### CED 461- Battery Technologies

-project report-

#### **Critical Raw Materials for Li-ion Batteries**

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**Abstract**: This project aims to examine the critical raw materials used in lithium-ion batteries, comprehensively exploring their fundamental principles, operational mechanisms, historical evolution, and elemental composition. Moreover, the study aims to examine the sustainable supply chain and industrial importance of these crucial materials. Additionally, the research delves into sustainability challenges and the environmental and social implications associated with critical raw materials.

#### Introduction

Batteries are utilized in nearly all aspects of daily lives. While non-rechargeable batteries hold a significant position in our lives, rechargeable batteries seem to be more widely preferred. In secondary batteries, the reversible electrode reaction and cell structure have made rechargeable batteries, particularly lithium-ion batteries, more appealing. The primary reason for the adoption of lithium-ion battery technology is lithium's status as the lightest and most electropositive metal, enabling it to provide high energy density. Li-ion batteries demonstrate a consistent life cycle; they can be manufactured in various sizes and require less maintenance compared to other types of batteries. A lithium-ion battery functions as an electrochemical device that both stores and dispenses electrical energy through a reversible process. This process involves the movement of lithium ions between two distinct electrode materials, with a lithium ion-conducting electrolyte solution serving as the medium that separates these electrodes [1]. Lithium-ion batteries are showing a rising trend among energy storage technologies and aim to transform the energy infrastructure into a more sustainable form than fossil fuels. Many of the batteries used in electric vehicles and grid energy storage have transitioned from Ni-MH batteries to lithium-ion batteries over the years.

#### **History of Li-ion Batteries**

Since the beginning of the 21st century, the goal has been to use energy efficiently, minimize certain emissions, and provide sustainable technology. In this regard, lithium-ion batteries have become a significant part of people's lives since the early 1990s when they began to commercialize [3]. The first commercial lithium-ion battery, introduced by Sony Corporation in 1991, contained LiCoO2 as the positive electrode and graphite as the negative electrode. Since then, these batteries have exceeded their original expectations in terms of

power, leading to the creation of new markets for portable electric devices. The lithium-ion battery

stands out as a remarkable success story, fuelling the wireless revolution in portable electronics (such as cell phones, laptops, digital cameras, power tools, etc.) and emerging as the preferred option for electric vehicles and the historical evolution of lithium-ion batteries over time shown as in Figure 1. [7] This is primarily due to its exceptional energy density and the continuous reduction in manufacturing costs. For the adoption of these developing projects, they must meet certain criteria, especially energy density, cyclic stability, and conductivity, among others. Cost also significantly impacts these criteria. Additionally, the ability to be produced on a large scale is an important criterion for the technology to globalize and be sustainable. The availability, quality, and the ability to be smoothly provided in the supply chain, usability of critical raw materials used in production also play a significant role [2].

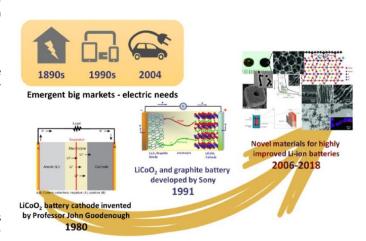


Figure 1: Schematic diagram of the Historical Development of Lithium-Ion Batteries. (Wentker, M., Greenwood, M., Asaba, M. C., & Leker, J. (n.d.).

A raw material criticality and environmental impact assessment of state-of-the-art and post-lithium-ion cathode technologies.)

suppliers due to the high consumption of valuable materials (Li, Ni, Co, graphite, etc.) for Lithium-ion batteries [5].

#### **Basic Principles of Lithium-Ion Batteries**

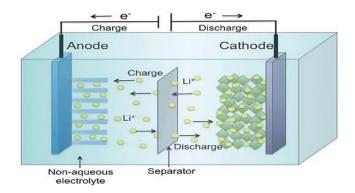


Figure 2: The Principle of the Lithium-Ion Battery

A lithium-ion battery, there are four main components: cathode, anode, separator, and electrolyte. The cathode and anode materials are applied to copper and aluminium foil current collectors, respectively, to store lithium ions. Graphite is frequently employed as the primary material for Li-ion batteries anodes because of its elevated negative potential [6]. Although cobalt is the most frequently used cathode material in lithium-ion batteries, other materials like manganese are also common. The electrolyte enables the movement of lithium ions between the cathode and anode, aiding in the flow of energy. When charging, lithium ions return from the anode to the cathode's crystal structure. Conversely, during discharging, lithium ions move from the anode to the cathode's internal structure. This process is essential for storing and using energy in a lithium-ion cell [4].

#### 3. Critical Raw materials in Li-ion Batteries

Critical raw materials are economically critical substances that, due to the lack of exact alternatives and the limited nature of resources coupled with the increasing world population, can cause production problems if the supply chain is disrupted. Critical raw materials are found in many everyday devices and products essential to the economy of each country, hence their absence can render many sections of society inoperable. The main critical materials for Li-ion batteries include lithium, cobalt, nickel, manganese, and graphite. The supply and prices of these materials can impact the overall cost and sustainability of lithium-ion batteries, making them critical points. Therefore, effective management of these materials, promoting recycling, and diversifying the supply chain are crucial for the future use of lithium-ion batteries. Especially in recent years, with the increasing use of Li-ion batteries, the importance of critical raw materials has been emphasized. The rapid growth in lithium-ion battery production has led to significant pressure on global Due to the developing and increasing demands, there is a rapid increase in the usability of lithium-ion batteries, leading to significant reserves flowing into the battery sector in the world and triggering interest in the sector, especially with the explosive growth of electric vehicle lithium-ion batteries driven by the popularity of electric vehicles. These rising demands pose serious challenges in the supply of raw materials for lithium-ion batteries, leading to the production of massive amounts of spent lithium-ion batteries and creating difficulties in resource allocation and environmental protection. Research indicates that several materials listed in the EU's critical raw materials list from 2020 are utilized in lithium-ion batteries, with the most significant ones outlined in Table 2. [8]

Table 1: List of critical raw materials for li-ion batteries.

RAW MATERIALS	CRITICAL STAGE	MAIN GLOBAL PRODUCERS	APPLICATION
Bauxite	Extraction	Australia (28%)	Aluminum
		China (20 %)	production
		Brazil (13 %)	
Cobalt	Extraction	Congo DR (59%)	Batteries
		China (7 %)	Super alloys
		Canada (5 %)	Catalysts
			Magnets
Lithium	Extraction	Chilie (44%)	Batteries
		China (39 %),	Glass and ceramics
		Argentina (13 %)	Steel and aluminum
			metallurgy
Graphite	Extraction	China (69 %)	Batteries
		India (12 %)	Refractories for
		Brazil (8 %)	steelmaking

Due to the proliferation of electric vehicles and energy storage systems, the demand for lithium-ion batteries is expected to increase rapidly in the next decade. This surge could require up to 18 times more lithium and five times more cobalt than the current demand by 2030. Furthermore, by 2050, this demand is projected to increase to 60 times more lithium and 15 times more cobalt. This highlights the growing importance of sustainable sourcing and recycling of critical raw materials such as lithium and cobalt [8].

### 4. Worldwide Sources and Applications of Critical Raw Materials in Lithium-Ion Batteries

#### 4.1 LITHIUM

One of the most important materials in Li-ion batteries is undoubtedly the element Lithium. This is supported by characteristics such as being the lightest of all solid elements (density of 0.53 g·cm-3 at 20 °C), having the highest specific heat capacity, the smallest ionic radius among alkali metals, and a high electrochemical potential. While metallic Lithium is found only in non-rechargeable batteries, in rechargeable batteries, it exists as ions in lattice structure in both the cathode

and electrolyte. In the cathode, it is synthesized within the cathode active material and shuttles between the anode and cathode during the battery's charge-discharge cycles. In the electrolyte, it is typically dissolved in an organic liquid containing a dissolved salt solution. Global lithium resources are concentrated, with 53% distributed in the lithium triangle of South America (Bolivia, Chile, Argentina), particularly in salt flats. Following closely are Australia, China, and the United States. In terms of reserves, in 2022, of the 26 million tons. Chile holds 9.3 million tons, accounting for 35.8%, Argentina has 2.7 million tons, making up 10.4%, Australia boasts 6.2 million tons, representing 23.8%, while China holds 2 million tons, accounting for 7.7%. Although China's lithium resources are abundant, they are dispersed, and the quality is relatively low [9]. The resources of lithium are primarily divided into three categories. The first are brines, which are by far the main source of lithium, accounting for more than 60% of the global identified reserves[10]. The other two categories are pegmatites and Sediment-Hosted Deposits. Since brines are the most widely utilized source, we will continue our study focusing on them. In traditional lithium brine processing, there is a phase dedicated to concentrating lithium through solar evaporation ponds. During this process, various salts precipitate out as water is removed, facilitating the elimination of primary impurities like sodium, potassium, and a portion of magnesium from the final lithium products. Typically, this step aims to achieve lithium concentrations of up to 6% by weight, although in certain instances, the target lithium concentration may be adjusted based on the impurity levels in the brine. Subsequently, this concentrated brine is directed to the final processing facility where lithium carbonate and hydroxide are produced [11].

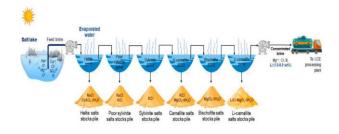


Figure 3: Conventional process to concentrate and purify lithium brines, based on evaporation ponds. Adapted from Cerda et al. (2021) [12].

Given the significant water loss due to evaporation in conventional lithium brine processing, it is relevant to mention that lithium processing also uses fresh water extracted from surface water sources. This type of water is typically considered to quantify the freshwater consumption of the process (water make-up) instead of the water loss from brines induced by evaporation[13]. The additional use of fresh water in the process, leading to significant water loss, has prompted researchers to explore alternative methods to mitigate water loss. Essentially, methods can be divided into two categories: Direct Lithium Extraction (DLE) and Lithium Brine Concentration (LBC), as depicted in Figure 4.

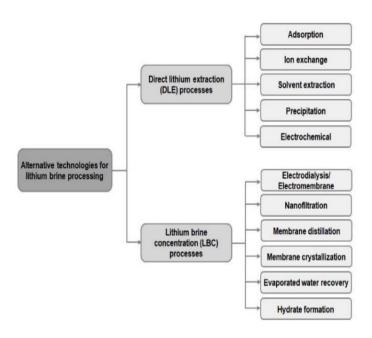


Figure 4: Classification of alternatives for lithium brine processing [14] .(Fuentealba, D., Flores-Fernández, C., Troncoso, E., & Estay, H. (2023).

The DLE processes aim to selectively extract lithium from the brine, facilitating efficient separation and enabling the production of final lithium products. LBC processes, meanwhile, concentrate lithium brine without separating lithium, allowing for the production of final products. The main distinction lies in DLE processes separating lithium from the brine to produce final products, while LBC processes concentrate lithium brine to obtain final products, determining the processes' operation and outcomes.

#### 4.2 NICKEL

The symbol of nickel is 'Ni'. Nickel's atomic number is 28. Nickel's atomic weight is 58,6934. Nickel is hard and white in color which is close to silver. Nickel melts at 1453 °C. It has magnetic properties. Nickel compounds are insoluble in water. Chloride, sulphate and nitrate are soluble in water. Nickel is found in the earth's crust at values between 58-94 mg/kg. The amount of nickel in water is very low. Nickel is used in iron production, alloys, catalysts, some batteries, and paint [15]. Nickel alloys can be recycled. Nickel-containing alloys are melted down and used to produce new alloys and stainless steel [16].

Nickel reserves are mostly found in Indonesia. This country is followed by Australia, Brazil, Russia, the Philippines, China, Canada.

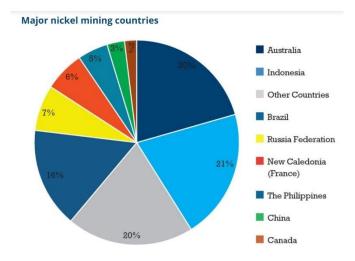


Figure 5 [17]: The amount of nickel produced by countries and their reserves.

The utilization of nickel electrodes involves the solid-state oxidation of Ni(OH)2 to NiOOH during the charging process and its reversal during discharge, resulting in a prolonged cycle life. The adoption of nickel electrodes in practical applications commenced between 1897 and 1903, facilitated by advancements in pocket-plate technology originating from the USA, Sweden, and Germany. In this technology, the active material is initially compressed into pellets with a conductive additive and binder, which then serve as the current collector. These pellets are encased in a nickel-plated perforated sheet to offer structural support. A significant breakthrough in this realm was made by Edison in 1908 when he devised a tubular plate to mitigate mechanical stresses and enhance the electrodes' durability during discharge cycles. The evolution of nickel electrodes traces back to the inception of sintered plate technology, pioneered by Pflider in 1928. Sintering involves a thermal process wherein loose nickel particles are fused into a cohesive structure just below the nickel's melting point. Presently, more than half of the nickel electrode batteries utilize this technique, with sintered nickel electrodes emerging as the dominant technology in recent years. These electrodes comprise porous nickel plates formed from sintered high surface area nickel particles, which are infused using chemical and physical methods. Modern preferences lean towards foam and bonded electrodes to achieve higher loadings. Bonded nickel electrodes entail nickel hydroxide particles interfacing with a high surface area conductive mesh or substrate. Foammetal bonded electrodes have entered the market due to their cost-effectiveness and superior energy density compared to sintered nickel electrodes. Nickel oxide electrodes serve as the positive plates in rechargeable batteries like Ni-Zn, Ni-MH, Ni-Cd, Ni-H2, and Ni-Fe. Among these, Ni-MH batteries exhibit the most promising commercial viability and developmental prospects. They find extensive use in electric vehicles, hybrid vehicles, and fuel cell electric vehicles. Notable advancements in both positive and negative electrode materials have propelled the production of Ni-MH batteries, leading to their prominent position in the battery industry. Consequently, the Ni-MH battery market is experiencing rapid growth, with ongoing efforts directed towards further enhancing Ni-MH battery technology [18].

#### 4.3 MANGANESE

The symbol of manganese is 'Mn'. Manganese's atomic number is 25. Manganese's atomic weight is 54,938. Manganese melts at 1246°C. The color of manganese is silver grey. Manganese is hard and brittle. Manganese is easily oxidized [19]. Manganese can be used in steel to reduce brittleness and increase strength. It is mainly used in batteries under renewable technology. Small amounts of manganese are also used in wind turbines and geothermal plants.

Manganese is a very common element. Manganese ores are produced by Australia, South Africa, China, Gabon and Brazil, India, Ukraine, Mexico, Georgia, Vietnam, Kazakhstan. South Africa ranks first in the world, accounting for 39% of production. Australia ranks second with 3.3 million tones followed by Gabon with 2.8 million tones. Apart from the earth, there are also manganese deposits under the sea [20].

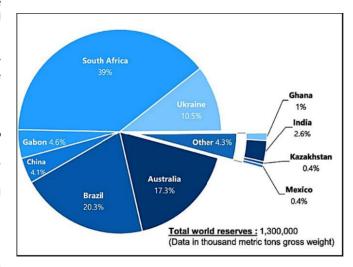


Figure 6 [21]: Graphically interpreted manganese reserves of countries.

Various electrodes have been produced until today. Mn-based electrode materials are one of the most important among the electrodes produced. Manganese has Mn2+, Mn3+, Mn4+ valence. Manganese redox has high redox potential. Manganese provides high capacity and high energy density by offering two electron transfer. Manganese's low cost and lack of toxicity make it an ideal choice for practical applications. Some issues related to manganese hinder the development of this element. For example, poor electronic conductivity leads to slow kinetics; dissolution of Manganese and reduced capacity of Mn3+. In recent years, this issue has been studied and significant progress has been made. As seen in Figure 7, there are three categories of Mn-based materials.

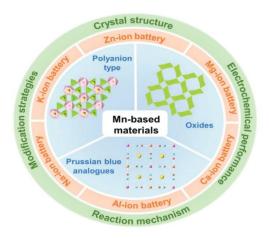


Figure 7 [22]: Graphical classification of Mn-based materials.

Manganese-based materials are predominantly represented by oxides, which encompass a diverse array of compounds including MnO,  $Mn^2O^{3}$ ,  $Mn^3O^4$ ,  $MnO^2$ , and  $Mn^2O^4$ . Each of these oxides demonstrates suitability for alkali-ion storage, exhibiting various crystal phases that offer adjustable properties. Manganese oxides possess the capability to combine with other cations, leading to the formation of different manganese species, highlighting manganese's versatility. Particularly, poly-anion type materials (PBAs) emerge as highly promising candidates for metal ion intercalation. Compared to oxides, the crystal structures of poly-anion type materials exhibit greater stability for ion intercalation. This enhanced stability is attributed to the "inductive energy" of poly-anion groups, resulting in higher redox potential and energy density. Consequently, a wide range of manganese-based poly-anion materials with diverse crystal structures, such as phosphates, pyrophosphates, polyanion compounds, and silicates, have been under scrutiny as potential electrode materials for both aqueous and non-aqueous rechargeable batteries [23].

#### 4.4 Graphite

Graphite, like other carbon-based materials employed as anodes, has attracted considerable interest in the field of Li-ion battery chemistry due to its impressive electrochemical properties and prolonged lifespan since its inception. The key factor contributing to graphite's outstanding performance is its composition as a crystalline form of elemental carbon, akin to substances such as fullerenes, diamonds, and carbon nanotubes. Physically, graphite presents as an opaque mineral with a grayish-black appearance and a metallic sheen, characterized by a soft texture and exceptional basal cleavage. Notably, graphite boasts the highest electrical and thermal conductivity among nonmetals, coupled with chemical inertness and non-toxicity. Graphite is typically divided into two primary categories based on its origins: Natural Graphite, which encompasses amorphous graphite, crystalline small flake graphite, and crystalline lump or chip graphite, and Synthetic Graphite. The genesis of graphite deposits is largely attributed to the metamorphism of carbonaceous sedimentary rocks. Amorphous graphite originates

from the thermal metamorphism of petroleum, coal, or carbon-rich sediments, while flake graphite is extracted from carbonaceous metamorphic rocks, and lump or chip graphite is sourced from veins in high-grade metamorphic regions. Synthetic graphite is produced through the heating of a carbonaceous precursor to high temperatures, commonly utilizing resources such as petroleum coke, coal, or other organic materials. In its final state, synthetic graphite is available in electrode, powder, or granule forms[24].

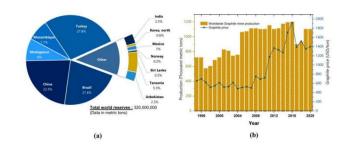


Figure 8 [25] (a) Global distribution of estimated Graphite Reserves in 2021, (b) worldwide Graphite mine production and prices (1995–2021).

#### 4.5 Cobalt

Cobalt is mostly produced through mining activities. It is mostly obtained as a by-product from nickel and copper mining. Since it is produced as a by-product predominantly, its production highly depends on nickel and copper mining activities thus resulting in price fluctuations and even shortages occasionally [27]

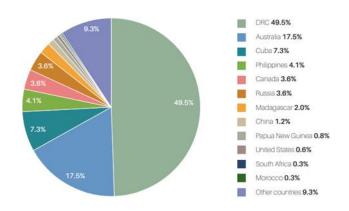


Figure 9: Global cobalt reserves [26].

As for main uses, Lithium-ion batteries are one of the leading fields. Cobalt is preferred as a cathode material component such as in  ${\rm LiCoO_2}$ . It provides good cycling performance along with high theoretical capacity. However, due to its high cost, inability to provide thermal stability and rapid capacity decline, studies are being carried out to reduce its composition in cathode material development. Nevertheless, it continues to be

widely used as it becomes difficult to achieve high theoretical capacity without cobalt [28].

Figure \* shows the main usage areas of cobalt-containing products however it is also critical in terms of civil and military technologies as it is used for drone production and 3D printing [29].

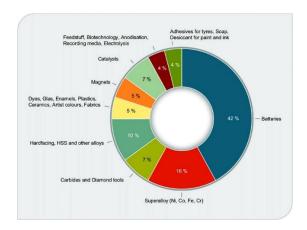


Figure 9: Shares of usage areas of Cobalt containing products in EU [28].

## Sustainability and Risks of Critical Raw Materials:

As the world becomes more globalized, the need for energy storage is increasing day by day, with lithium-ion batteries taking a prominent place among the options. Societies have begun to realize the importance of sustainability and the limits of resources. People are seeking more sustainable resources. Access to resources and sustainability are of vital importance from both industrial and economic perspectives. Sustainable product design requires more efficient use of resources and opportunities for recycling. Therefore, the sustainable management of resources and the strengthening of supply chains are crucial for enhancing industries competitiveness and ensuring economic stability. Additionally, conserving natural resources, reducing environmental impacts, and improving societal welfare are also important. In this context, the EU and other countries are developing policies and strategies to ensure the effective and sustainable management of critical raw materials and therefore, the production and consumption of batteries must be socially and economically responsible, environmentally sustainable, and innovative. [30]

# Supply Chain and Industrial Importance of Critical Raw Materials

When considering supply chain, one of the most important criteria is to be able to obtain elements from various countries, thus a uniform distribution is expected. Another issue to take into account is the economic importance of the material, meaning an assessment has been made by looking at end-use applications and value added into corresponding industries. Index modeling has been performed by various studies to predict supply risk and Figure\* below shows that lithium and cobalt have high risk, nickel and graphite medium risk while other elements are in low-risk zone [Song].

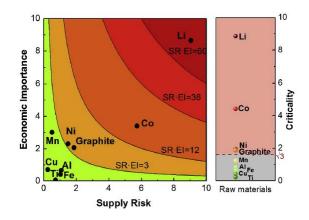


Figure 10: Criticality evaluation of raw materials [31].

In terms of production methods, based on Figure 11, it can be observed that cobalt and lithium pose challenges in the mining phase, manganese in the refining phase and nickel in the production phase.

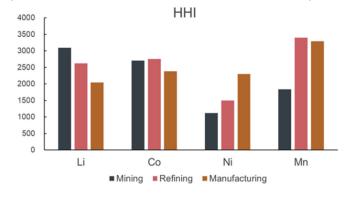


Figure 11: Difficulties in production methods based on element [32]

A more detailed examination of the supply chain reveals Asian dominance in the production of cathode materials such as NCA, NMC, LCO, graphite separator and cell. The leading Asian countries are China, Japan and South Korea, and these countries account for most of the global production. Asian countries account for 86% of global production, while China accounts for 48% by itself, a fact that highlights Europe's dependence on imports for batteries. Therefore, battery supply being dependent on Asia, leading to uncertainties and high prices for Europe. The need for batteries has increased, especially with the development of electric vehicle technologies, which has put pressure on the supply of both raw and processed materials. In the case of lithium and cobalt, which are in the risk group, although cobalt is being replaced with less harmful and cheaper

materials, there is no decrease in its demand due to the increase in sales per unit. When lithium is examined, the price increase continued until 2015, but then there has been a decline in the last 5 years due to the fact that lithium hydroxide is more preferred in battery production. Nevertheless, there are major problems in terms of supply due to the limited distribution of lithium on earth. These challenges have brought up the necessity of waste management and recycling up to an important point along with start-up companies [33].

#### **Conclusion:**

The analysis of critical raw materials in lithium-ion batteries is crucial for understanding complex dynamics such as resource availability, sustainability, and supply chain resilience in the rapidly expanding energy storage sector. This article has examined the fundamental principles of lithium-ion batteries, the definition and significance of critical raw materials, their sources, and applications, as well as their supply chains and industrial importance. It is emphasized that with increasing demand and needs in various fields such as electric vehicles, portable electronic devices, and grid storage systems, the stable supply and use of critical raw materials for Li-ion batteries has become increasingly important.

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Seray:Introduction,history,basic principles,critical raw materials,conclusion,sustainibility parts.

Ahmet Musab: Lithium and Graphite parts.

Enes:Nickel, Manganese parts.

Ebru: Cobalt, Suply chain parts.