

Review

Global Lithium Sources—Industrial Use and Future in the Electric Vehicle Industry: A Review

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Abstract: Lithium is a key component in green energy storage technologies and is rapidly becoming a metal of crucial importance to the European Union. The different industrial uses of lithium are discussed in this review along with a compilation of the locations of the main geological sources of lithium. An emphasis is placed on lithium's use in lithium ion batteries and their use in the electric vehicle industry. The electric vehicle market is driving new demand for lithium resources. The expected scale-up in this sector will put pressure on current lithium supplies. The European Union has a burgeoning demand for lithium and is the second largest consumer of lithium resources. Currently, only 1–2% of worldwide lithium is produced in the European Union (Portugal). There are several lithium mineralisations scattered across Europe, the majority of which are currently undergoing mining feasibility studies. The increasing cost of lithium is driving a new global mining boom and should see many of Europe's mineralisation's becoming economic. The information given in this paper is a source of contextual information that can be used to support the European Union's drive towards a low carbon economy and to develop the field of research.

Keywords: lithium; electric vehicle; source; industrial use

1. Introduction

Presented is a review of the available literature regarding the industrial uses and sources of lithium, with a focus on the European Union (EU) and electric vehicle (EV) market. The work organises the literature in order to review and evaluate the state of the art in this field of research. There is a trend in the literature showing an increasing amount of interest by both developed and developing countries in previously uneconomic mineralisations of lithium globally. Here we present detailed information on historic and new lithium mineralisations. The industrial uses of lithium are varied and often go unreported in any great detail in publications relating to lithium. In this paper, the main industrial uses of lithium have been collated. This work is designed to highlight and summarise research findings regarding lithium's use, presence in the environment, mining, and occurrence. The impetus for lithium's future recycling is also discussed as a requirement for a future sustainable circular lithium economy [1].

The last century has seen an increase in the amount of all metals, including lithium, consumed globally. In the last twenty years, there has been an exponential increase in the number of metals consumed. This rapid increase has been correlated with China's economic reforms and development. China's vast manufacturing capacity and ability to sell lithium products cheaply has led to the country dominating the lithium product manufacturing industry. Even though China has its own lithium resources, it still imports massive amounts of the metal [2]. World leading Chinese lithium manufacturing companies like "Tianqi" and "Ganfeng Lithium" currently control almost half of the

worlds lithium production. China has invested in lithium projects all around the world and has the power to distort the market. China has already limited its export quotas of rare earth elements (REEs); a similar limit on the export of lithium to the EU could give rise to a real supply security issue. Within the EU, demand for lithium is growing increasingly quickly [3]. The United Nations (UN) Environment Programme launched an international resource panel in 2007, with an aim to gather and share information on global metal resources, the availability of critical raw materials (CRMs), and the concept of a circular economy [4]. The European Commission (EC) uses a CRM approach to describe materials which are essential to the EU's economy. The EC defines a CRM as a material which forms a strong industrial base, producing a broad range of goods and applications used in everyday life and modern technologies [4]. CRMs are crucial to the EU's economy. The EC has created a list of CRMs which includes 27 materials (Table S1, Supplementary Material [4]). The EC revises its CRM list every three years and the list was last updated in 2017 [4]. Lithium is not currently considered a CRM, rather a near critical material. Factors contributing to lithium not being classified as a CRM include its relative global abundance (although it rarely appears in large deposits) and the current availability of suitable substitutes available for some lithium technologies, for example, other battery technologies using manganese and nickel [1]. Nickel and manganese are globally abundant and not classified as CRMs [3]. Lithium is likely to be classified as a CRM in 2020 when the EC revises its CRM list, because of current and expected future demand. Lithium has a high economic importance and is essential to the growth of green technologies in the EU. The EU has the potential to become self-reliant for lithium supplies by developing its own domestic lithium resources reducing reliance on other suppliers (Table S2, Supplementary Material [5–16]). In the EU, hard rock mineralisations of lithium offer the best potential to provide the EU with lithium in the future. New mining investment in the EU will strengthen the competitiveness of its lithium industry.

1.1. Methodology

There is an ever-increasing output of scientific publications concerning lithium resources driven by recent demand for this, until now, relatively unfamiliar metal. This paper provides an up to-date overview of the literature in this specific area and brings together relevant material from various sources. Articles included in this review were accessed from journal databases, bibliographic databases, and subject-specific professional websites. The inclusion criteria for articles comprised of only relevant peer-reviewed qualitative and quantitative articles related to both the uses and sources of lithium globally.

1.2. Lithium

Lithium is the third element on the periodic table and the first element in the alkali metal group. It has an atomic mass of 6.94 g/mol, an atomic radius of 1.33 Å, a melting point of 180.5 °C and a boiling point of 1342 °C. With a density of just 0.534 g/cm³, lithium metal floats in water even as it reacts. Lithium has a hardness of 0.6 on the Mohr scale, is softer than talc (Mg₃Si₄O₁₀(OH)₂), the softest mineral on the Mohr scale (talc hardness = 1). Lithium is harder than carbon = 0.5, caesium = 0.5, and sodium = 0.5 but softer than lead = 1.5 [15]. Lithium has the highest specific heat capacity (at 25 °C) of any solid element at 3.56 J/g K. Lithium is the most polarising of all the alkali metals and more electronegative than H so it can accumulate chemical energy very efficiently. At a pressure in excess of 40 gigapascals (400,000 atmospheres) lithium becomes a superconductor [17]. There are several radioisotopes of lithium (⁴Li to ¹²Li). Their half-lives range from 9 × 10⁻²³ s for ⁴Li to 8 × 10⁻¹ s for ⁸Li. Naturally occurring lithium exists as the two stable isotopes ⁶Li (at 7% abundance) and ⁷Li (at 93% abundance) [17]. Lithium has a single valence electron on its outer shell which is freely given up for reaction to form a variety of compounds [18]. The highly reactive nature of lithium (the least reactive of the alkali metals) towards oxygen, a trait it shares with other group 1 alkali metals, means that it never occurs as a pure metal in nature, instead, it occurs as various salts and minerals. One property of lithium is its apparent cosmological discrepancy. Lithium follows in the periodic table after the two most abundant elements in the universe hydrogen and helium, but it is far less abundant in the

universe than it has been predicted to be, according to the standard cosmological model (SCM) [19,20]. During the first few minutes of the “Big Bang” H, He, and Li were created. The amounts of hydrogen and helium occurring in the universe agree with those figures proposed by the SCM, lithium (and beryllium and boron) estimates, however, are too low [20]. This lithium discrepancy question has not been solved to date although some authors have attempted to provide explanations [21]. The leading theory is that lithium is transmuted to other elements early within stars.

The chemical history of lithium began with the characterisation of the aluminosilicate minerals petalite ($\text{LiAlSi}_4\text{O}_{10}$) and spodumene ($\text{LiAlSi}_2\text{O}_6$). They were discovered at the start of the 18th century by the Brazilian statesman and naturalist José Bonifácio de Andrada e Silva on the island of Utö, near Stockholm, Sweden [22]. In 1817 the Swedish chemist Johan August Arfwedson discovered a previously unknown element in the new mineral petalite. Arfwedson was working at the time for another Swedish chemist, Baron Jöns Jacob Berzelius. Lithium, according to the author Berzelius (1964) (who coincidentally shares the same name as Jöns Jacob Berzelius) formed compounds similar to those of sodium and potassium [22], although lithium’s carbonate and hydroxide forms are less soluble in water and more alkaline [23]. Together the two chemists named the mysterious element lithion/lithina from the Greek for stone. Arfwedson went on to discover lithium in lepidolite ($\text{K}(\text{Li},\text{Al})_3(\text{Al},\text{Si},\text{Rb})_4\text{O}_{10}(\text{F},\text{OH})_2$). In 1818 Christian Gottlieb Gmelin a colleague of Arfwedson was the first to observe that lithium salts, when exposed to flames, gave off an intense red flame [24]. Although Arfwedson had discovered the element he never managed to isolate pure metallic lithium. In 1821, the English chemist William Thomas Brande, a colleague of Sir Humphry Davy, obtained lithium by the electrolysis of lithium oxide [25]. In 1855, the German chemist Robert Wilhelm Eberhard Bunsen and English chemist Augustus Matthiessen isolated lithium from lithium chloride by electrolysis [24]. Their production method was later commercialised by the German company Metallgesellschaft AG (1923), who produced metallic lithium electrolytically from a mixture of 55% lithium chloride and 45% potassium chloride at a temperature of 450 °C [24].

2. Lithium in the Environment

2.1. Lithium in Water

Lithium occurs in barely trace amounts in fresh water, rivers, lakes, and surface waters. Its concentrations in fresh waters depend on numerous variables like local geology and topography. The range is from 0.001 to 0.020 mg/L lithium [26–31]. Groundwater concentrations are much more variable mainly due to geological factors and, in some places, can reach concentrations >500 mg/L. [10]. Generally, a range between 0.5 and 19 mg/L lithium in groundwater is agreed upon [32]. Although there are exceptions; in Northern Chile where lithium is actively mined from brines the water lithium concentrations are exceptionally high [33]. In Chile, the daily dietary intake of lithium may be as high as 10 mg/day [34], although a lithium intake this high has not shown any harmful effects on humans [35]. Lithium intake of adults has been calculated in several countries, ranging from 0.35 mg/kg in Vienna Austria to 1.6 in Xi’an China [34]. Lithium is the 14th most abundant element in seawater. Its concentration varies across different oceans, despite this it is largely accepted to occur in seawater at a concentration between 0.14 and 0.20 mg/L (Table S3, Supplementary Material [14,17,26,36–42]). An average lithium concentration of 0.17 mg/L is often reported. Seawater is known to contain vast amounts of lithium between 230,000 and 250,000 megatons (Mt) [39,43–48]. The low level of lithium in seawater makes it difficult to create a process to extract it efficiently or profitably [49]. Despite this, several attempts have been made to extract lithium economically from seawater using different techniques like electrodialysis and membrane filtration. [46,47,50–54]. Aluminium salts are widely used to precipitate lithium from seawater [48,55,56]. Another common method of extracting lithium from seawater involves using a manganese-based absorbent which has a high selectivity for the lithium ion, followed by a precipitation process [43]. In a 1986 Japanese study, manganese oxide was evaluated for its ability to sequester lithium from seawater [57]. The majority

of downstream seawater processing includes the following steps, flotation, sorption, ion exchange, membrane filtration, and solvent extraction [43]. Tin antimonate $\text{Sn}_3(\text{SbO}_4)_4$ has been used as a lithium ion absorber [57]. A massive amount of seawater would have to be processed in order to extract economic amounts of lithium [12] and this approach may never become economically viable; the process is just too expensive compared to current mineral and brine mining [58].

2.2. Lithium in Soil

Lithium is found in trace amounts in all soils. Several figures are given in the literature for the abundance of lithium in the Earth's crust (Table S4, Supplementary Material [14,17,37–39,59–69]). An average of 20 mg/kg of lithium is commonly cited. However an average value is minimally informative given 4 orders of magnitude of lithium concentrations recorded in different geological situations; skewed towards the lower end of the range. Lithium is slightly more abundant in the Earth's crust than Cu, Cr, Ni, and Zn and less abundant than Al, Mg, Mn, and Ti. Lithium does accumulate to economic levels in some areas as aluminosilicate minerals, in some specialised clays, and in lake evaporate. Clay minerals are a group of hydrous aluminosilicates. These minerals are similar in chemical and structural composition to the primary minerals that originate from the Earth's crust [60]. A range between 10 and 40 mg/kg is generally accepted as the "background" concentration of lithium in soil with average values of 20 mg/kg in the soil and 30 mg/kg in granites (Table S5 [14,20,32,45,60,63,66,70–75] and Table S6, Supplementary Material [32,34,39,45,60,76–85]). According to some authors, the lithium content of soils is determined more by the conditions of soil formation rather than by its initial content in parent rocks [70,86]. Lithium has been reported to correlate strongly with aluminium in the clay fraction of soils [79]. It has also been shown to be positively correlated with calcium and magnesium in soils and negatively correlated with sodium. Yalamanjali (2012) also reported correlations between lithium and Al, B, Fe, K, Mg, Mn, and Zn in the soil of New Zealand [60].

2.3. Lithium Industrial Resources

Lithium is not a particularly rare metal, rather it is widely distributed globally. It is only found in suitably large concentrations in two types of material; silicate minerals and mineral-rich brines [20]. Prior to the 1980s, all lithium was mined from hard rock mineral sources. The production of cheap lithium from mineral-rich brines like those found in the Andes, resulted in the closure of several lithium mineral mines [87]. The capital expenditure required for lithium production from a brine source is lower than that required for a mineral source. Mineral sources may have valuable accessory elements like Be, Cs, F, P, Sn, Ta, and Rb; brine sources tend to have a larger concentration of accessory minerals like B, K, Na, and Mg. Today approximately 59% of the world's lithium resources are found in brines and 25% in minerals, the remainder is found in clays, geothermal waters, and oil field brines [82,87]. Relatively few lithium sources contain high concentrations or commonly occur in any great amount. In 2009, 13% of worldwide lithium reserves, expressed in terms of contained lithium, were reported to be within mineral deposits, and 87% within brine and mineral water deposits [88]. Gruber et al. (2011) state that 57% of the world's lithium resources are contained in just three locations, the Salar de Atacama, Chile; the Salar de Uyuni, Bolivia, and the Kings Mountain belt, USA (Salar is Spanish for Salt Lake) [87]. Given the expense associated with lithium mineral mining, the majority of lithium on the market today is sourced from brines. Salt brines (dry saline lake beds) are the main source of lithium today (approximately 50%), but extraction from minerals is still significant (40%), the other (10%) is sourced from clay deposits and other sources [8].

Mineral deposits are viewed as a means of offsetting any deficit in lithium production from brines as well as mitigating some concerns about the security of lithium supply in the future [67]. The high concentration of lithium in mineral sources can often offset additional costs associated with the process. Despite the cost-effectiveness of extracting lithium from brines rather than minerals, the increased demand in lithium means that it is still being processed from mineral sources all over the world.

Mineral deposits in countries like Afghanistan and Ireland are currently being prospected for lithium resources [89–91]. In Ireland, lithium occurs in the south-east of the country and is associated with the Leinster granitic batholith [10]. Afghanistan has been identified as a major future potential lithium market supplier if its vast resources are utilised [91]. Afghanistan's lithium deposits occur in dry lake beds located in the western provinces of Herat and Nimroz and in the central-eastern province of Ghazni. The geologic setting is similar to that found in the Andes. Lithium mineral deposits are also found in the north-eastern provinces of Badakhshan, Nangarhar, Nuristan, and Uruzgan [91]. Afghani lakes such as Lake Namaksar-e-Herat, Dasht-e-Nawar, and Godwe Zareh in the west of the country contain lithium at concentrations between 41 and 99 mg/L [92].

The language used to describe minerals identified in a deposit is divided into two major groups, resources and reserves. Resources refer to the amount of those minerals that are known to exist in a deposit that may be extracted economically and are reasonably well defined with regard to grade and quantity. Resources are further subdivided into three more categories [93]. An inferred resource refers to reasonable estimates on the amounts of minerals present in a deposit, based on early limited information. Indicated resources refer to estimates given when more information about the deposit like grade and size are known. Measured resources refer to an estimate given after all the characteristics of a deposit are known. Reserves refer to the quantity of target mineral which can be feasibly/economically extracted from a resource. Factors which determine reserve figures include current mining technologies, environmental factors, and available infrastructure. Reserves may be subdivided into proven and probable reserves. Probable reserves have the potential to be economic while proven reserves are known to be economic [93,94]. Estimates of global lithium reserves and resources have been published extensively in the literature. It is difficult to estimate the world's lithium reserves, because of the abundance of contradictory estimates which are typically made by both investors and venture capitalists rather than researchers in the field [49]. As the price of a metal rises some resources may become economically feasible to recover and also become classified as reserves [87]. Mohr et al., (2012) provide an extensive list of the global lithium resources and reserves at different sites around the world [8]. Some countries are known to contain lithium resources, but little data is available. All resource and reserve estimates are subject to change as new projects come online, others close, and some go unreported [66]. Lithium resource and reserve estimates are expected to increase in the future as new deposits are discovered and technology advances. Lithium global resource estimates vary from author to author and have varied over the years (Table S7 [5,6,8,12,18,41–43,58,87,95–105] and Table S8, Supplementary Material [5,18,41,43,66,87,96,99,102,105–107]).

2.3.1. Lithium in Brines

Commercial quantities of lithium exist in brines (a high concentration salt solution). The main type of brine deposit mined for lithium is found in interior saline desert basins, these basins in the past contained water before the rate of evaporation exceeded the rate of recharge, leaving behind a dry lake bed. The terminology used to describe these dry lake beds is varied. They are referred to as salt pans, salt flats, salt marsh, alkali flats Playas or, most commonly, Salars. Sediments in salars are primarily lacustrine, but some are derived from modern depositional processes. Many mineral rich and hot geothermal waters contain elevated concentrations of lithium, between 0.1 and 500 mg/L lithium [14,83]. Geothermal waters become enriched in lithium because hot water is more effective than cold water at leaching lithium from rocks. The lithium in geothermal brines can come from volcanic activity, weathering of silicates, and leaching from lake sediments [15]. In geologically active countries like Iceland (the Reykanes geothermal field), Japan (the Hatchobaru and Oguni geothermal fields), and New Zealand (Wairakei), the potential commercial extraction of lithium from geothermal waters has been studied [108–111]. Other potential lithium sources in geothermal waters are found in Cesana, Italy, and Alsace, France [20]. Recovery of lithium from geothermal sources often involves methods such as ion-exchange; precipitation, often as a lithium aluminate; and membrane filtration [14,83]. Efforts have also been made to extract lithium from saline water bodies like the Dead Sea [64].

Mineral-rich brines, known as oilfield brines, are produced as a waste product of certain oil extraction process. The brines can occur at a depth >2 km. Oilfield brines in the United States contain 0.1 to 700 mg/L lithium [43,83]. Oilfield brines, such as the Smackover oilfields in southern Arkansas, USA, have been investigated for their potential as an economic source of lithium [43,97,112,113]. The Smackover oilfield has been shown to contain lithium at concentrations between 100 and 500 mg/L [114]. Other oilfield brines being investigated occur in areas such as the oilfield brines at Leduc, Alberta, Canada; the Heletz-Kokhav oilfields in Israel; and the gas fields of Altmack, Germany [20]. The United States has several oilfield brine deposits, including East Texas, the Devonian formation in North Dakota, Rock Springs Formation in Wyoming; Wilcox Formation in Oklahoma; Paradox Basin in Utah; and the Pennsylvanian Minnelusa formation [20,97,112]. Lithium is produced directly from oilfield brine and does not require evaporation ponds. Lithium extraction from oilfield brines can be an expensive process because of the need for pumping from such depths [87]. Currently, there is enough lithium being produced from other sources, although geothermal waters and oil field brines may become an economic source of lithium in the future depending on demand [14].

The most abundant source of lithium-rich brine are the high-altitude continental brine aquifers of the Andean mountain region in South America. The Andes is a major subduction zone, which has resulted in a series of endorheic basins [66]. The brine deposits of South America occur at high altitude, which promotes the evaporation process due to the inverse relationship between atmospheric pressure and altitude. Salars exist in three countries, Argentina, Bolivia, and Chile, collectively known as the Lithium Triangle, where 50% of global lithium reserves are found [6]. Argentina has several salars, including the Salar de Muerto Hombre, the Salar de Olaroz, and the Salar de Marianna, all of which contain substantial amounts of lithium. The Salar de Atacama in Chile is currently the largest producer of lithium from a brine source [87]. By far, the largest reserve base of lithium in the world is in the Salar de Uyuni in the southwest of Bolivia [96,107]. Bolivia alone may hold up to 25% of world lithium reserves. According to the Bolivian government, their resources add up to 100 Mt. Lithium reserve estimates for the Salar de Uyuni have been placed at 0.6 to 9 Mt [5,43,96].

Lithium is extracted from brines as lithium carbonate or lithium chloride by solar evaporation. Broadly, the process involves evaporation, precipitation, adsorption, and/or ion exchange [43]. Usually, the brine is pumped to open man-made ponds, where solar evaporation is used to concentrate the lithium into a smaller volume of brine. The brine is transferred through a series of these ponds, becoming progressively more concentrated by solar evaporation. The process from start to finish can take 18 to 24 months. Since the brine is open to the environment, the process may be slowed down by rain or flooding, and sheet flooding of the South American salars is a common occurrence. After sufficient concentration of the brine, the lithium is eventually extracted by chemical means, as lithium chloride or, more commonly, lithium carbonate. To extract magnesium from the brine calcium carbonate is added to precipitate out magnesium carbonate ($\text{CaCO}_3 + \text{MgCl}_2 \rightarrow \text{CaCl}_2 + \text{MgCO}_3$). This results in a brine that is between 5.5 and 6.5% lithium chloride. Finally, sodium carbonate is added (at 90 °C) to precipitate out lithium carbonate at a ratio of 1.8:1 ($\text{LiCl} + \text{Na}_2\text{CO}_3 \rightarrow \text{Li}_2\text{CO}_3 + 2\text{NaCl}$) [66]. Lithium and magnesium have similar chemistries and are difficult to separate in brine deposits. The higher the Mg/Li ratio, the more expensive it is to separate the two in the production process. The Mg/Li ratio of seawater is 7000, and the Mg/Li ratio of several salars are given in (Table S9 Supplementary Material [14,15,20,45,87,89,97,115–117]). Swain (2017) discusses, in detail, the different techniques, mechanisms, and chemistry by which lithium is extracted from brines [83]. Apart from the Lithium Triangle, there are numerous brine deposits around the world in countries like Canada, China, India, Israel, and the United States [12]. China has numerous Salt Lake deposits in areas like the Qaidam basin (>30 lakes) and the Tibetan plateau (>300 lakes). These deposits include the Tajjinaier Salt Lake (Qinghai Province), and Lake Zabuye (Shigatse Prefecture). The Qaidam Basin, where Lake Tajjinaier is located is the largest salt bed lithium reserve in China [20]. In the United States, brine deposits include the Searles Lake, Nevada; the Salton Sea in California; and Utah's Great Salt Lake [15,36,87,97].

2.3.2. Lithium in Minerals

Lithium minerals fall into three general classes: complex aluminium silicates, phosphates, and micas [45,115,118]. Micas are normally classified as aluminium silicates [115]. There are 145 named lithium-bearing minerals, given in (Table S10 Supplementary Material [15,37,43,119]). Not all of these minerals are of commercial value. There are only a few lithium minerals, like spodumene, petalite, and lepidolite, that are economically worthwhile to process for lithium if a large-enough deposit is found [43]. The aluminium silicate, spodumene, is the most commonly available economic lithium-bearing mineral. Its colour can be white when it is low in iron, and dark green when rich in iron [15]. Lithium minerals mainly occur as a subset of a type of rock called a pegmatite. Pegmatites are coarse-grained igneous rocks associated with the late crystallisation stage of postmagmatic fluids in intrusive granitic plutons [15]. The main constituents of pegmatite are feldspar, quartz, and mica. Pegmatite rock is the last to solidify during the emplacement of a pluton, and because it cools slowly, pegmatite tends to become enriched with more diffuse elements like lithium. When pegmatites are cooling, the process is controlled by the presence of lithium and other volatile elements like fluorine and boron, resulting in fewer and larger crystals [66]. These volatile elements remain in solution until late in the cooling process, so they become concentrated in late-stage pegmatites. The distribution of lithium within minerals is controlled by the $(\text{MgO} + \text{Fe})/\text{Li}_2\text{O}$ ratio [15,120]. Lithium has similar chemical properties to magnesium. Lithium has been shown to substitute for magnesium in many systems, both inorganic and organic [39]. The Mg/Li ratio varies from 2900 in ultramafic rocks to 120 in granites [72]. Lithium substitutes for Mg, Fe, Al, and Ti in magmatic melts. In a magmatic melt, when the ratio $(\text{MgO} + \text{FeO})/\text{LiO}$ is large, crystals which precipitate out of the melt first contain little lithium [72]. In melts, both magnesium and iron are removed by ferromagnesian minerals in preference to lithium; this contributes towards the enrichment of lithium in pegmatite [15]. There are two main types of pegmatites [121]. The NYF (niobium, yttrium, fluorine) group predominantly accumulates the elements niobium, yttrium, and fluorine. The LCT (lithium, caesium, tantalum) groups accumulate lithium, caesium, and tantalum, and are typically associated with late tectonic peraluminous (S-type) granites [67]. The NYF pegmatites are typically associated with A and I-type granites [67]. Generally, S-type granites are derived from sedimentary rocks and I-type granites are derived from igneous rocks, usually plagioclase-rich and muscovite poor [122]. A-type granites typically occur in rift zones and in the interiors of continental plates. Pegmatites are fairly common throughout the Earth's crust; however, lithium-bearing pegmatites make up only 1% of the world's pegmatite resources. LCT pegmatites typically contain 12 to 30% spodumene, 22 to 27% quartz, 30 to 50% feldspar, and 3 to 5% mica and accessory minerals, such as cassiterite (SnO_2) and columbite ($\text{Fe}_2\text{Nb}_2\text{O}_6$) [115]. Of the two-main economic lithium-bearing minerals, spodumene has a maximum theoretical percentage Li_2O of 8.03% (3.7% lithium), and petalite has a maximum percentage Li_2O of 4.88% (2.2% lithium). Other minerals with less lithium, that are often mined when they occur in large enough quantities, are lepidolite ($\text{K}(\text{Li},\text{Al},\text{Rb})_2(\text{Al},\text{Si})_4\text{O}_{10}(\text{F},\text{OH})_2$) and amblygonite ($(\text{Li},\text{Na})\text{AlPO}_4(\text{F},\text{OH})$) [43]. There are two significant clay sources of lithium; hectorite ($\text{Na}_{0.3}(\text{Mg},\text{Li})_3\text{Si}_4\text{O}_{10}(\text{OH})_2$) a magnesium, lithium smectite clay mineral, and jadarite ($\text{Na}_2\text{OLi}_2\text{O}(\text{SiO}_2)_2(\text{B}_2\text{O}_3)_3\text{H}_2\text{O}$) a monoclinic silicate mineral [43]. Hectorite occurs in the Kings Valley California, USA, where it has an estimated reserve of 2 Mt, while jadarite is found in the Jadar Valley, Serbia, with an estimated reserve of 1.4 Mt [102]. Global lithium reserves, as hectorite and jadarite, have been estimated to be 9.9 Mt [96]. In hectorite, the lithium tends to replace magnesium. Jadarite is a boron, lithium, and sodium-rich silicate hydroxide mineral [87]. Vine (1976) provides a detailed description of clay-like minerals [14].

Normally, lithium is extracted from minerals such as lithium carbonate, which is a precursor for nearly all lithium commercial compounds. Initially, the process for the majority of minerals follows the same sequence. Crushing and grinding (comminution) is the first stage in the process, as it liberates the lithium minerals from the rock matrix. Aluminosilicate minerals are hard and abrasive. As a consequence, comminution is energy intensive, and accounts for up to 50% of the processing cost. The lithium ore is then separated using physical, electrical, and magnetic processes. The next step

involves chemical processing, after which final processes like froth flotation and/or dense media separation are used to further concentrate the lithium [66]. Chemical processing is usually carried out by specialised companies. Spodumene in nature exists as α -spodumene, a monoclinic aluminosilicate that is very resistant to most chemical breakdown, although, hydrofluoric acid can dissolve the silicate matrix over time. A method for the extraction of lithium from β -spodumene by leaching with hydrofluoric acid, has been described as; $\text{LiAlSi}_2\text{O}_6 + 19\text{HF} \rightarrow \text{LiF} + \text{H}_3\text{AlF}_6 + 2\text{H}_2\text{SiF}_6 + 6\text{H}_2\text{O}$, [123]. Often, during processing, α -spodumene is converted to β -spodumene by roasting at a temperature of 1100 °C (calcination). The crystal structure is changed during roasting, resulting in the β -spodumene becoming more reactive and susceptible to chemical breakdown. Sulphuric acid is heated to different temperatures, the specific temperature is dependent on the mineral treated (e.g., spodumene at >1050°C). Chen et al. (2011) describe a method for the extraction of lithium from spodumene using a sodium carbonate autoclave process. β -Spodumene is mixed with hot sulphuric acid, then water is used to leach out lithium as Li_2SO_4 ; $\text{Li}_2\text{O} \cdot \text{Al}_2\text{O}_3 \cdot 4\text{SiO}_2 + \text{H}_2\text{SO}_4 \rightarrow \text{Li}_2\text{SO}_4 + \text{Al}_2\text{O}_3 \cdot 4\text{SiO}_2 + \text{H}_2\text{O}$ [124]. Finally, sodium carbonate is added to extract the lithium as Li_2CO_3 , $\text{Li}_2\text{SO}_4 + \text{Na}_2\text{CO}_3 \rightarrow \text{Li}_2\text{CO}_3 + \text{Na}_2\text{SO}_4$. The sodium carbonate method has a low energy requirement compared to other extraction methods. The separation of lithium from β -spodumene concentrates, using the physical methods of froth flotation with oleic and naphthenic acids followed by heavy media separation processes, has been described [125]. Petalite is not as resistant to chemical attack as spodumene, and it is still roasted prior to processing. Sitando and Crouse (2012) describe a method using sulphuric acid at 300 °C to process lithium carbonate from petalite $\text{Li}_2\text{O} \cdot \text{Al}_2\text{O}_3 \cdot 4\text{SiO}_2 + \text{H}_2\text{SO}_4 \rightarrow \text{Li}_2\text{SO}_4 + \text{Al}_2\text{O}_3 \cdot 4\text{SiO}_2 + \text{H}_2\text{O}$ [126]. Sitando and Crouse (2012) also describe an alkali/gypsum process where petalite is mixed with calcium carbonate heated to 1050 °C, and, lithium is extracted by hydrochloric acid as lithium chloride [126]. A method for the separation of lithium from lepidolite, called chlorination roasting, uses sodium chloride and calcium chloride as reacting agents rather than hydrochloric acid [126]. This process is usually followed by a water leaching technique which has been described [127]. The reaction is heated to 750 °C in the presence of a chloride salt, and lithium is eventually converted to lithium chloride. More commonly used methods for extracting lithium from lepidolite are roasting in the presence of sodium sulphate or potassium sulphate at 860 °C [126]. Barbosa et al. (2014) demonstrated the extraction of lithium from β -spodumene using pure gaseous chlorine at temperatures >1000 °C [128]. Vu et al. (2013) report on the extraction of lithium and rubidium from the mineral zinnwaldite ($\text{KLiFeAl}(\text{AlSi}_3\text{O}_{10}(\text{OHF})_2$) using an alkali digestion method [129]. Their process heats the ore (825 °C) in the presence of calcium carbonate followed by water leaching (90 °C) to extract the lithium. Other valuable elements, like caesium, tantalum, and rubidium, are often produced, along with lithium from a mineral source.

The three main global suppliers of lithium from mineral sources today are Australia, Canada, and Zimbabwe [15]. In Australia, the Greenbushes pegmatite mine in southwest Australia is currently the largest producer of lithium from a mineral source [130]. There are other locations in Australia that have substantial lithium pegmatite deposits: at Broken Hill, New South Wales; at Mt Cattlin, 2.2 km north of Ravensthorpe, Western Australia; and at Mt Marion, 40 km southwest of Kalgoorlie, in the Goldfields region of Western Australia [58,97,131]. In Canada, there are numerous pegmatite mines, such as LaCorne, Val d'Or, Nemaska mines in Quebec, and Tanco pegmatite mine at Bernic Lake, Manitoba; where caesium, lithium, and tantalum are mined from LCT pegmatites [15,43,97]. Sub-Saharan Africa is exceptionally rich in minerals. The Bikita mine in the Masvingo province of Zimbabwe is one of the largest lithium mines in Africa and has been operating since the 1950s. Lithium mineralisations are also known to exist in the Bauberton, Benson, Fort Rincon, Harare, Kamativi, and Uredefort regions of Zimbabwe. Other locations in Sub-Saharan Africa, like Karibib in Namibia, the Democratic Republic of Congo, Rwanda, Mozambique, and the Noumas and Norrabees areas of South Africa, also contain lithium pegmatite mineralisations. Lithium pegmatites also exist in Bougouni, Mali, as the mineral amblygonite; in the Indian regions of Chhattisgarh, Jharkhand, Karnataka, Rajasthan as spodumene; and the pegmatites of the Republic of Suriname in

South America [6,8,12,15,97]. In the EU, old tin mines are receiving renewed interest as sources of lithium in places like Cornwall in England and the Czech/German border town of Cinovec. (Table S11 Supplementary Material [5,8,12,15,43,87,91,97,122,126]) contains a listing of some of the more well-known lithium pegmatites deposits globally.

2.4. Lithium Mining and the Environment

A priority and legal necessity for all modern mining companies is the sustainable management and stewardship of the environment. Modern mining companies are responsible, practice low impact mineral extraction processes, and take stewardship of the environment seriously. In the past, however, and even today, in some small-scale mining operations, this has not been the case. Poorly managed mining operations have left a legacy of environmental problems. For example, in India, large-scale coal mining operations have affected local communities due to land transformation, resulting in a loss of forestry and agricultural land, in one of the most densely populated countries in the world [132,133]. Other notable examples include small-scale gold mining operations in Africa and South America, which have severely increased mercury concentrations in rivers. Mines are sometimes huge in scale, the ecosystem of a mined area is effectively destroyed during mining, although, nowadays, most mining companies are concerned with efforts to reclaim previously mined sites and rehabilitate the local ecosystem. Open-pit mines associated with mineral lithium deposits are often small compared to other mines. Although not a phenomenon which has been related to lithium mining, “conflict minerals”, in countries like the Democratic Republic of Congo (D.R. Congo), which contains a vast mineral wealth, may also be considered a potential mining-related impact. Lithium mining has a relatively low environmental mining impact compared to the mining of other metals like platinum group metals (PGMs) and REEs.

Another legacy of poorly managed mining operations is acid mine drainage (AMD), the acidification of waters leached from mine tailings or old mines that have been left to fill with both surface and groundwater. These waters contain toxic metals, like copper and lead, and have been shown to have a negative effect, at a reduced pH, on fresh waters [134]. The negative effects associated with AMD often do not manifest until several years after mining has begun and can persist for centuries. Nowadays, preventative measures, which are normally compulsory in most countries, are in place to mitigate AMD [135]. Treatments for AMD problems include alkaline neutralization, bioremediation, and constructed wetlands, and have been described elsewhere [135,136]. Mine tailings normally take the form of a slurry and are, therefore, easily stored in a pond/dam construction usually on the same site as the mine, preventing them from entering the wider environment. This technique is effective, but there have been cases of dam failures. Tailings contain compounds like sulphides and, typically, a large number of heavy metals which are normally only found deep underground. These heavy metals, using a pathway which usually involves water, can find their way into the surrounding environment with potentially toxic effects on both flora and fauna. It is estimated that, globally, the total volume of mine tailings generation is about 18 billion m³/year and is expected to double in the next few decades [137]. Mining of ores increases the presence of metals in environments and physically rearranges land formations which can interfere with groundwater carrying soil layers. Metals originating from mining activities have been found in a wide variety of environmental media, including soil, plants (including food products), air, and fresh waters. The extraction of lithium from brines requires a large amount of fresh water in the process. In the areas where the salars of South America occur, fresh water supplies are relatively scarce. This has led to some “water conflicts” in the area between the brine mineral extraction industry and traditional farming [33]. Lithium brine production may have negative effects on the local environment. One source of potential pollution is from the large PVC (polyvinylchloride) lined ponds used to evaporate the brine, which could leak substances like lime to the environment [138]. The PVC itself may also leach harmful substance to waters that find their way back into the local environment. Volatile organics and substances, like organotin, albeit at very low concentrations, have been described as leaching from PVC pipes [138,139].

Wanger (2011) describes how a reduction in the flamingo population may result in an increase of harmful cyanobacteria [101]. Flamingos have a variety of habitats, including mangrove swamps, tidal flats, and salars. Flamingos eat cyanobacteria (blue-green bacteria) in these salars, and naturally keep their number in check. The extraction of lithium can have significant environmental and social impacts if not properly regulated and controlled. Water pollution and toxic chemical releases, through leaching and air emissions, are the main concerns. The inhalation of siliceous dust associated with hard rock mining is known to be harmful. The mining of lithium, just like any other mining process, can have an effect on the environment if poorly managed. However, it is important to state that mining is an important part of our global economy. For decades mining has provided millions of people with employment and helped developing nations with economic security [140]. Mined metals are also indispensable for the production of technology that reduces environmental impacts, technologies like wind generators and solar panels would not be possible without metals. Metals are invaluable to our society and it is not an option to just not use them.

3. Lithium Uses

Lithium is a versatile metal, with a wide range of uses. Its applications vary from its use, in the form of lithium carbonate, as a medication to treat mental illness to its use in the manufacture of lightweight alloys for the aeronautics industry. In this section, we have compiled the information given in the literature concerning the main industrial uses of lithium.

3.1. Glass and Ceramics

For a long time, the principal use of lithium ore was in glasses, glass ceramics, porcelain enamels, fritted glazes, raw glazes, and refractories [14]. The glass and ceramics industries are still major consumers of lithium. In these industries, lithium ores, like spodumene, are used as a fluxing agent (chemical cleaning, flowing or purifying agent) [15]. Spodumene concentrate is often used rather than lithium in combination with other lithium-bearing minerals, like amblygonite, lepidolite, and petalite. Lithium is used to reduce the viscosity and lower the production temperatures of glass and ceramic manufacturing processes, thereby reducing costs. Due to lithium's small ionic radius, it has a low coefficient of thermal expansion ($46 \mu\text{m}/(\text{m}\cdot\text{k})$) [17]. When added to molten glass, it reduces the thermal expansion and fluidities (elasticity) of the mix. Adding 0.17% Li_2O to glass lowers the melting temperature by 25°C and reduces energy consumption by 5 to 10%. When used in ceramic production, it lowers the firing temperatures and increases the strength of ceramic bodies. The addition of lithium provides additional durability, particularly in heatproof ceramic and glass cookware. The addition of lithium produces pyroceramic products with prolonged furnace refractory lifespans, greater surface tension, resistance to thermal shock, and increased mechanical strength. Lithium also improves the colour fastness of glazes and decreases shrinkage during production and increases resistance to corrosion.

Lithium fluoride crystals are used in specialised optics. Lithium fluoride forms a simple ionic crystal lattice structure, which is useful in the ultraviolet (UV) and infrared (IR) optics. The lithium fluoride crystals are transparent to short wavelength ultraviolet radiation, more so than any other material. The lithium fluoride crystal has one of the lowest refractive indexes and the farthest transmission range in the deep UV of most common materials. Due to these properties, lithium fluoride is commonly used in the manufacture of prisms, and lenses in monochromators, as well as the focal lenses in large telescopes. Double-glazed windows (using heat-reflective glass) are coated with a thin layer of metallic chemicals, which includes lithium, to improve the insulating properties of the glass. The glass for the Californian Institute of technology's 5.1 m telescope (Hale telescope) at the Mount Palomar Observatory in Pasadena California, USA, contains lithium as a minor ingredient [17]. The addition of lithium to the telescopic mirror helps the glass withstand prolonged heating and slow cooling annealing manufacturing processes [14]. Lithium niobate and lithium tantalate also have specialised applications in optics in the production of electronic grade crystals for use in electronic oscillators. Lithium has been found effective in assisting silicon nanowelds in electronic components

for electric batteries and other devices. Glass lenses, such as those in car headlights which are exposed to rapid temperature changes, contain lithium to reduce thermal shock [14]. The production of high barium, containing monochromatic television tubes, in the past, required lithium as a melting aid [14]. Lithium is also used in the production of monochromatic computer monitors [141]. It is used in the production of glass foam as an alternative to other more polluting ingredients, glass foam is an insulating building material [14]. A blue glaze is acquired when lithium is combined with copper, a pink glaze results from the combination of lithium and cobalt [66].

3.2. Lithium as a Desiccant

Lithium chloride and lithium bromide are extremely hygroscopic and used as desiccants for gas streams. Lithium chloride is one of the most hygroscopic compounds and is commonly used in sophisticated air conditioning systems. Lithium bromide solutions at 55% are used in the air conditioning systems of large buildings. Lithium chloride is used in industrial dehumidification and drying. Lithium bromide and lithium chloride have low vapour pressures and have been used in adsorption refrigeration [15]. Anhydrous lithium hydroxide and lithium peroxide are used in submarines and the international space station as chlorofluorocarbon-free, carbon dioxide removers (scrubbers). The lithium hydroxide takes carbon dioxide from the air and converts it to lithium carbonate. Lithium peroxide reacts in the same way, but also releases oxygen. When lithium is burned in air, it will produce lithium oxide and lithium peroxide. Lithium chromate has also been used in air conditioning systems. Lithium perchlorate is used in the manufacturing of candles that provide oxygen. Lithium hydroxide was used as a desiccant in the rebreather systems used in the Apollo space missions.

3.3. Organolithium Chemistry

Due to the high electropositive nature of lithium, organolithium compounds are extremely powerful bases and nucleophiles. Organolithium compounds are sold as bases commercially and used in the production of high-grade pure chemicals. Butyllithium is used in both polymer and pharmaceutical industries as an intermediate. Lithium and its compounds are used to catalyse the polymerization of conjugated dienes and the copolymerisation of alkenes [142]. Butyllithium is used as a catalyst in the polymerisation of butadiene, isoprene, and styrene, and to produce styrene butadiene and polybutadiene synthetic rubber [15]. It is used to catalyse polymer reactions with thermoplastic properties [6]. Organolithium reagents are used as exceptionally powerful and selective reducing agents in organic synthesis. Lithium aluminium hydride is the most common lithium compound used as a reducing agent. It is used in reactions such as in the Birch reduction, Grignard-type reactions and in the synthesis of vitamin A [143]. Unlike other alkali metals, lithium is soluble in organic solvents like pyridine, diethyl ether, and 1-pentanol [115]. This property is often exploited in the lab as a means of separating lithium from a solution using a liquid/liquid extraction process. Lithium's solubility in diethyl ether is also used to create an organolithium compound in a Wurtz-type coupling reaction, where two alkyl halides are reacted with sodium in a diethyl ether solution to form higher alkanes ($RX + 2Li \rightarrow RLi + LiX$) [142]. This reaction is used to produce many organic compounds. Organolithium compounds will bond to an alkene [142]. The alkylation (transfer of an alkyl group from one molecule to another) of organolithium compounds is a common and useful reaction in organic chemistry, for example, reaction of organolithium compounds with a ketone produces a tertiary alcohol ($R_2C=O + R'Li \rightarrow R_2R'COLi$) [142].

3.4. Lithium as a Lubricant

Lithium grease is waterproof, capable of maintaining its viscosity for a long time, has an extremely low melting point, high mechanical strength, and high thermal resistance. Since lithium grease first came onto the market in the early 1940s, it has practically replaced sodium-based greases [60]. Essentially, lithium grease is an oil mixed with an emulsifying agent like soap. Lithium stearate and lithium 12-hydroxystearate are often used in the saponification of triglycerides (lipids) to manufacture high-temperature resistant greases [144]. These greases are commonly used as a lubricant

in metal-on-metal mechanisms, both indoor and outdoor, and are commonly used in automotive applications. Lithium hypochlorite is used as a disinfectant in swimming pools and as a reagent for some chemical reactions. Lithium hydride is used in the synthesis of hydrides of certain metalloids like silane (compounds with four substituents on a silicon atom) in the Sundermeyer process ($4\text{LiH} + \text{SiCl}_4 \rightarrow 4\text{LiCl} + \text{SiH}_4$) [145]. Lithium-based chemicals have other applications, such as in hydrogen and oxygen generation, and in flavours, colourings, and fragrances [15]. Lithium burns bright red, and because of this property, lithium compounds are often used in fireworks and flares as pyrotechnic colourants. When lithium oxide is extracted from spodumene by roasting, the gangue is used as an additive to cement, where it reduces cement kiln operating expenses and increases setting time [115]. Lithium is also used as a tracer in soil and water contamination studies because it mimics the movement of metals in the soil solution and water body closely and can be used to accurately predict residence time.

3.5. Lithium in Medicine

Lithium's beneficial neurological effects have been exploited since the height of the Roman Empire. Perhaps the first recorded use of lithium as a therapeutic agent was between the years 98 and 138. The Roman physician Soranus of Ephesus (modern-day Turkey) discovered that patients suffering from mania who repeatedly bathed and drank the alkaline waters of the area showed improved conditions [146]. These waters contained high levels of lithium salts. Without knowing it, Soranus had discovered the therapeutic effects of lithium on people suffering from mania. Lithium was first used to treat gout in 1845, the reasoning for this being that a lithium solution was observed to dissolve uric acid crystals in urine, the formation of which is a symptom of gout [34,147]. At the time "urate imbalances" were proposed to be responsible for a number of medical ailments like gout. Uric acid was also known to be a psychoactive substance, so it was postulated that treatment with lithium would reduce uric levels in patients suffering from mania [148]. Lithium was seen as a miracle neuroprotective agent and was added to tonics to boost mental fitness. Its growing popularity even saw it been added to products like "Bib-Label Lithiated Lemon-Lime Soda" the precursor to 7-up (where lithium was the original "up" ingredient) and "Lithia water" in the 1920s [149]. Lithium chloride was also used as a replacement for common table salt for people requiring low sodium diets. The widespread use of lithium eventually led to several cases of lithium toxicity, resulting in it being banned in soft drinks [147].

Some groups suggest there are beneficial effects to be had from taking lithium supplements, such as lithium orotate. Claimed benefits include enhancing mental development, the protection from use of psychoactive medications such as serotonin reuptake inhibitors, and protection to the brain from alcohol abuse [150–152]. In the 1880s, it was noted that lithium had a beneficial therapeutic effect on patients suffering from mania, and also reduced suicidal tendencies in patients [147]. Credit for rediscovering the therapeutic properties of lithium goes to the Australian psychiatrist Dr John Cade in the 1940s [153–157]. Cade treated patients suffering from mental ailments successfully using lithium carbonate [147]. He determined that lithium carbonate had a calming effect. Cade's findings went unnoticed for some time: "*Made by an unknown psychiatrist with no research training, working in a small chronic hospital with primitive techniques and negligible equipment, was not likely to command attention*" [157]. Lithium carbonate, as well as lithium acetate, lithium aspartate, lithium citrate, lithium borate, lithium orotate and lithium sulphate, has been used since then to treat people with bipolar disorder (manic depression) and to alleviate suicidal thoughts in patients [148]. It has also seen some use in the treatment of schizophrenia and addiction. Lithium is known to interact with neurotransmitters and receptors in the human brain, increasing serotonin levels and reducing brain production of norepinephrine, a hormone and neurotransmitter. Lithium's interactions in human biochemistry are complex and the topic of much research [34]. The exact mechanisms by which lithium acts neurologically are not fully understood, however, at least nine theories having been put forward [148].

Lithium has been used to treat headaches, hypertension, diabetes, epilepsy, and even dental caries [77,158]. Lithium bromide was used as a sedative/hypnotic in the past, but its use was discontinued due to some complications caused to patients with pre-existing heart conditions [148]. Lithium is also used in the chemotherapeutic treatment of inflammation in joints. It accumulates preferentially in the thyroid gland, where it can cause problems like hypothyroidism and thyrotoxicosis, which has only been observed in patients receiving lithium treatments [158]. Autopsies have shown that lithium also accumulates in the cerebellum, cerebrum, and kidneys [34]. Lithium has been investigated as a possible preventative/treatment for Alzheimer's disease. One symptom of Alzheimer's is a "tangling" of microtubules in cells. Lithium's presence reduces the amount of "tangles" by limiting the amount of a protein produced which propagates these "tangles" [147,159]. Lithium may have a preventative effect on dementia in mice [160]. There are also studies investigating whether lithium in humans can prevent dementia [161]. There are no cases in the literature relating a natural source of lithium to any acute or chronic toxicities. Ingestion of approximately 5 g of lithium chloride is enough to cause fatal toxicity in humans [35,45]. Shahzad et al. (2017) provide an extensive list of the symptoms associated with lithium acute and chronic toxicity in humans associated with people receiving lithium treatments [35]. Lithium has been reported to reduce reproduction in some fish and crustaceans [45,162]. Lithium is an important micronutrient that has a function in metabolism, cell proliferation, and neural communication [35].

There is evidence to suggest that lithium at low concentrations in the human diet has a beneficial effect on human behaviour. Lithium's beneficial effect on risk factors associated with atherosclerotic heart disease, like hypertension and serum lipid levels, have been described in detail [163]. Voors, (1969) work showed a negative correlation existed between atherosclerotic heart disease and lithium in drinking water ($r = -0.426$ at $\alpha = 0.05$) in white males [163]. A sustained increase in the amount of lithium in the human diet can result in its accumulation in the body, where it could potentially have undesired effects. Lithium easily enters human cells but finds it more difficult to leave [164,165]. Schou (1958) reported on the distribution of lithium in mammalian bodies [165]. Physiological symptoms in humans due to a lithium-deficient diet, have not been observed.

Evidence linking low lithium levels with behavioural abnormalities has been shown. In 1990, a study carried out in Texas, USA, over 10 years found lower rates of suicide, homicide, and rape in areas with relatively higher concentrations of lithium in the public drinking water (0.07–0.160 mg/L) [166]. Their work suggested that lithium has moderating effects on suicidal and violent criminal behaviours at levels that may be encountered in municipal water supplies [167]. It has been suggested that putting minuscule amounts of lithium into public drinking water supplies would have a beneficial effect on the general population by improving the mood of people and lowering suicide rates. In a Japanese study, the lithium levels in the drinking water of eighteen municipalities in Oita prefecture were measured and used to investigate if there were any associations between suicide rates and lithium levels. It was found that suicide rates were significantly and negatively associated with lithium concentrations [168]. A study which involved >6000 drinking water samples taken across ninety-nine Austrian, districts, was carried out to evaluate any correlation between local lithium concentrations and suicide mortality rates. The study showed that there was strong evidence that Austrian regions with higher lithium drinking water levels were associated with lower suicide mortality rates [169]. A similar study was carried out in the east of England, and the study found that the lithium drinking water concentration in forty-seven subdivisions of the east of England was significantly and negatively associated with suicide rates [170]. Another observational study in Japan, involving eighteen neighbouring Japanese municipalities with a total of 1,206,174 individuals, suggested that naturally occurring lithium in drinking water increased human lifespan [171]. In the Aomori prefecture of Japan, which has the highest suicide mortality rates in Japan, findings from a similar study indicated that the natural concentrations of lithium in drinking water reduce the risk of suicide among females [172]. The Ministry of Health, Labour and Welfare, who are the authority in charge of water supply for domestic use in Japan, has recommended that lithium could be added

to the drinking water at a level of 2 mg a day per adult to promote mental health and lower suicide rates [173].

These studies provide strong evidence that regions with high concentrations of lithium in the drinking water are associated with lower suicide mortality rates. In some of these studies, confounding variables to do with physiological and economic factors were not taken into account, so it is difficult to say the results are conclusive [174]. Several authors suggest that these associations do not establish a causal relationship, their argument generally being that the parameters measured are too variable, and subject to many other societal issues. Despite this, there are numerous studies which suggest that lithium in drinking water can modulate behaviour [174–184].

3.6. Lithium in Warfare

Both stable isotopes of lithium ^6Li and ^7Li are used in the production of nuclear weapons. The first man-made nuclear fusion reaction using ^7Li was achieved by Mark Oliphant in 1932 [185]. On 16 July 1945 in the Jornada del Muerto desert of New Mexico, the United States carried out their first successful nuclear weapon test (The Trinity test) [186]. Only a matter of weeks later, on 6 and 9 August, the United States dropped nuclear weapons on the Japanese cities of Hiroshima and Nagasaki, effectively ending the Second World War in the Pacific. In January 1946, the United Nations called for the elimination of nuclear weapons. However, in August 1949, the United Soviet Socialist Republic (USSR) test fired its first nuclear weapon, a major contributing factor to the already ongoing Cold War between the two world superpowers, the United States and the USSR. The demand for lithium increased significantly during the Cold War, along with the proliferation of thousands of nuclear fusion weapons. Lithium produces net energy through nuclear fusion. ^6Li acts as a neutron absorber, and ^7Li is used as an enriched lithium fluoride coolant in the nuclear power industry. Both isotopes, when exposed to a stream of neutrons in an exothermic (^6Li) and endothermic (^7Li) reaction, produce the radioactive hydrogen isotope tritium, an important component in nuclear weapons. In the 1950s, the USA military required vast amounts of lithium as lithium hydroxide, from which they harvested ^6Li to produce staged thermonuclear weapons [187]. Tritium is also important for the future production of thermonuclear fusion reactors, a technology which has the potential to cleanly meet the future energy needs of the world [14,15]. The estimated future requirement of lithium to meet the demand of a mass production of thermonuclear the fusion reactors is 200 to 1000 t/1 GW electric power [12]. Lithium hydride was used to store hydrogen for warships in World War Two, and as a means of rapidly producing hydrogen to inflate lifting balloons, emergency signalling, and barrage balloons used as a means of protection from enemy plane attacks [14,15]. Lithium hydride and lithium aluminium hydride are used as a high energy additive to liquid and solid rocket fuel propellants [187]. The propellants Li, F_2 , and H_2 , together, produced the highest specific impulse ever test-fired in a rocket engine (5320 m/s) [188]. Sulphur hexafluoride reacted with metallic lithium is also used as a propellant fuel in military applications. The advent of rocketry also necessitated the need for high-temperature resistant materials. The properties of lithium make it an ideal candidate to produce these materials, like the composite ceramic (Pyroceram[®], which expands very little and resists cracking at high temperatures and is used as a heat shield in rocketry [15]. Pyroceram[®] is manufactured by Corning incorporated, New York, NY, USA. Lithium ion batteries (LIBs) are used extensively by military around the world, favoured because of their lightweight efficiency and ability to conform to almost any required shape.

3.7. Metallurgy

Similar to the glass and ceramics industries, lithium is primarily used in metallurgy as a flux to reduce energy costs. It promotes the fusing of metals when soldering or welding. In continuous steel casting, it reduces the melt viscosity, improving flow rates and assisting in thermal insulation. It has a lubricating effect on the surface of the steel, making the continuous casting process more efficient by reducing friction. In the production of high conductivity copper and the copper–tin alloy bronze, lithium is used as a degasifier; since, in very low amounts, lithium metal scavenges

available oxygen and other gases from molten metals. When casting iron, lithium reduces defects in the process by reducing the incidence of veining (a sheet-like casting defect). Lithium fluoride is used to adjust the melting points during the smelting and refining of aluminium in the Hall–Héroult process. Lithium is used in the electrolysis of aluminium oxide to lower the temperature of the reaction, increase electrical conductivity, decrease viscosity, and reduce the amount of the mineral cryolite (Na_3AlF_6) used. Cryolite is also used as a flux to reduce reaction temperatures and dissolve oxide minerals from ores, allowing the easy extraction of aluminium by electrolysis. Lithium is the lightest of all the solid elements; because of this property, it is ideal for making high-strength-to-weight-ratio alloys, and several of its alloys are produced on an industrial scale. Lithium alloys of Al, Cd, Cu, and Mn are used in the aeronautical industry to make lightweight parts. Other lithium alloys are common, and include alloys with metals such as Ag, Au, Mg, and Pb. Mg/Li alloys have a low density, which makes them an attractive material for several industries, including engineering and armour-plating [189]. Cu/Li alloys are used in the copper-casting industry. Lithium is used in the degasification of copper castings because of its affinity for oxygen, hence, it is added prior to pouring as a means of creating denser casting free of pinhole porosity, which is a common problem [142]. Al/Li alloys are used in the aerospace and aeronautics industries, where their strength and weight reduction properties allow better fuel consumption. Lightweight lithium alloys used in the manufacture of aircraft have the potential to reduce weight by as much as 10%. Li/Al alloys contain up to 7.5% lithium and Li/Mg alloys can contain up to 13% lithium, while most other lithium alloys contain 2 to 3% lithium [20]. These alloys are quite expensive, and consequently, plastics are often used in their place. In 1918 in Germany, an Al, Zn, Cu, Mn, and Li alloy containing 0.1% lithium, called Scleron, was manufactured as one of the first commercial lithium alloys [190]. Another such alloy created in Frankfurt am Main, Germany, during World War One, was Bahnmetall (bearing metal) an alloy of Li, Ca, Na, and Pb. Bahnmetall is still used today in the manufacturing of specialised (anti-friction) railroad car bearings [191].

3.8. Lithium Batteries

In 1912, Gilbert Newton Lewis investigated the electrochemical properties of the lightest and one of the most electropositive stable elements lithium [192]. Early lithium batteries used lithium metal as the cathode and could not be recharged. A common problem with these batteries was the build-up of dendrites (microscopic fibres of lithium) on the lithium electrodes, caused by the repeated removal and addition of lithium ions. If the dendrites bridged the gap between the two electrodes, the battery would short circuit, often resulting in fire. In 1972, while working for the company Exxon, Michael Stanley Whittingham developed the first rechargeable lithium battery. This advance in battery technology was based on a lithium disulphide cathode and a lithium metal anode, with lithium perchlorate in dioxolane as the electrolyte. The technology was still susceptible to dendrite formation, often resulting in thermal runaway. Credit for developing the modern LIB goes to John Bannister Goodenough. The presence of lithium in its ionic rather than metallic form in the Goodenough design, effectively solved the dendrite problem [193]. According to Goodenough (2018), Professor Akira Yoshino, a fellow at the Asahi Kasei Corporation, Japan, manufactured the first commercial LIB by combining a lithium cobalt oxide cathode with a graphitic-carbon anode [194]. Sony and Asahi Kasei commercialised the technology in 1991. The battery was used by the Sony Corporation to power the very first portable phone and, since then, the demand for LIBs has consistently grown [194]. Tarascon and Armand (2011) provide a detailed account of the development of the modern LIB [193]. Today, LIBs are used in most of our everyday portable electronic devices, from pacemakers to smartphones. In recent years, the consumer electronics and energy storage industries have driven the demand for LIBs.

Primary lithium batteries use metallic lithium with compounds like manganese dioxide and sulphur dioxide as the cathode [41]. Primary batteries are not rechargeable. Secondary batteries are rechargeable (LIBs) and use a lithium metal oxide as the cathode and, often, lithium-based compounds, such as lithium perchlorate, as the electrolyte [41]. A modern LIB contains a graphite anode, a lithium

metal oxide cathode, and an electrolyte solution doped with a lithium solution, such as lithium hexafluorophosphate in a mixed organic solvent (often ethylene carbonate or dimethyl carbonate [195]). The design of EV LIBs consists of a number of battery cells arranged in sequence in a module, a group of modules becomes a battery pack, and a group of packs is referred to as the battery system [133]. The terms battery and battery cell are often used interchangeably in the literature, and a battery is made from a number of cells (e.g., a 12 V lead-acid battery contains 6 cells) [133]. According to Tahil (2007), a 30 kWh LIB system for an EV cost €7500 in 2007 [96]. The price of Li/kWh has steadily decreased since then, from €800/kWh in 2010 to just over €200/kWh in 2018 and is expected to fall to €100/kWh by 2025 [196,197].

LIB advantages include high energy density, low self-discharge rate, long life cycle (1000 cycles), no memory effect, low maintenance, fast charging, and low weight (40 to 60% less than lead-acid batteries). Some of the disadvantages of LIBs include the need for a protection circuit and travel restrictions, in order to prevent thermal runaway. Current LIBs operate best at a temperature between 20 °C to 60 °C [133]. Nickel metal hydride is currently used in some HEVs (hybrid electric vehicles) and Ni–Cd-based batteries are also used in some EVs. These batteries, despite not being as powerful as LIBs, are still vying for a share of the EV market. However, any future technology using these metals is not expected to impact significantly on lithium's dominance of the market. LIB production is the largest consumer of lithium resources today. LIBs are replacing known nickel metal hydride and Ni–Cd batteries as the battery of choice for new EVs [193]. LIB batteries provide more voltage than previous battery technologies (Table S12, Supplementary Materials [19,107,133]). The amount of electrical energy in a battery is best given by the specific energy (Wh/kg), the nominal battery energy per unit mass.

To manufacture a 5 kWh LIB for each of the estimated 1 billion cars in the world today, would require 20% of current lithium reserves [96]. However, a 5-kWh battery is a conservative estimate for the size of a standard EV battery; the capacity of EV LIBs will undoubtedly increase as technology advances [96]. According to Tahil (2007), a 60 kWh LIB in every car would use up 50% of world lithium reserves [96]. These figures do not take into account heavy and light goods vehicles, which would require a battery at least 10 times larger than a generic EV LIB [96]. According to Speirs et al. (2014), generally, an EV battery requires 0.165 kg of lithium carbonate for each kW/h, a plug-in hybrid electric vehicle (PHEV) battery 0.176 kg/kWh, and an HEV 0.375 kg/kWh [198]. A lithium carbonate-based LIB requires 0.18 kg of lithium carbonate per kW/h [198]. The Tesla Model S Performance EV contains an 85 kWh LIB pack with approximately 50.8 kg of lithium carbonate. The Tesla Model S, LIB can fully recharge in 20 to 40 min, and has an electric range of 539 km, higher than any other EV [199]. A battery of 8 kWh capacity would give 50 km range [96]. Lithium carbonate is one of the lowest cost components in a LIB [67]. Different LIBs require different amounts of lithium carbonate, depending on their application. A smartphone requires at least 3 g, a laptop computer 10 to 30 g, and a power tool 40 to 60 g [12]. EV batteries, depending on their capacity, may require anything from 8 to 100 kg of lithium carbonate.

There is a race to develop the next big thing in battery technology. LIBs may not continue to dominate the EV battery market, as other battery technologies currently at the research stage, like metal–air, bio-electric, foam, graphene, and gold nanowire batteries, may be more efficient than LIBs. Solid state lithium batteries are making a comeback as well. The development of solid electrolytes, which allow the passage of ions and prevent the formation of dendrites, are currently being developed. These solid electrolytes can be made from plastic or even glass, the batteries also have the advantage of being able to work at low temperatures (–20 °C). Goodenough (2018) describes a dielectric amorphous-oxide solid electrolyte (developed by Maria Helena Braga of the University of Porto). The battery is comparable to modern-day LIBs [194]. Goodenough (2018) has used this electrolyte material to develop all-solid-state rechargeable batteries that are dendrite free, have a long-life cycle, and have acceptable charge and discharge rates [194]. Figure 1 shows the increasing use and production of lithium from 2003 to 2020. Figure 2A–D shows the percentage of lithium use in each main industry since 2005.

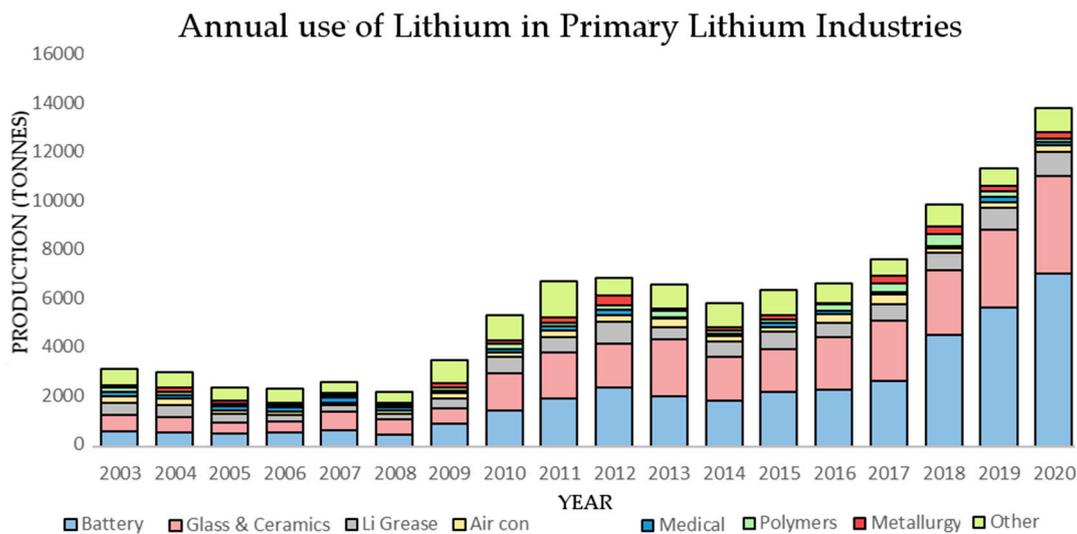


Figure 1. Annual use of lithium in tonnes in each of the primary lithium usage industries from 2002 to 2020 [5,6,15,83,88,96,104,105,128,129,141,200].

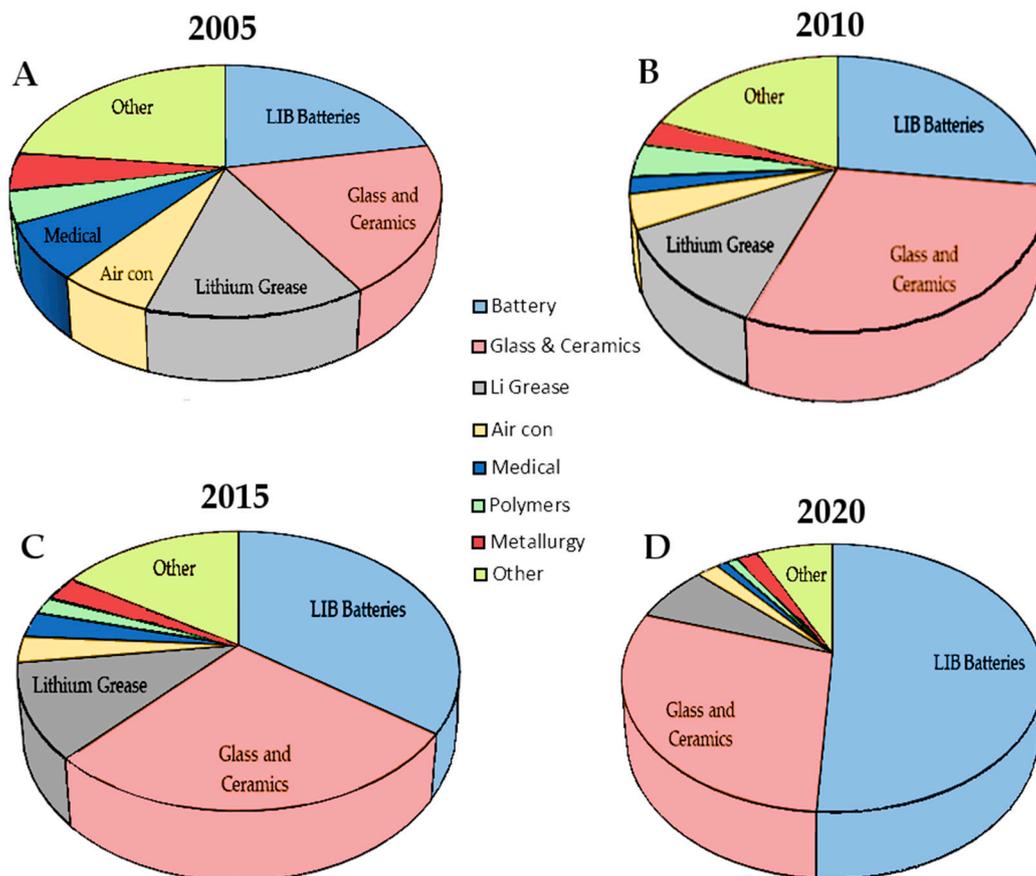


Figure 2. (A) Percentage lithium use in each of the main lithium using industries in 2005. (B) Lithium use in 2010, (C) lithium use in 2015, and (D) lithium projected use in 2020. Sources, [43,83,88,96,104,105,141].

4. Lithium Recycling

Less than 1% of lithium is currently recycled. There is currently no great incentive to recover lithium from waste streams because of its relative abundance. The majority of mined lithium is still in use in our society, for example, as LIBs. There is not a large enough lithium waste stream yet to justify the development of a lithium recycling industry. If demand increases for lithium resources, there will be a future imperative

to recapture lithium before it is lost in waste streams. One such waste stream is old mobile phones. Over a billion mobile phones are produced globally every year. These phones contain approximately 30 to 40 g of lithium. These phones also contain, on average, metals like gold at approximately 9 mg, palladium at 24 mg, and silver at 250 mg [1]. The amount of metal present is largely dependent on the model of phone. Gold, palladium, and silver are currently recycled from old mobile phones. In the future, it should make economic sense to also recover lithium from old mobile phones and other waste streams. Unlike oil, lithium is easily recyclable, its low melting point (180 °C) and the low solubility of its fluoride, carbonate, and phosphate salts make its recovery quite easy [49]. The recovery of valuable metals from spent batteries is a common procedure which can be easily applied to LIBs. LIBs usually contain aluminium, copper, and cobalt, which are often recovered during recycling [201]. Lithium recycling has not yet taken off as an industry [6]. The recycling of LIBs will require an already well-established EV market functioning for several years. Any large-scale recycling of lithium will come online in a few years; the demand for lithium should fuel strong investment in its recycling in the future.

Lithium can be recycled from LIBs using the following methods, leaching, precipitation, ion exchange or solvent extraction [43]. Meshram et al. (2014) estimate that 250 t of ore or 750 t of brine or 28 t of LIBs are needed to produce 1 t of recycled metallic lithium [43]. Large EV LIBs will be easier to recycle than smaller batteries, also, the economies of scale for the LIB recycling industry should emerge when the use for LIBs in EVs increases [12]. Swain (2017) describes three methods by which lithium is recovered from batteries: (1) hydrometallurgy (dissolution, leaching, solvent extraction, precipitation, and electrochemical methods); (2) pyro-metallurgy (mechanical shredding, thermal, calcination, roasting, reduction, and chlorine metallurgy); and (3) biological processes (bio-leaching and phytomining) [83]. Peiró et al. (2013) describe a cryogenization process (freezing, shredding, leaching, and precipitation) [41]. According to Swain (2017), as of 2017, only 3% of LIBs were recycled and <1% of Li was recovered, globally [83]. The recycling of LIBs is in compliance with the Waste Electrical and Electronic Equipment Directive (collection, recycling, and recovery) WEEE Directive, 2012/19/EU and the RoHS Directive, 2002/95/EC, which sets restrictions on European manufacturers as to the material content of new electronic equipment placed on the market [202,203]. The recycling of LIBs is an important factor and should facilitate any future shortfalls in lithium resources [101]. Environmental pollution from battery materials is a concern for the future [17]. Lithium's newfound popularity means that it is now considered an emerging environmental contaminant. Improper LIB disposal is one way in which lithium can infiltrate the environment, where it can be absorbed by plants, enter the food chain and potentially accumulate in humans.

5. Discussion

Demand for lithium today is largely driven by the applications of LIBs in EVs. It has been predicted that there will be between 3.8 and 4.5 million EVs in use by 2020 [41]. Lithium demand is expected to increase by 8 to 11% every year from 2017 [6,60]. LIB production in the United States nearly doubled between 2005 and 2010 [12]. Currently, 35–39% of global lithium production is used for LIBs [83]. The LIB market is estimated to grow to €180 billion by 2024 and require at least 66% of all lithium produced [83]. The European Union (EU) has put in place directives to encourage the spread of EVs. These include the Clean Vehicle Directive 2009/33/EC and the Energy Efficiency Directive 2006/32/EC [41]. Also, individual countries offer incentives, like free road tax and free charging points, to encourage people to buy EVs [41]. Most major vehicle companies are actively pursuing the development and production of EVs using LIBs [204]. EV companies include Nissan, Tesla, General Motors, Ford, and Toyota. Fossil fuels currently account for 95% of the total energy used for global transport [12]. Predicting the future demand for lithium resources is a complicated issue which requires predicting the future growth of the various industries that use lithium, rather than just the LIB industry [14]. Most of the data regarding the price and demand of lithium are found in commercial reports rather than in scientific journals [6]. Gruber et al. (2011) report on global lithium resources and demand in 2011, and list 103 lithium-containing deposits. Drivers for the lithium market

include targets for carbon dioxide emissions, lowering LIB costs, and extended EV ranges [49,87]. Some authors predict that there will be a shortfall in the amount of lithium produced in the future, but this argument has been going on since the 1970s [14,101,198]. Sverdrup (2016) believes that there will be enough lithium to meet demand until 2050, after which, the price of lithium will rise, although lithium recycling, by then, should help offset some of the cost [104]. Financial market analysts at the Macquarie Group noted that lithium prices have increased 50% since the start of 2015 and are continuing to increase rapidly [205].

The EV market is on the verge of large-scale commercialisation and implementation. However, there are some doubts as to whether or not infrastructure like charging points will be in place to ensure a seamless transition from fossil fuel to electric power. The perceived limited range of EVs also creates uncertainties among customers. Sverdrup (2016) points out that for an EV to be comparable to the performance of a fossil-fuelled car, it should have a range of at least 300 km; this corresponds to a battery pack that would contain approximately 10 kg of lithium [104]. LIBs are still very expensive, which could explain the persistence of nickel metal hydride battery technology in PHEVs. The obvious incentive for consumers to buy an EV is that they are cheaper to run than fossil fuel vehicles. Wright (2010) worked out that the cost of running an EV is €0.012/km, while fossil fuel vehicles cost €0.155/km to run [107]. The EV global market is experiencing a rapid market evolution. In 2016, the number of EVs worldwide was greater than 2 million. New registrations of EVs hit a new record in 2016, with over 750 thousand sales worldwide. Tens of thousands of EVs are already on our roads in countries like Norway, where they have a market share of 29%, and the Netherlands, with a 6.4% EV market share [206]. Tesla Incorporated's new Gigafactory in Nevada, USA, is projected to supply >30% of the world's LIBs by 2020 and have an annual output of the production of 500,000 EVs [207]. Tesla's energy storage home Powerwall battery pack has also received \$800 million worth of presale orders. The United Kingdom and France have stated that there will be a ban on the sales of all of petrol and diesel cars by 2040. China represents one of the largest and fastest growing markets in the world, and the Chinese government is working on a timetable to end the production and sales of traditional energy vehicles and are developing several new EV models for production. In 2016, China was by far the largest electric car market, accounting for more than 40% of the electric cars sold in the world, and more than double the amount sold in the United States [206]. Several major car manufacturers including Volvo, Toyota, and Volkswagen, have set dates by which they plan to phase out vehicles powered solely by the internal combustion engine.

6. Conclusions

Film directors Andreas Pichler (Italian) and Julio Weiss (Bolivian) first coined the term "The Lithium Revolution" in their documentary of the same name [208]. That title effectively paints an optimistic vision for the future of lithium. Their documentary illustrates our unsustainable dependence on oil and the search for an alternative energy source. If the alternative energy source is renewable green energy produced from technologies like solar and wind, then storing that energy in LIBs is an important element in the equation. The propagation of EVs globally, and a reduction in the number of fossil fuel-burning vehicles, would effectively reduce greenhouse gases and perpetuate the green energy economy. The responsible mining of lithium resources could very well be the key that sets us on a path towards a low carbon energy future, a future in which the EU cannot afford to be left behind. The EU needs lithium in order to meet its commitments to the green economy.

Lithium demand is growing along with the LIB. The distribution of lithium deposits both brine and mineral around the world should be sufficient to meet future demand and to ensure a security of supply for the EU [8,87]. Resource estimates should increase as new deposits are discovered and mining and recycling technology advances. This also means that sites, such as that in Ireland, could perhaps become commercially valuable [10]. Some authors predict that there will not be enough lithium to meet future demands, and that we are just switching one diminishing resource, oil, for another, lithium [14,83,101]. According to some, the demand for lithium may also overtake production in the

future, unless at least 90% of lithium is recovered by recycling [83]. Some of the largest deposits of lithium exist in countries that lack the infrastructure to mine it, thus, the supply of cheap lithium in the future is not guaranteed. An enormous resource of lithium exists unmined in Bolivia. The Bolivians are understandably reluctant to allow their valuable resource to be taken from them, having experienced the “resource curse” first hand in their past [209]. Afghanistan also contains a massive lithium resource. Countries like Bolivia and Afghanistan have the potential to become, as many authors have suggested, “The New Saudi Arabia of Lithium” [91,107].

It is likely that demand for future lithium resources will be dominated by the battery industry, especially in the EV market. Other applications of lithium-based battery technology that should come online in the coming years including grid electrical storage, as well as applications in the nuclear power industry, will undoubtedly increase demand on lithium resources. With the vast resource of lithium in the world, albeit in as many different locations as deposits, there still should be enough to meet demand. If the industry passes a certain threshold, then it will likely boom like the smartphone market at the start of the century. Our fossil fuel resources are depleting and becoming more difficult to extract. On top of that, there is constant and growing concern over the security of future oil supplies. There is an urgent need to find new sources of energy, and industrialised nations are looking towards lithium. As more nations develop and their people need transport, lithium technology can ensure that this need for transport will not come at the cost of our environment. Due to the efficiency and environmental cleanliness of lithium technology, worldwide financial and political support for its development is increasing. It is in our interest to advance the production of EVs. The world lithium market is rapidly growing, although it is essentially still in its infancy, prior to the mass production of EVs. The EU should have enough lithium deposits to ensure a future security of supply.

Supplementary Materials: The following are available online at <http://www.mdpi.com/2079-9276/7/3/57/s1>, Table S1: CRMs listed by the EC in 2017. HREEs—heavy rare earth elements, LREEs—light rare earth elements, PGMs—platinum group metals. Table S2: Known EU lithium mineralisation’s. Main mineral present, percentage lithium oxide and estimated lithium reserve. Table S3: Lithium concentrations in seawater given in the literature, units—mg/L. Table S4: Lithium’s average crustal abundance, units—mg/kg lithium. Table S5: Lithium concentrations in various rocks, units—mg/kg, Sources. Table S6: Lithium concentration in different soils, units—mg/kg. Table S7: Global lithium resource estimates, units—Mt (megatons). Table S8: Estimates of global lithium resources by country from the literature. Units—Mt (megatons), (D.R. Congo—Democratic Republic of Congo). Table S9: Location and parameters of some of the main lithium containing brines. Table S10: List of 145 named lithium minerals. Table S11: Location and parameters of some lithium pegmatites mines globally.

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