poly(ethylene oxide), PEO, and a lithium salt, LiX , like LiPF_6 or LiCF_3SO_3 . These are also referred to as high molecular weight dry polymers. In all cases, the battery electrolyte film is an amorphous lithium phosphorous oxynitride (Fergus ; Hong H 1977; Laudise R 1980; Korepp, Santner et al. 2006; Nakahara, Yoon et al. 2006; Tsujikawa, Yabuta et al. 2009), Recently K. Sit et.al., have shown that the crystalline complexes PEO: LiXF_6 ($X = \text{P}, \text{As}, \text{Sb}$) demonstrate good ionic conductivity. It has also been shown that the conductivity of the crystalline polymer electrolytes may be raised by two orders of magnitude by partial replacement of the XF_6 ions with other mono or divalent anions. Nanoscale inorganic fillers such as Al_2O_3 , TiO_2 and SiO_2 have been proved effective in enhancing the mechanical strength and conductivity of the polymer electrolyte (Bates, Dudney et al. 2000; Kawamura, Okada et al. 2006).

1.4.5 SEPARATORS

Separators main function is to keep the cathode and anode apart to prevent electrical short circuits and at the same time allow rapid transport of ionic charge carriers that are needed to complete the circuit during the passage of current in an electrochemical cell. A separator is a porous membrane placed between electrodes of opposite polarity, permeable to ionic flow but preventing electric contact of the electrodes. There are many different types of separators used in batteries; manufactured from cellulosic papers and cellophane to nonwoven fabrics, foams, ion exchange membranes, and microporous flat sheet membranes made from polymeric materials. As batteries have become more sophisticated, separator function has also become more demanding and complex. This requires the separators to be strong to avoid any contact between the electrodes through the separator. The separator also must not yield and reduce in width with either charge or discharge cycles, or else the electrodes may contact each other. Separators can be broadly classified into six types – micro-porous films, nonwovens, ion exchange membranes, supported liquid membranes, solid polymer electrolytes, and solid ion conductors (Arora and Zhang 2004). The solid polymer electrolyte usually used in thin polymer film Li-ion battery acts both as an electrolyte and separator.

2. LITHIUM: RESOURCES & ITS APPLICATIONS IN OTHER INDUSTRIES

Lithium can be found in brines, pegmatites, and sedimentary rocks. Brines containing lithium make up 66% of the world's lithium resource; pegmatites make up 26% and sedimentary rocks make up 8%, (Paul Gruber 2010)

The lithium content on average in earth's crust is about 20 ppm. The lithium content is divided between the lithologies and aquatic regimes as: basic rocks 17 ppm lithium, intermediate rocks 20 ppm lithium, syenite 28 ppm lithium, granite 40 ppm lithium, shales 66 ppm lithium, sandstone 15 ppm lithium, carbonate rocks 5 ppm lithium, river water 3 ppm lithium, seawater 180 ppb lithium; (Dill). In this section the sources of reserves, major producers and consumers are presented along with a brief note about industries which also use lithium in their products other than the battery industry.

2.1 LITHIUM SOURCES

Lithium is widely distributed in trace amounts in most rocks, soils and natural waters. However, the actual concentration can vary greatly. The different minable sources can be broadly classified to rock forming ores and brines.

2.1.1 LITHIUM MINERALS

Pegmatites are an exceptionally coarse-grained igneous rock with interlocking crystals, normally found as irregular dikes, lenses or veins, especially at the margins of large bodies of (solidified) magma flow. Most grains are 1 cm or more in diameter and the pegmatite's composition is usually that of granite. The need for favorable circumstances such as continued flow of magma with slow cooling has resulted in only a small fraction of the world's pegmatites having high lithium content. Some common lithium based minerals are spodumene (8.03% Li_2O), lepidolite (7.7% Li_2O), petalite (4.5% Li_2O) and amblygonite (7.4% Li_2O). It has been studied that concentrations exceeding 0.5% Li_2O are feasible to extract lithium.

The pegmatite ore is first crushed and ground to 100% finer than 0.3 mm and cleared with caustic, sometimes with sodium sulphide added as a dispersant. Then the ore is conditioned with a collector like oleic acid (Averill and Olson 1978). But when it is in a mineral form such as spodumene then the lithium is leached out of the mineral using acids such as sulphuric acid and the lithium sulphate is purified by addition of other salts and evaporating.

2.1.2 LITHIUM BRINES

Brines are mineral salt concentrated waters undergoing evaporative concentration and precipitating a sequence of minerals in order of increasing solubility (Risacher, Alonso et al. 2003). The brine is pumped from subsurface deposits in dry salt lakes for concentration by evaporation, due to the evaporation of water, other salts present in the brine precipitate first and get separated. The lithium-containing concentrated brine is then precipitated as Li_2CO_3 by carbonation. The efficiency of the concentra-

tion depends on the evaporation rate (influenced by average temperature, wind, humidity and therefore of topography (Paul Gruber 2010).

ELECTROWINNING

To get pure lithium, electrowinning of the precipitated lithium carbonate from brines or pegmatite is used. Lithium metal is extracted by a process in which the the lithium is electrolytically reduced from a fused mixed salt of potassium chloride and lithium chloride with 40% lithium chloride,(Averill and Olson 1978).

Table 4: Ore deposit estimates and Brine reserve estimates around the world in various countries(1990-2002) (Garrett 2004).Estimated Lithium Reserves of Various Lithium Deposits, 1000 mt lithium.

Countries	Ore Deposits	Brine Lakes	Reserves
Africa (other)	>0.3	Salar de Uyuni , Bolivia	5000
Bikita, Zimbabwe	23	Salar de Atacama , Chile	4300-4600
Mali	26	Salar de Hombre Muerto	800
Manono-Kitotolo, Zaire	309	Clayton Valley	115-382
Namibia	9.8	Zabuye Salt Lake, China	1000
Argentina	0.2	Qinghai Lake, China	1000
Australia (Greenbushes)	150	Smackover oilfield brine	1000
Austria	10	Great Salt Lake	526
Brazil	3.3	Searles Lake	31.6
Canada (total)	240.5	Salton Sea	1000
Bernic Lake, Manitoba	73	Dead Sea	2000
Ontario, Quebec	139		
China	500		
Portugal	10		
Russia	130		
United States (other)	44.3		
North Carolina	71		
Total	1739 approx	Total	14718 approx



Figure 12: A photo of the Salar² de Atacama, Chile(Scrosati 1997)(Scrosati 1997)(Scrosati 1997)(Scrosati 1997)(Scrosati 1997)(Scrosati 1997)(Scrosati 1997)

² A salar is a salt pan, created when water repeatedly evaporates from a shallow lake, leaving behind a crusty layer of salt minerals, which are brilliant white in this image. Unlike many salt pans in the region in and near the world's driest desert, the Atacama Desert, Salar de Atacama receives enough rainfall to occasionally be covered by a thin layer of water. The water evaporates or percolates through the salt crust to form a layer of brine. The brine in Salar de Atacama is rich in lithium

2.2 PRODUCERS AND CONSUMERS

Although the mineral production is dominated by South America, with more than 50% concentrated between Chile and Argentina, production companies are dominated by the developed countries like Australia, Germany, USA, Canada and Norway ; and in that order, (Jungst, G. Pistoia et al. 2001). The published production with respect to reserves for 2008-2009 are shown in [Table 5](#).

Table 5: World Mine Production and Reserves(1000mt)

Country	2008	2009 (estimate)	Reserves ³	Reserve Base ⁴ (2007)
Chile	10,600	7,400	7,500,000	3,000,000
Argentina	3,170	2,200	800,000	2,000,000
China	3,290	2,300	540,000	1,10,000
United States	---	---	38,000	410,000
Australia	6,280	4,400	580,000	260,000
Canada	690	480	180,000	360,000
Portugal	700	490	---	---
Zimbabwe	500	350	23,000	27,000
Afghanistan	----	---	----	----
World total (rounded)	25,400	18,000	9,900,000	13,800,000

It should be noted that the revised 138×10^8 mt seen above, is very low compared that quoted by the Lithium-handbook ([Table 4](#)). Also the reserve bases have not been updated since 2007 and show an obvious disagreement with reserves in 2009..

³ Reserves are that part of the Reserve Base which could be economically extracted or produced at the time of determination. The term 'reserves' need not signify that extraction facilities are in place and are operative. Reserves include only recoverable materials.

⁴ Reserve Base is that part of an identified resource that meets specified minimum physical and chemical criteria related to current mining and production practices, including those for grade, quality, thickness, and depth.

2.3 OTHER CONSUMERS

The major consumer until 2006, [Figure13](#), was the ceramics industry; The United States is at present the leading consumer of lithium minerals and compounds and the leading producer of value-added lithium (using) materials, (Jungst, G. Pistoia et al. 2001). Few of the many utilities of lithium in other industries other than batteries have been described below.

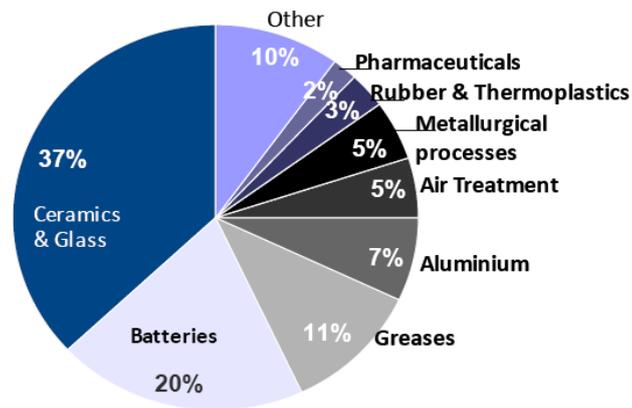


Figure 13: Share of lithium using Industries

2.3.1 GLASS , CERAMICS , ENAMEL INDUSTRIES

Lithium is used in many glass and ceramic industries for varied purposes. It reduces melting temperatures and improves forming properties. In Pyro-ceramic ware lithium additions helps achieve zero coefficient of expansion and improves forming characteristics. In fibreglass it reduces viscosity, improves continuity of fibre production and in safety glasses it helps improve strength. Lithium is also used in optical glass ceramics for high performance telescopes requiring extremely low linear thermal expansion. Lithium imparts desirable properties to both enamels and glazes. Enamel is a glass-like coating bonded to a metal. Lithium addition can prevent against forming frits, to make aventurine, corrosion-resistant (“glass”) coatings for steel tanks, in high-voltage porcelain because of its low coefficient of expansion, leadless glazes for dinner ware, opaque and crystalline glazes, and to produce white ware. (Garrett 2004).



Figure 14: Examples of glass ceramics for telescopes; left, support; right, 8.6 m dia mirror (Garrett 2004)

2.3.2 GREASE INDUSTRY

Lithium hydroxide is used in making greases like lithium stearate (Fenton Walter, Esmay Donald et al. 1957). About 60% of all industrial greases contained lithium in 1993. Lithium stearate is a matrix or sponge-like gel lubricant where the lithium attaches to the metal, and the long-chain multi-hydroxyl end of the stearate molecule extends outward in the form of interlocking spirals to hold the petroleum lubricant and cushion the wearing surface. Mixtures containing 5–10% of the lithium soap are an excellent lubricant for bearing surfaces, since they are almost totally water insoluble, and stable in consistency over a range of shear and temperatures from -55 to 200°C. The gel holds a high volume of oil, resists oxidation and hardening, and on liquefaction will reform as stable grease upon being cooled. Because of these qualities the grease is used over a wide variety of demanding industrial & machine applications.

2.3.3 ALUMINUM ELECTROLYSIS

Lithium is used in the aluminum industry (Garrett 2004) to lower the (electric) reduction cell's temperature and reduce the fluorine emissions from the electrolytic cells by 25–50%. About 1–3% LiF in the bath or 2 kg lithium carbonate/mt of aluminum is needed. Lithium carbonate reacts with the cryolite (Na_3AlF_6) “solvent” in the cell to form lithium fluoride, which has a very high fluxing ability, electrical conductivity and low volatility. Lithium is most beneficial for older plants, where it can reduce the energy costs by 5–10%, and bring the cell efficiency up to 90–95%. However, most of the lithium was used to initially charge the cells. However, the more modern cells the energy efficiency is already at 90–93% and lithium can only add 1–3% greater efficiency. Lithium alloys with aluminum retain high strength even at high temperatures up to 204 °C and increases the modulus of elasticity by about 8%.

2.3.4 AIR TREATMENT

Concentrated lithium bromide brines (54%) are widely used in aqueous solution as an absorption medium in the industrial absorption refrigeration (absorbs heat and uses heat to power the cooling systems) (Goldstein, Eckert et al. 2002). These refrigerating units are used mainly in hotels, apartment buildings, hospitals, etc. for air conditioning and process cooling. Lithium chloride solutions are used in industrial humidity control and drying systems of comparable construction. These systems have the added advantage that the lithium chloride destroys micro-organisms, bacteria, etc. Anhydrous lithium hydroxide and peroxide serve for the removal of carbon dioxide from the air (Garrett 2004).

2.3.5 CLINICAL USAGE

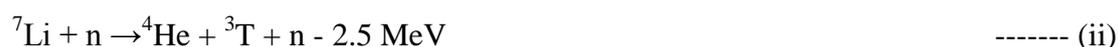
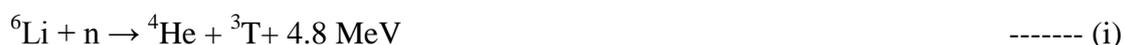
Lithium salts have had a major impact in the medical treatment of bipolar affective disorder. Long term treatment of bipolar patients has resulted in considerable reduction in the re-hospitalization rates for this condition. Lithium clinics provided an early model for the psychopharmacologic treatment of individuals with other mental disor-

ders and the medical approach to the treatment of depression and in some trial cases alcoholism and drug abuse (Soares and Gershon 1998; Audet, Carney et al. 2008).

Li_2CO_3 is used in drugs treating asthma, thyroid diseases, granulo-cytopenia, headache, bowel disease, anaesthesiology, cardiology, and sleep disorders (Dunner, Neumaier et al. 2000).

2.3.6 NUCLEAR AND FUSION REACTORS

Lithium carbonate is both a raw material for the solid-state synthesis of some nuclear compounds and a pellet detector for estimation of tritium production rate in irradiated samples. Lithium as a solid compound, a pure melt, or a molten alloy is used for tritium breeding in at least the first generation of fusion reactors. To simulate sun's fission reaction and produce energy, we need both deuterium and tritium, the latter is not readily available on earth. But it can be produced by bombarding lithium with neutrons (Blink J, Krikorian O et al. 1982).



The two isotopes of natural lithium contribute to this breeding of tritium according to (i, ii) reactions. Lithium is also being used in fusion devices as a coating on vacuum vessel walls. It increases plasma performance by reducing impurities sputtering into the plasma (Blink J, Krikorian O et al. 1982). Lithium compounds are also used as coolants for the walls.

3. LI-ION BATTERIES FOR VEHICLES

There are many types of vehicles. These range from very large ones such as trams, trains, aircrafts, and cargos trucks to small ones such as forklift trucks and golf carts, all having different fuel needs. Cars and vans together are responsible for 17% of world locomotive emissions, which is higher than the share of aviation (12%) (Mock, Schmid et al. 2010).

For fuel cell hybrid electric vehicle (FCHEVs) and especially for (EVs), specific energy consumption is significantly lower than for Internal combustion engine (ICE) vehicles, owing to their higher degree of efficiency of energy conversion, [Figure15](#). The specific energy density of a battery (X-axis, figure15) is the nominal battery energy per unit mass, also called the gravimetric energy density, previously. Batteries play a major role as a critical component in many respects, such as energy and power capability, life, safe use and cost. Li-ion batteries can offer superior characteristics as mentioned earlier (Chapter2).

Li-ion batteries using the chemistries described in Table 2, are under consideration for many hybrid and fully electric car batteries. An overview of hybrid and electric cars is given below. A brief survey of the fleet of cars, their respective companies is also presented along with the chemistry of the battery on board.

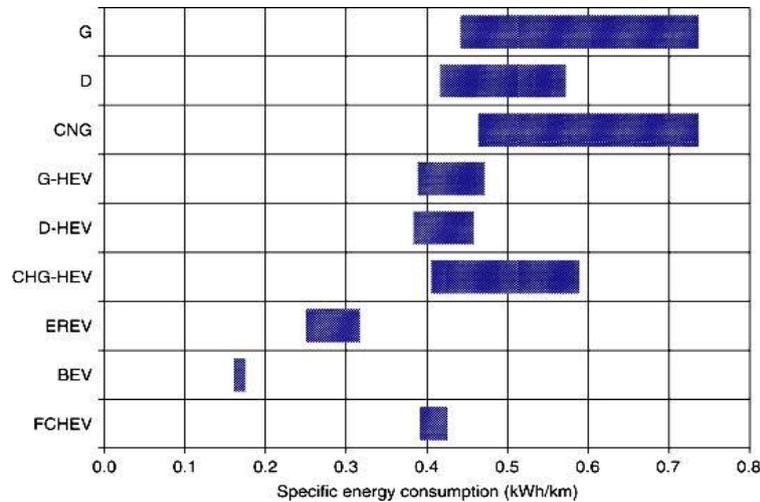


Figure 15 Specific energy consumption vs. vehicles types assessed (for a medium size passenger car). BEV- battery electric vehicle; CNG-compressed natural gas; D-diesel; EREV- extended range electric vehicle; FCHEV-fuel cell hybrid electric vehicle; G-gasoline; HEV- hybrid electric vehicle; ICE- internal combustion engine (Mock, Schmid et al. 2010)

3.1 HYBRID ELECTRIC VEHICLES (HEV) AND PLUG-IN HYBRID VEHICLES (PHEV)

The HEV does not need to be plugged into an electrical outlet to recharge. Hybrids use a conventional fuel or an alternative fuel along with a battery. Fuel motors switch on automatically when the battery gets low, and proceed to charge the battery. Therefore, hybrid cars still use gasoline unlike the electric cars.

A (full) hybrid vehicle allows starting and driving with the electric motor alone. It has however limited motor and battery size because of its dependence on conventional fuel for power/ even battery charging. There are micro, mild versions of hybrid depending on the battery capabilities. In a full-hybrid system, the following characteristics are present; Power supply to electrically driven accessories, Stop & start, Inactive timing system, Power supply for traction purposes; in particular the electric motor provides power when torque peaks must be reached. For example, at the start brake energy regeneration Regenerative braking uses kinetic energy to recharge the battery when the vehicle slows down. An idling or stopped hybrid car automatically uses electrical power. Once the car begins to accelerate, it reverts to using the fuel engine. Different models of cars vary in terms of when the electric power is used (German and Cutler 2004).

As many as 47 auto-mobile manufacturers and many small scale manufacturers are putting out their models of Hybrid electric Vehicles most of which were brought in to

market already (2010) and the rest are predicted to be brought in by 2011 (Ritchie 2001). Although their (various HEV's) initial battery chemistries are unknown, it is noted that most of them are switching to Li-ion batteries (Orecchini and Santiangeli).

Table 6: Some of the HEV's whose battery chemistry is lithium- based

Battery Developer	Chemistry	Company (Hybrid)	Year
A123	Doped Lithium phosphate (nano)	-Saturn view plug-in	2010
Panasonic EV	Li Ni Co Al Oxide	-Toyota Plug-in	-2010
EnergyJohnson Controls or Saft		-Mercedes	-2009
		-Saturn view plug in	-2009
Hitachi	Li/Mn Oxide	Future GM Hybrids	2010

Plug-in hybrid electric vehicles (PHEV) offer the possibility of recharging the batteries onboard from an electrical socket and the capacity to guarantee all-electric driving for a distance that is sufficient at least for daily average urban driving, i.e. from approximately 15 to above 100 km. It can also run on internal combustion engine (ICE) or any other alternative fuel depending on requirement.

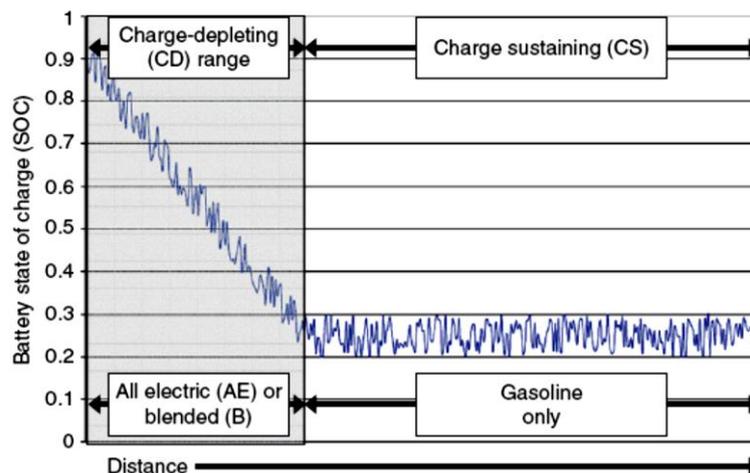


Figure 16 Typical charge of PHEV discharge cycle; 65% DOD (Axsen, Burke et al.)

In contrast to HEV a PHEV is charged from electricity output and not from fuel combustion within the ICE (Orecchini and Santiangeli). A PHEV can operate in one of

two modes: Charge Sustaining (CS) or Charge Depleting (CD) which is illustrated in , [Figure 16](#). In practice, the battery's maximum State of Charge (SOC) may be limited to less than 100% , and the minimum SOC constrained to more than 0%, both to preserve battery life and to improve safety. The difference between the maximum and minimum SOC is known as the usable Depth of Discharge (DOD), which varies across battery and vehicle designs (Axsen, Burke et al.). A comprehensive list of the HEV's put forward by various automotive industries is provided at Annex C (Ritchie 2001).

Table 7: PHEV Battery chemistries and their respective qualitative assessment(Axsen, Burke et al.)

Name	Description	Automotive status	Power	Energy	Safety	Life	Cost
NiMH	Nickel-metal hydride	Commercial production	Low	Low	High	High	Mod
LCO	Lithium cobalt oxide	Limited production	High	High	Low	Low	High
NCA	Lithium nickel cobalt and aluminum	Limited Production	High	High	Low	Mod	Mod-High
LFP	Lithium iron phosphate	Pilot	Mod-High	Mod	Mod-High	High	Low
NCM	Lithium nickel, cobalt, manganese	Pilot	Mod	Mod-High	Mod	Low	High
LMS	Lithium manganese spinel	Development	Mod	Low-Mod	Mod-High	Low-Mod	Low-Mod
LMO	Lithium manganese oxide	Development	High	Mod-High	Mod-High	Mod-High	Mod
LTO	Lithium titanium oxide	Development	High	Low	High	High	Mod
MNS	Manganese titanium	Research	High	Mod	High	Unknown	Mod

3.2 COMPLETE ELECTRIC VEHICLES (EV)

EV's use electricity directly as a fuel and the source of electricity can be traditional power grid, solar cells or other sources of electricity. Since there is no internal combustion engine (ICE) the efficiency is almost 90-95% and vehicles run noiselessly.(Dhameja 2002) There are no emissions from EV's; hence they are environment-friendly (although it depends on the source of electricity). Once the charge units are placed and the infrastructure is built, EVs may require lesser investment on maintenance (van Vliet, Kruithof et al.). Now many of the major manufacturers are gearing up for complete electric vehicle.

A market study of the EV battery chemistry presented in [Table 8](#), will signify the role of the Li-ion battery in the electric car technology.

Table 8: Some of the EV's which employ Li-ion batteries (Li, Ge et al. ; Motors ; Pranolo, Zhang et al. ; Shin, Kim et al. 2005; Balakrishnan, Ramesh et al. 2006; Nan, Han et al. 2006; Pistoia 2009; Wang, Lin et al. 2009)

Company	Model Name	Battery	Battery Developer	Price USD	Vehicle preview	Sales Sold vs. Estimate
BYD, China	E ₆	60kWh Lithium ion, Fe based	BYD	\$43k		2900 test lease contracts, as opposed to 1100 target
Tesla	Roadster sport, Roadster	53 kWh Li-ion	Tesla	\$109-59k		1200 as of June 2010
BMW	Megacity	35kWh Li-ion (Ni-Mn-Co)	Bosch JV	— due 2013		---
CODA made in China (US market)	Hafei Saibao 3	37kWh Li-ion (LiFePO ₄)	Lio Energy Systems (Coda & Lishen Power Battery)	\$40k		9000 in 2010 and 30,000 there after.
Mercedes	Blue ZeroE-Cell	35kWh Lithium	---	due 2011		----
Ford	Focus	23kWh Li-ion	Ford	due 2011		5000-8000
Volvo	C ₃₀	24kWh Hard carbon/ Li-ion	EnerDel	2011		----
Nissan	Leaf	24 kWh Li-ion battery	Automotive Energy Supply Corporation (AESC)	\$32k		25000 orders for delivery in 2011 confirmed

Renault	Fluence ZE	22kWh Li-ion battery	-----	due 2012		660 in 2010 as test car models
BMW	Mini E	35kWh Li-ion	Hybrid Technologies	850\$/month ; 1 year lease		Only 500 released
Tayota	FT	Vn based i think based on iQ	Panasoni-c EV Energy Compan-y LTD	2012		-----
Subaru	R ₁ e G ₄ e	Mn/Li-ion Batteries Vn based lithium-ion	NEC			40 cars in Japan in 2008, 3000 was the target for 2009 -----
Mitsubishi	iMiEV	16kWh Li-ion	Lithium Energy Japan	small 2009 \$44k		2400 test lease units sold
EnerDel (former ford)	Th!nk City	22kWh Li-ion , zebra so- dium	EnerDel	Small 28kUSD		Atleast 60,000 every year in only US by the end of 2012 5000in Norway, Netherlands, Elkhart by 2011
Chevrolet GM	Volt	16kWh	LG Chem	2010		-----

4. NECESSITY TO RECYCLE LITHIUM BATTERIES (FROM ELECTRIC VEHICLES)

Electric vehicles (EVs) have been considered as a means to meet some of the CO₂ emissions and resource challenges of today's road vehicle system. EVs can be non-polluting, (if the source of charging can be derived for alternative sources and not conventional fuels) they are more energy efficient than pure internal combustion engine vehicles. However, mineral resource constraints and environmental concerns due to excessive mining, can become a severe problem. Large scale EV battery production will add to the stress on several metals the battery contains, inclusive lithium.

4.1 LITHIUM NEED

The lithium-requirement per cell (depending on the cell chemistry) can be of the range 0.24-12.7kg including cathode active material, lithium additive in electrolyte and additive anode, [Table 9](#), per battery pack (60 – 150 cells), Argonne Laboratory, 2009, (Gaines 2009).

Table 9: Predictions for the lithium-requirement per cell [29]; Lithium - nickel, cobalt, and aluminum - NCA-graphite batteries; Lithium-iron and phosphorus - LFP batteries; Lithium-manganese for both the LMO - graphite and LMO- titanium, LMO-TiO

Battery Type	NCA-G				LFP-G				LMO-G				LMO-TiO			
	4	20	40	100	4	20	40	100	4	20	40	100	4	20	40	100
Autorangeat 300Wh/mile	4	20	40	100	4	20	40	100	4	20	40	100	4	20	40	100
Li in cathode (kg)	0.34	1.4	2.8	6.9	0.20	0.80	1.6	4.0	0.15	0.59	1.1 8	3.0	0.29	1.2	2.3	5.8
Li in electrolyte(kg)	0.04	0.1	0.2	0.55	0.05	0.14	0.26	0.66	0.03	0.09	0.1 7	0.43	0.05	0.17	0.34	0.85
Li in anode (kg)	0	0	0	0	0	0	0	0	0	0	0	0	0.30	1.21	2.4	6.1
Total Li in Battery Pack (kg)	0.37	1.5	3.0	7.4	0.24	0.93	1.9	4.7	0.17	0.67	1.4	3.4	0.64	2.5	5.1	12.7

According to the survey made, [Table 8](#), if the EV production for 2011-2012 reaches 200,000 EV's, and then requirement for lithium be of the range 48 tonnes – 2.4 thousand tonnes. This implies that the growth rate of lithium consumption from 2009-2011 will be almost 150% considering only EV production, ignoring other manufacturing industries. From resources point of view this need for lithium growth will not be sustainable only depending on mining sources, [Table 7](#), also taking in to consideration growth in other lithium-using manufacturing sectors. With the need for more electric vehicles, the demand for lithium will increase.

In 1970, there were 200 million cars in the world. In 1990, there were almost 500 million, now there are about 600 million cars, and at-least half as many public transport vans, military vehicles, goods transport vehicles together. In 2011 (December) 56 million cars (worldometers) have been produced. If green future and minimizing carbon dioxide emission is the objective to achieve through electric transportation, then

the amount of lithium required to replace as many vehicles by battery run EVs just for just this half of year is above the produced lithium today. Other lithium dependent industries will add to the pressure on the lithium market, [Figure18](#) (Dundee 2009) . Recycling is a solution which will sustain the lithium-ion battery industry, recycling ensures the battery manufacturer with continuous supply of lithium (Baylis), [Figure17](#).

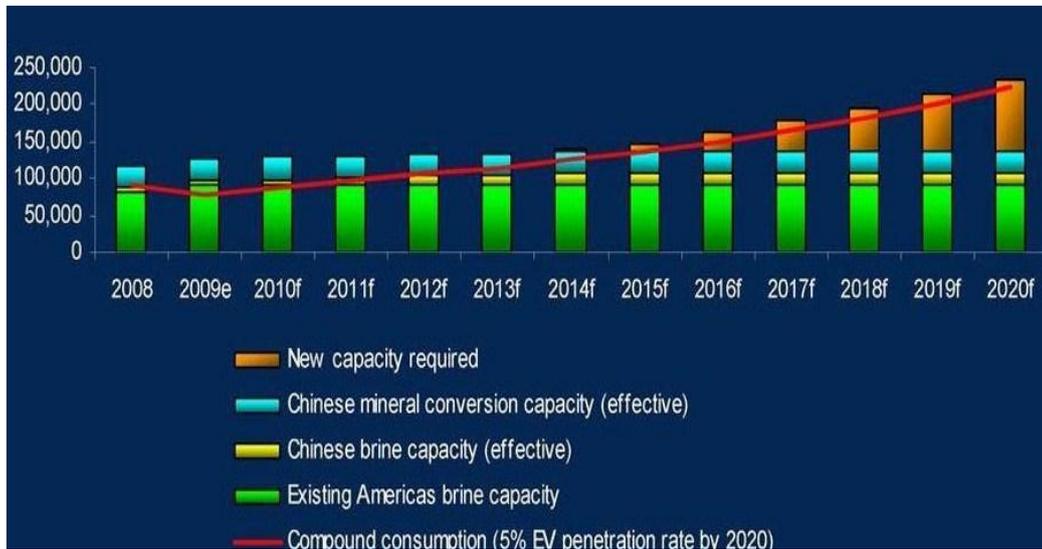


Figure 17: Analysts predict that the world production will not match the need for lithium as early as 2015 (Baylis).

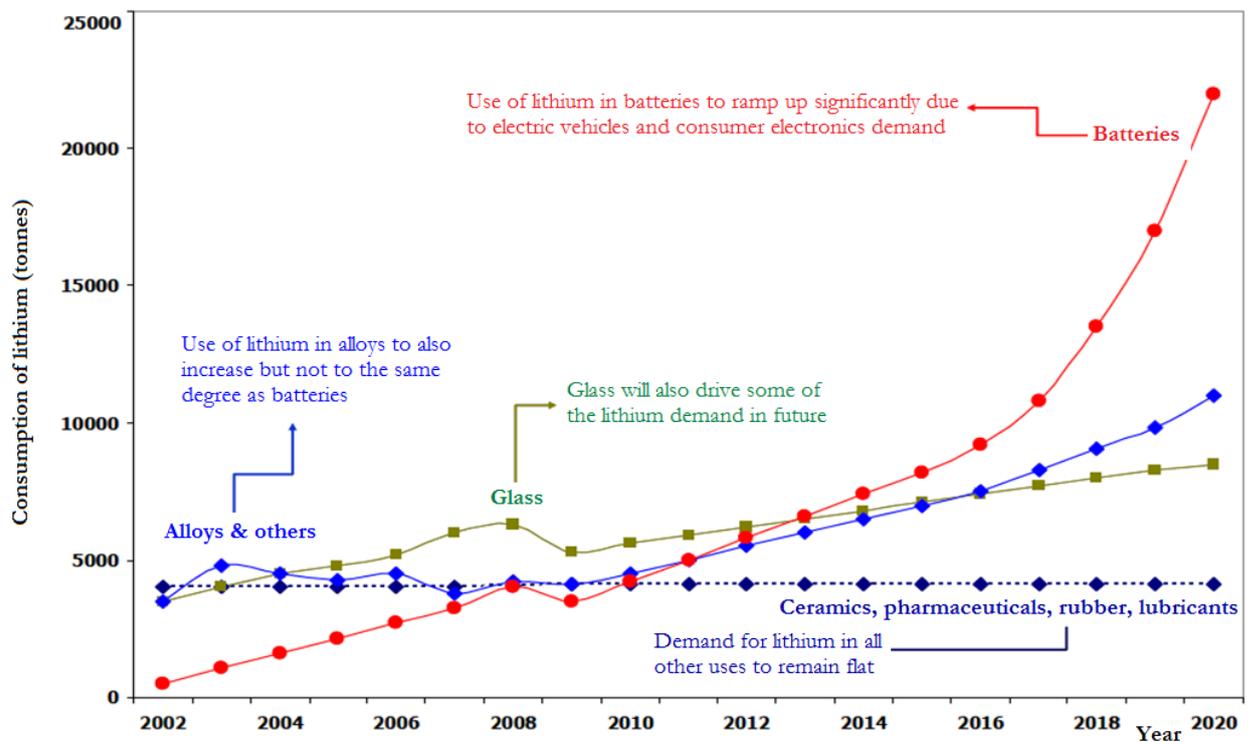


Figure 18: Estimates of the increase in consumption of lithium by various industries

4.2 THE CASE OF OTHER METALS

The batteries have other metals of value such as cobalt, nickel, aluminum, iron, manganese, titanium. The recovery of lithium will include recovery of these metals as well.

Table 10: Demand scenario of other metals present in the Li-ion battery (Gaines 2009)

Material	Availability (million tons)	Cumulative demand	Percent demanded	Basis
Co	13	1.1	9	World reserve base
Ni	150	6	4	World reserve base
Al	42.7	0.2	0.5	US capacity
Iron/steel	1320	4	0.3	US production
P	50,000	2.3	~0	US phosphate rock production
Mn	5200	6.1	0.12	World reserve base
Ti	5000	7.4	0.15	World reserve base

Recovery of metals from wastes have been reported (in an early study conducted by (Tytgat)) to be better in terms of energy saving resulting in their profitability in comparison to mining for minerals and processing the ores for their metallic content (in case of lithium, ores with percentages ranging from 0.6-10%, see Chapter 4) .

4.3 ENERGY RECOVERY AND ENVIRONMENTAL SAFETY

A battery recycling company (Tytgat) reported that their preliminary research shows recycling scenario result in a 51.3% natural resource savings, not only because of decreased mineral ore dependency but also because of reduced use of fossil resource (45.3% reduction) and nuclear energy demand (57.2%).

Land filling /dumping batteries is a waste of the metals, also the electrolytes might be harmful for earth. The European battery directive has not made a recycling suggestion specifically for Li-ion batteries yet but it might be in order very soon judging by the introduction of electric cars in to the market and EU's environmentally responsible directives. The present battery directive suggests that the manufacturers should be responsible for recycling. A brief summary of the present battery direct is given below. The recovery process has also shown to considerably reduce the release of greenhouse gas by replacing recovered metals instead of mineral mining operations for the production of new batteries (Tytgat).

The battery directive (Shin, Kim et al. 2005) is a comprehensive agreement which puts forth a number of regulations for the member states for the purpose of ensuring

better recycling of batteries and to eliminate any form of environmental pollution by producers, distributors, third party and end users due to the carelessness or due to lack of information, or regulations. The present directive quotes that the recycling of the batteries for hazardous substances is a must and is the responsibility of the producer, distributor and economic operators. Few of the regulations which are pertinent to industrial/automotive batteries have been isolated below for the purpose of this review, as Annex A. (Annex III is as quoted in the battery directive, hence the naming sequence is left as is, in the original document).

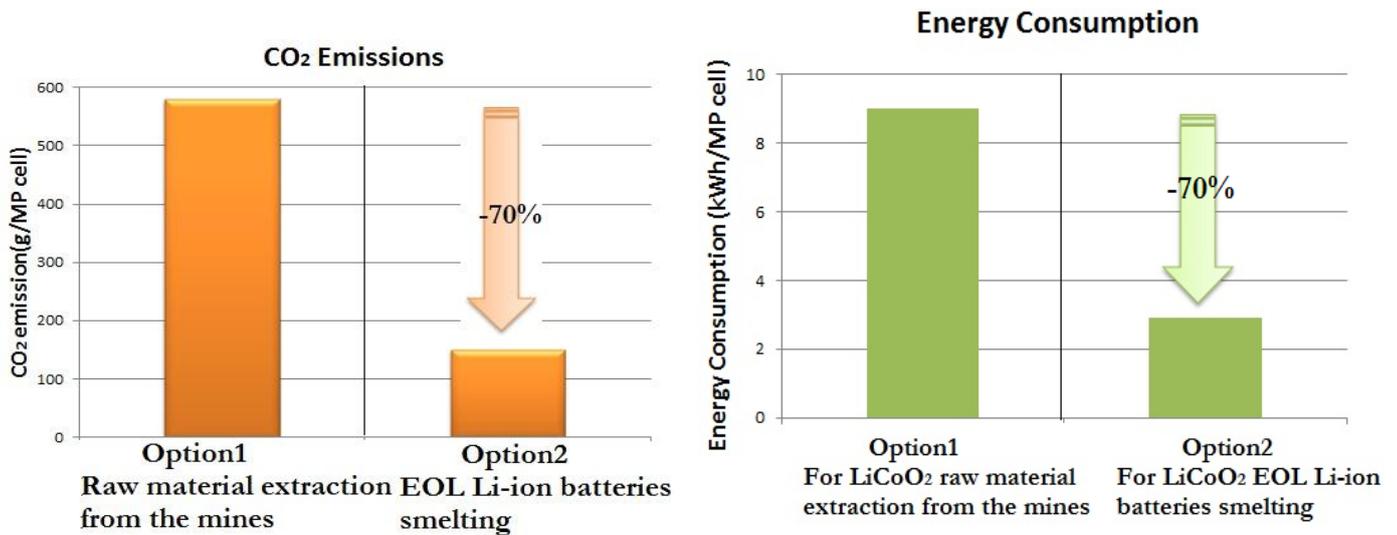


Figure 19: Preliminary recycling results indicate: (a) large energy conservation (b) Greenhouse-gas Emission reduction - with battery industry sustained by recycling.

For the reasons stated above, i.e., metal recovery, energy saving, environmentally friendly objectives a review of recycling process specifically for Li-ion batteries has been presented below. This review will yet give the reader a perspective and possible methods for recycling batteries, if not to the scale of electric car batteries or particularly lithium.

5. LI-ION BATTERY RECYCLING PROCESSES

The following recycling processes have been tried and few of them have been commercially established, many times in congruence with each other and more for the recovery of Cobalt in device scale batteries.

The first step in recycling is the stripping and separation of packaging, encasing so as to reach the chemically reactive substances, usually the anode, cathode, electrolyte and (sometimes) the separators.

5.1 PHYSICAL PROCESSES

Physical processes for recycling include any mechanical processes for the separation of materials according different properties such as density, conductivity, magnetic behavior, etc. Sometimes thermal processes are used with the production of steel, ferromanganese alloys or other metallic alloys. A common mechano-chemical (MC) process is a special grinding technique for LiCoO_2 chemistries that exposes greater surface areas so that the acid leaching is successful for the recovery of cobalt and lithium. Dissolution process use organic reagents (such as N-methylpyrrolidone) to dissolve the adhesive substance usually pVdF (Xu, Thomas et al. 2008).

5.1.1 MECHANICAL SEPARATION PROCESSES

Inert, dry atmosphere is suitable for mechanical processing of the batteries, as it avoids exposing the cell contents to water vapor which can hydrolyze the electrolyte. It also reduces the impact of internal short circuits which can be violent in contact with oxygen (Lain 2001). Mechanical processes involve crushing, sieving, magnetic separation, fine crushing and classification to yield a concentrated material for recovery using other processes. Two stages of crushing and sieving has been noted to give a satisfactory separation of the metal-bearing particles from the waste. A magnetic separator can be used for removal of steel casing. It has been studied (Shin, Kim et al. 2005) that mechanical separation done before leaching process not only improves the recovery efficiency of target metals but also eliminates the need for a purification process of the leachate.

Filtration is used both at the first level of stripping of casing and concentrating and at an intermediate step for example to separate pVdF, because it does not dissolve in acid solution, remains in the cake after filtration. Also, carbon from the cathode does not dissolve in acid solution, and instead it floats on the solution. When defining mechanical separation processes the factors that play an important role besides separating all the components from each other such as metals, organic substances, and inorganic substances is to minimize penetration and cross contamination (Shin, Kim et al. 2005).

5.1.2 THERMAL TREATMENT

Thermal process usually consists of furnace heating in controlled atmosphere to 100-150°C to separate out the insoluble organic additives and adhesives. This process is

also used as an intermediary step after each step of hot acid leaching. The time of heating is not standardized but never exceeds two hours (Xu, Thomas et al. 2008).

Sometimes the residues are also heated to separate metallic compounds from organic materials. For example; The solid residue coming from the HNO₃ acid leaching of spent lithium-ion batteries, consisted of iron, cobalt and nickel hydroxides mixture and some traces of Mn(OH)₃ (Shin, Kim et al. 2005). They were heated in a muffle furnace at 500°C for 2h to eliminate carbon and organic compounds.

Though thermal processes are useful for improving the recycling process, issues such as recovering organic compounds, purifying the smoke and gas resulting from combustion of carbon and organic compounds and any energy recovery, should all still be addressed.

5.2 CHEMICAL PROCESSES

Recycling through chemical processes include dissolution, acid and or base leaching, and precipitation.

5.2.1 ELECTROLYTE EXTRACTION

The liquid electrolyte is dispersed in the pores of the electrodes and separator. By immersing in a suitable solvent for a few hours, the electrolyte can be extracted. After separation from the residual solids, the solvent can be recovered by evaporation at reduced pressure, leaving pure electrolyte. Several liquids can be used as the extraction solvent. The main requirements are that the boiling point at reduced pressure is below the lithium salt decomposition temperature ($\sim 80^\circ\text{C}$), and that the material is available in an anhydrous state. If the electrolyte does not have volatile additives, the thermal treatment stated above is also often preferred to separate out the solvent (Lain 2001).

5.2.2 ELECTRODE DISSOLUTION PROCESS

The PVDF electrode binder is dissolved in an organic solvent. This process can be reversed to recover the electrode particles. The cell pieces are immersed in the solvent, which is stirred, heated to around 50°C. The binder re-dissolves, separating the electrode particles from the residual copper, aluminum, steel and plastic. The active material particles and substrate metals can be further separated based on their physical properties, e.g. density, magnetism. The electrode particles are filtered from the binder solution, which is then concentrated to recover the bulk of the solvent for reuse(Lain 2001).

In a method quoted in (Xu, Thomas et al. 2008) the battery rolls were treated without the separation of anode and cathode electrodes with (NMP) at 100°C for 1h and CoO₂ was efficiently separated from their support substrate and recovery of the substrate metals both Copper and Aluminum. This method is useful only in case of only a certain adhesive agent and electrode rolling method. The solvent used for dissolving the PVDF (binder) is N-methylpyrrolidone (NMP)

5.2.3 ACID LEACHING

The electro-chemically active material that has been separated from its packaging such as plastic, ferrous materials through preliminary treatment step, is leached by an acidic solution in order to transfer the metals from the used compound form in to the leachate solution. As shown in [Table 11](#). Almost all the experimental results indicated that the leaching efficiency of Co is highest in hydrochloric acid (Xu, Thomas et al. 2008). These experiments are only valid with the LiCoO_2 compound.

Table 11: Selective leaching (Xu, Thomas et al. 2008)

Leaching Agent mol.l^{-1}	Temperature $^{\circ}\text{C}$	Time (h)	S/L ratio (g.ml^{-1})	Reduction agent	Result
4 HCl	80	1	1/10	No agent	100% Li, Co
2 HNO_3	80	2	-	No agent	100% Li
1 HNO_3	75	1	1/50	1.7% H_2O_2	85% Li, Co

5.2.4 SOLVENT EXTRACTION

Some special extractants were studied to recover cobalt, lithium and copper from batteries; For example di-(2-ethylhexyl) phosphoric acid (D2EHPA), bis-(2,4,4-trimethyl-pentyl) phosphinic acid (Cyanex 272 or BTMPPA), trioctylamine (TOA), diethylhexyl phosphoric acid (DEHPA) or 2-ethylhexyl phosphonic acid mono-2-ethylhexyl ester (PC-88A) (Pranolo, Zhang et al. ; Contestabile, Panero et al. 2001; Shin, Kim et al. 2005; Nan, Han et al. 2006; Wang, Lin et al. 2009).

A hydrometallurgical plant involving metal purification/separation by liquid–liquid extraction with Cyanex 272 (bis-2,4,4-trimethylpentyl phosphinic acid) as extractant, was found to be technically viable to separate base metals from NiCd, NiMH and Li-ion Batteries [86].The method comprised leaching with sulphuric acid and metal purification/separation by liquid–liquid extraction with Cyanex 272 (bis-2,4,4 trimethylpentyl phosphinic acid) as extractant, after the preliminary separation. It was reported that high recoveries of recycled metals such as cobalt, nickel, copper and lithium could be achieved at high purities.

5.2.5 CHEMICAL PRECIPITATION

Chemical precipitation methods for recycling spent Li-ion Batteries are methods which use precipitation agents like basic solutions. To precipitate metals dissolved in the acidic medium, the following procedure was followed; sorting, crushing and riddling, selective separation of the active materials, lithium cobalt dissolution and cobalt hydroxide precipitation. The cobalt dissolved in the hydrochloric solution (in the acid leaching phase) was recovered as cobalt hydroxide $\text{Co}(\text{OH})_2$ by addition of one equivalent volume of a 4M NaOH solution.

The precipitation of cobalt hydroxide begins at a pH of 6 and can be considered to be completed at pH 8. Ideally, $\text{Co}(\text{OH})_2$ precipitation can be obtained by using an ammonia solution, a weak base, which forms a buffer solution at pH 9. However, ammonia forms stable complexes with cobalt causing the partial dissolution of the hydroxide and thus, preventing from a quantitative recovery. Therefore, NaOH, remains the best choice (Shin, Kim et al. 2005; Xu, Thomas et al. 2008).

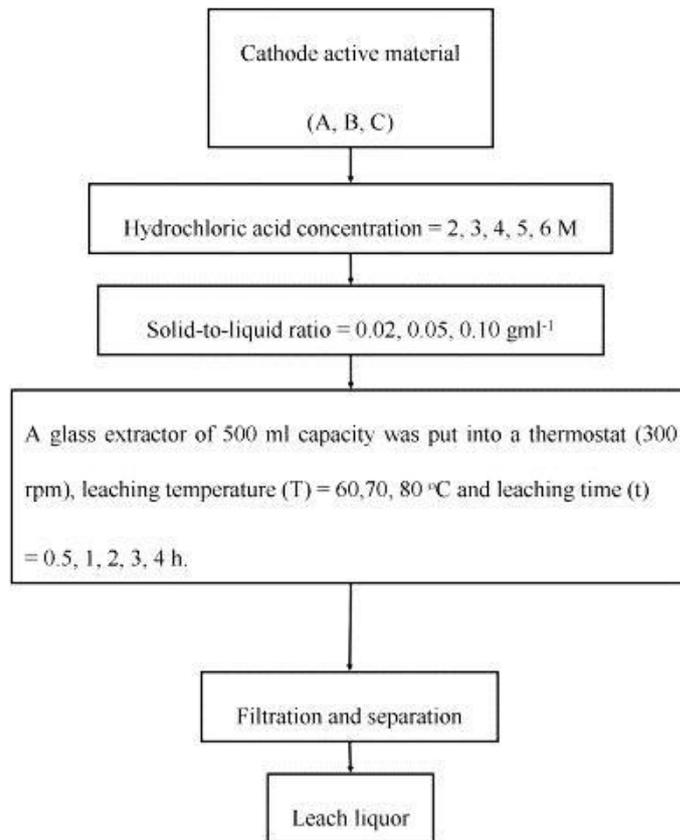


Figure20:Experimental sequence for leaching using HCl (Xu, Thomas et al. 2008).

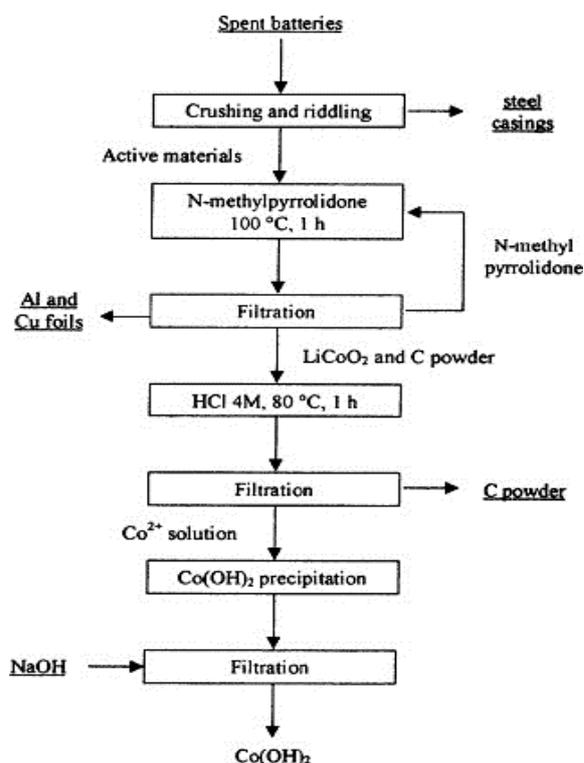
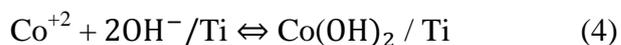


Figure 21: Sheet of recycling process, inclusive of precipitation method (Xu, Thomas et al. 2008).

5.3 ELECTRO CHEMICAL SEPARATION

(Xu, Thomas et al. 2008) reported that cobalt can be extracted from waste LiCoO_2 batteries by using a nitric acid as leaching solution. Cobalt hydroxide is deposited on a titanium electrode and cobalt oxide is then obtained by dehydration procedure (such as heating at low temperatures). The detailed reactions were reported to be:



Compared with other processes for recycling metals from spent Li-ion batteries, the electrolysis process can achieve the cobalt compound of very high purity since it does not introduce other substances giving no scope for impurities. However, the weight of electricity used should be considered.

5.4 PYROCHEMISTRY

Pyro-chemistry involves incinerating/ melting, used batteries at high temperatures in a furnace with controlled atmosphere. There are two established recycling processes

for Li-ion cells and batteries, using higher temperatures (Pistoia and Gianfranco 2005).

The Toxco process is designed for all types of lithium containing waste. The material is cooled in liquid nitrogen, before being mechanically shredded and mixed with water. The lithium reacts to produce hydrogen, which burns off above the reaction liquid. The main product is lithium hydroxide, but other components are “targeted where appropriate” (i.e. cobalt) (McLaughlin).

The Sony process uses higher temperatures; the cells are incinerated. The metallic waste is recovered for processing to recover the cobalt, using standard hydro-metallurgical techniques. The organic components, lithium, and fluoride are separated, though a scrubbing system on the incinerator to avoid emission problems. Larger cell sizes have to be punctured before they are introduced into the incinerator (Smith 1998).

5.5 BIO LEACHING

A novel (Rohwerder, Gehrke et al. 2003) study using chemo-lithotrophic and acidophilic bacteria, acidithiobacillus ferro-oxidants, which utilized elemental sulphur and ferrous ion as the energy source to produce metabolites like sulphuric acids and ferric ion in the leaching medium has shown that bio leaching can be an effective method, but the results are still very preliminary and laboratory scale.

The bacteria were able to grow in the medium containing elemental sulphur and iron as their energy source. Results revealed that a culture of ferro-oxidants can produce sulphuric acid to leach metals indirectly from the Li-ion batteries. Cobalt was leached faster than lithium. The main advantage of the bio-hydrometallurgical processes is that it is of lower cost and needs few industrial requirements and is also environmentally favorable. Bio-hydrometallurgical processing of solid waste is similar to natural biogeochemical metal cycles and reduces the demand of resources, such as ores, energy and landfill space.

5.6 COMMERCIAL RECYCLING PROCESSES

Some commercial methods have been mentioned below. These processes are mainly a combination of two or more mechanical separation methods in conjunction with one or more chemical methods discussed above. Commercial recycling processes run have two criteria one is two separate and treat toxic material in batteries and second is to recover valuable metals.

5.6.1 VAL'EAS CLOSED-LOOP PROCESS

Umicore (Cheret, Broussely et al. 2007) is one of major producers of materials for lithium-ion cathodes (LiCoO_2 or other mixed-metal materials). The aim of the Val'E-as closed-loop process, shown in [Figure 22](#), is to provide to treat end-of-life lithium-ion batteries and production scraps. Batteries are directly introduced into a furnace without any pre-processing, e.g. crushing or dismantling. The increase in temperature

and reducing conditions are closely managed so that no explosion can occur and the totality of Co and steel is recovered in the metallic phase.

This metallic phase is then atomized into a very fine powder and further refined in the Co refinery. The other product formed during the first smelting step is a pure inert slag. By managing the smelting conditions, no metal can be found in the slag. The slag can be re-used in construction, concrete or even as raw material in replacement of pure limestone and silica in the special steel industry.



Figure 22: Umicore's, Val'Eas closed-loop process for recycling Li-ion batteries, (Bernardes, Espinosa et al. 2004)

5.6.2 ETOILE-REBATT TECHNOLOGY

Etoile-Rebatt (Ra and Han 2006) is a recycling process which is a combination of mechanical dismantling and separation, electrochemical and thermal treatment, [Figure 23](#). The lithium cells were soaked in brine and completely discharged for security. Then, anode, separator, electrolyte, and cathode in the unit cell were separated. Black pastes separated from cathode were electrochemically and thermally treated in a laboratory-made recycling instrument. The separated pastes were immersed in the ER-MRT-13 solution containing 4M LiOH and KOH, and located on the bottom of the reaction vessel and at a distance of 70 cm from the platinum electrodes located in another vessel for product collecting. The recycling reaction was carried out at a fixed temperature between 40 and 100 °C.

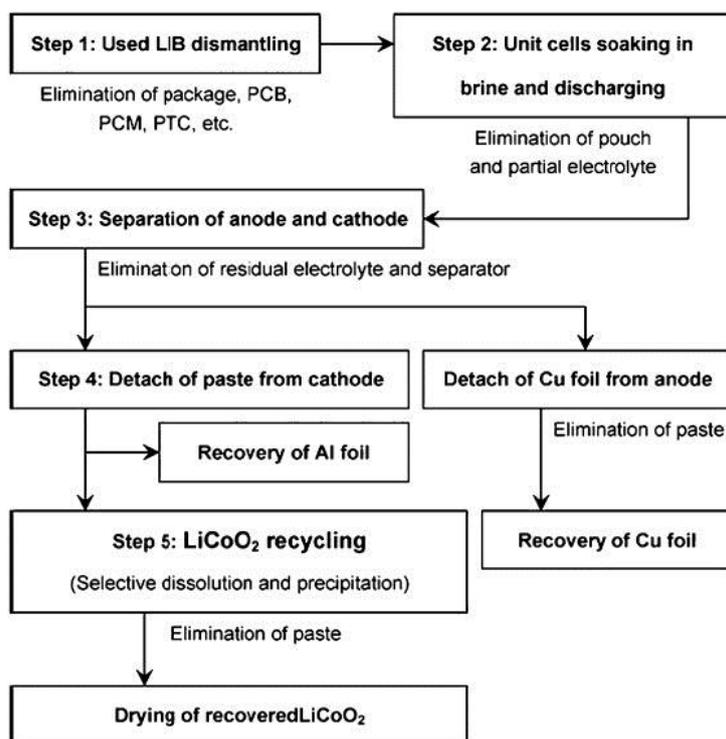


Figure 23: Flowchart of process prescribed by the Etoile-Rebatt method to recycle, (Ra and Han 2006).

The structural and compositional purities of the recovered and renovated LiCoO_2 were confirmed by elemental analyses, X-ray diffraction pattern analyses, and Raman spectroscopy. Since recycling using the Etoile–Rebatt technology is performed in an open system, its upper limit in capability depends on just volume scale of recycling instrument. While the renovated LiCoO_2 phase was simply obtained from spent Li-ion batteries, in an economical recycling way, the recovered and renovated LiCoO_2 was reported to exhibit a prospective electrochemical activity and battery performance: an initial discharge capacity of 134.8 mAh g^{-1} and the discharge capacity retention of 95.9% after 50 cycles. In detail, recycling reaction simultaneously consists of the dissolution of the used LiCoO_2 , the deposition of the dissolved LiCoO_2 on the platinum working electrode, the formation of the recovered and renovated LiCoO_2 film, as well as the precipitation of the recovered and renovated LiCoO_2 powder from the surface of the LiCoO_2 film. The recycled LiCoO_2 was filtered and washed with doubly distilled water, and then dried at $80 \text{ }^\circ\text{C}$ for 10 h. 12.564 kg of LiCoO_2 was recovered from 16.678 kg of black pastes separated from cathode.

There other technologies which combine different physical processes and chemical processes (explained above) and are uniquely designed based on the metal recovered.

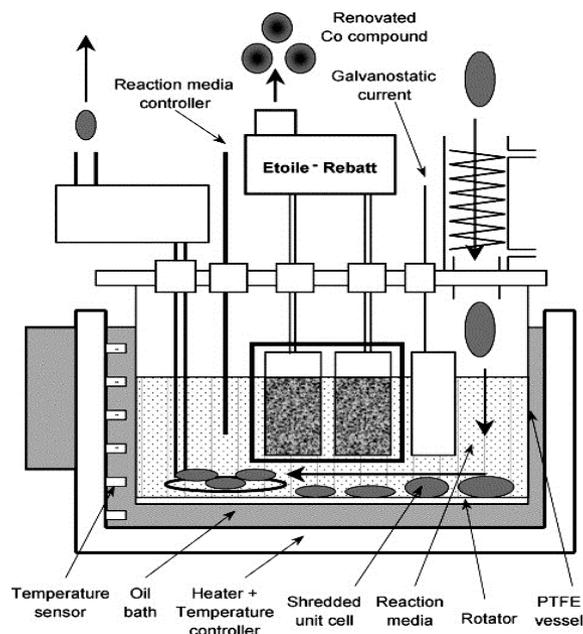


Figure 24: Schematization of the recycling instrument using the Etoile-Rebatt technology

6. CONCLUSIONS

The resources of lithium are limited in comparison to the needs projected for the possible electric car revolution. There is concern over the interpretation of the reserves. The total brine reserve base estimate around the world is about 11 million tonnes (Table 6-7), while the estimate for the reserves is much smaller about 8-9 million tonnes. That leaves much of those numbers to be realised into material, yet there is currently no technology set up at the source sites to extensively use it. Of the total world reserves (8-9 mt) at-least 60% is present in Bolivia alone. Its government has now taken a strong stance against any trade of raw materials in-spite of an already acute international pressure (PAZ 2009). Recycling of batteries is important not only for recovery of lithium, but also the recovery of many valuable metals and waste battery management. Using metal recovered from waste back in to the production process will greatly reduce emissions and energy usage related to mining. It will also be much more financially viable for the producer than to collect the waste battery and treat it for hazardous materials(producer responsibility). With recycling processes, much needs to be studied in terms of making it more environmentally friendly, because as the battery chemistries get more stable they become difficult to treat chemically.

ANNEX A

The Battery directive 2006/66/EC issued by the European Parliament and the Council on batteries and accumulators and waste batteries and accumulators and repealing Directive 91/157/EEC suggests that

1. Article 2 : Scope:

(only the concerned definitions for this report quoted below from those listed in the actual Article)

This Directive shall apply to all types of batteries and accumulators, regardless of their shape, volume, weight, material composition or use. It shall apply without prejudice to Directives 2000/53/EC and 2002/96/EC.

2. Article 3: definitions:

(only the concerned definitions for this report quoted below from those listed in the actual Article)

Automotive Battery or Accumulator means any battery or accumulator used for Automotive starter, lightning or ignition power;

Industrial Battery or Accumulator means any battery or accumulator designed for exclusively industrial or professional uses or used in any type of electric vehicle;

Waste Battery or Accumulator means any battery or accumulator which is waste within the meaning of Article 1(1)(a) of Directive 2006/12/EC;

Recycling means the reprocessing in production process of waste materials for their original purposes, but excluding energy recovery;

Disposal means any of the applicable operations provided for in Annex II A to directive 2006/12/EC;

Treatment means any electrical or electronic equipment, as defined by directive 2006/12/EC which is partly or fully powered by batteries or accumulators or is capable of being so;

Producer means any person in a Member State that, irrespective of selling technique used, including by means of distance communication as defined in directive 97/7/EC of the European parliament and of the Council of 20 May 1997 on the protection of consumers in respect of distant contracts (also defined), places batteries or accumulators, including those incorporated in to appliances or vehicles, on the market for the first time within the territory of that Member State on a professional basis;

Distributor means any person that provides batteries and accumulators on a professional basis to the end user;

Placing on the market means supplying or making available whether in return for the payment or free of charge, to the third party within the community and includes import in to the customs territory of the Community;

Economic Operators means any producer, distributor, collector, recycler or other treatment operator;

3. Article 8: Collection Schemes

(only the concerned definitions for this report quoted below from those listed in the actual Article)

Member States shall ensure that producers of industrial batteries and accumulators, or third parties acting on their behalf, shall not refuse to take back waste industrial batteries and accumulators from end-users, regardless of chemical composition and origin. Independent third parties may also collect industrial batteries and accumulators;(3).

Member States shall ensure that producers of automotive batteries and accumulators, or third parties, set up schemes for the collection of waste automotive batteries and accumulators from end-users or from an accessible collection point in their vicinity, where collection is not carried out under the schemes referred to in Article 5(1) of Directive 2000/53/EC. In the case of automotive batteries and accumulators from private, non-commercial vehicles, such schemes shall not involve any charge to end-users when discarding waste batteries or accumulators, nor any obligation to buy a new battery or accumulator;(4).

4. Article 12 : Treatment and Recycling

(only the concerned definitions for this report quoted below from those listed in the actual Article)

1. Member States shall ensure that, no later than 26 September 2009:

(a) producers or third parties set up schemes using best available techniques, in terms of the protection of health and the environment, to provide for the treatment and recycling of waste batteries and accumulators; and

(b) all identifiable batteries and accumulators collected in accordance with Article 8 of this Directive or with Directive 2002/96/EC undergo treatment and recycling through schemes that comply, as a minimum, with Community legislation, in particular as regards health, safety and waste management;(1a-b).

Treatment shall meet the minimum requirements set out in Annex III, Part A;(2).

Recycling processes shall, no later than 26 September 2010, meet the recycling efficiencies and associated provisions set out in Annex III, Part B;(4).

5. Article 14: Disposal

Member States shall prohibit the disposal in landfills or by incineration of waste industrial and automotive batteries and accumulators. However, residues of any batteries and accumulators that have undergone both treatment and recycling in accordance with Article 12(1) may be disposed of in landfills or by incineration.

6. Article 16: Financing

(only the concerned definitions for this report quoted below from those listed in the actual Article)Member States shall ensure that producers, or third parties acting on their behalf, finance any net costs arising from:the collection, treatment and recycling of all waste industrial and automotive batteries and accumulators collected in accordance with Articles 8(3) and (4);(1b).

Member States shall oblige producers, or third parties acting on their behalf, to finance any net costs arising from public information campaigns on the collection, treatment and recycling of all waste portable batteries and accumulators;(3).

The costs of collection, treatment and recycling shall not be shown separately to end-users at the time of sale of new portable batteries and accumulators;(4).

Producers and users of industrial and automotive batteries and accumulators may conclude agreements stipulating financing arrangements other than the ones referred to in the first paragraph above;(5).

This Article shall apply to all waste batteries and accumulators, irrespective of the date of their placing on the market ;(6).

ANNEX III

DETAILED TREATMENT AND RECYCLING REQUIREMENTS

PART A: TREATMENT

1. Treatment shall, as a minimum, include removal of all fluids and acids.
2. Treatment and any storage, including temporary storage, at treatment facilities shall take place in sites with impermeable surfaces and suitable weatherproof covering or in suitable containers.

PART B: RECYCLING

3. Recycling processes shall achieve the following minimum recycling efficiencies:

(a) Recycling of 65% by average weight of lead-acid batteries and accumulators, including recycling of the lead content to the highest degree that is technically feasible while avoiding excessive costs;

(b) recycling of 75% by average weight of nickel-cadmium batteries and accumulators, including recycling of the cadmium content to the highest degree that is technically feasible while avoiding excessive costs; and recycling of 50% by average weight of other waste batteries and accumulators.[28]

ANNEX B

Quotes on Lithium

Thom Calandra, Stockhouse (07/21/10) "Lithium's price has about tripled in the past 10 years. As Ticker Trax subscribers know, some junior producers' shares have risen 600%–1,100% since I first profiled them about 16 months ago. These include Western Lithium in Nevada and Canada Lithium in Quebec"

ANNEX C

[HEV](#) List

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What gets people to help recycle old batteries?



Battery Recycling slogans and their affectivity in waste battery collection as surveyed by (Hansmann, Loukopoulos et al. 2009), the most effective slogans were when people were presented with factual statements than with witty or funny ones, the collection increased.