UNIVERSITY OF THESSALY

SCHOOL OF ENGINEERING

DEPARTMENT OF MECHANICAL ENGINEERING

Diploma Thesis

Sustainable Recycling Technology for Li-Ion Batteries: Challenges and Future Prospects

by

Karasakalidis Kyriakos and Nekos Nikolaos

Under the supervision of Prof. Panagiotis Tsiakaras

Submitted in partial fulfillment of the requirements for the degree of Diploma
in Mechanical Engineering at the University of Thessaly

Volos, 2023

ΠΑΝΕΠΙΣΤΗΜΙΟ ΘΕΣΣΑΛΙΑΣ

ΠΟΛΥΤΕΧΝΙΚΗ ΣΧΟΛΗ

ΤΜΗΜΑ ΜΗΧΑΝΟΛΟΓΩΝ ΜΗΧΑΝΙΚΩΝ

Διπλωματική Εργασία

Βιώσιμη τεχνολογία ανακύκλωσης μπαταριών ιόντων λιθίου: προκλήσεις και μελλοντικές προοπτικές

υπό

Καρασακαλίδης Κυριάκος και Νέκος Νικόλαος

Επιβλέπων: Καθ. Παναγιώτης Τσιακάρας

Υπεβλήθη για την εκπλήρωση μέρους των απαιτήσεων για την απόκτηση του Διπλώματος
Μηχανολόγου Μηχανικού του Πανεπιστημίου Θεσσαλίας

Βόλος, 2023

Approved by the Committee on Final Examination:

Advisor	Dr. Tsiakaras Panagiotis (Supervisor) Professor of Department of Mechanical Engineering School of Engineering University of Thessaly
Member	Dr. Charalampous Georgios Assistant Professor of Department of Mechanical Engineering School of Engineering University of Thessaly
Member	Dr. Brouzgou Angeliki Assistant Professor of Department of Energy Systems School of Technological Sciences University of Thessaly

ACKNOWLEDGEMENTS

This thesis represents the final step for the integration of the academic cycle. We would like to express our thanks to our professor and supervisor, Mr. Panagiotis Tsiakaras for the valuable help, scientific expertise and guidance he offered us for the completion of this dissertation. We thank him very much for his patience and the trust he has shown in this cooperation as well as for the opportunity he gave us to make our goals a reality.

Of course, we would like to express our warm thanks to our beloved families for both their financial and psychological support. On the one hand, Nikolaos Nekos would like to thank his parents Achilleas Nekos and Cleopatra Vasdeka as well as his brothers Thanasis and Chris Nekos and on the other hand Kyriakos Karasakalidis would also like to thank his parents Andronikos Karasakalidis and Evangelia Michalopoulou as well as his sister Maria Karasakalidou.

Finally, we could not omit the contribution of our dear friends. Their support and the encouragement they offered us at all the stages of our studies were essential supplies for achieving our goals.

ΕΥΧΑΡΙΣΤΙΕΣ

Η παρούσα διατριβή υποδηλώνει το τελικό βήμα για την ολοκλήρωση του ακαδημαϊκού κύκλου. Θα θέλαμε να εκφράσουμε τις ευχαριστίες μας στον καθηγητή και επιβλέποντα μας, κ. Παναγιώτη Τσιακάρα για τη πολύτιμη βοήθεια, την επιστημονική επάρκεια και τις οδηγίες που μας πρόσφερε για την ολοκλήρωση αυτής της διπλωματικής εργασίας. Τον ευχαριστούμε πολύ για την υπομονή του και την εμπιστοσύνη που έδειξε σε αυτή τη συνεργασία καθώς και για την ευκαιρία που μας έδωσε να κάνουμε τους στόχους μας πραγματικότητα.

Φυσικά θα θέλαμε να εκφράσουμε τις θερμές μας ευχαριστίες στις αγαπημένες μας οικογένειες τόσο για την οικονομική όσο και για τη ψυχολογική υποστήριξή τους. Αφενός ο Νικόλαος Νέκος θα ήθελε να ευχαριστήσει τους γονείς του Αχιλλέα Νέκο και Κλεοπάτρα Βασδεκά καθώς και τα αδέρφια του Θανάση και Χρήστο Νέκο και αφετέρου ο Κυριάκος Καρασακαλίδης θα ήθελε επίσης να ευχαριστήσει τους γονείς του Ανδρόνικο Καρασακαλίδη και Ευαγγελία Μιχαλοπούλου καθώς και τη αδελφή του Μαρία Καρασακαλίδου.

Τέλος, δεν θα μπορούσαμε να παραλείψουμε την συνεισφορά των αγαπημένων μας φίλων. Η συμπαράστασή τους και η ενθάρρυνση που μας πρόσφεραν σε όλα τα στάδια των σπουδών μας ήταν απαραίτητα εφόδια για την επίτευξη των στόχων μας.

ABSTRACT

Tremendous efforts are being made to develop electrode materials, electrolytes, and separators for energy storage devices to meet the needs of emerging technologies such as electric vehicles, decarbonized electricity, and electrochemical energy storage. However, the sustainability concerns of lithium-ion batteries (LIBs) and next generation rechargeable batteries are received little attention.

Recycling plays an important role in the overall sustainability of future batteries and is affected by battery attributes including environmental hazards and the value of their constituent resources. Therefore, recycling should be considered when developing battery systems.

Herein, we provide a systematic overview of rechargeable battery sustainability.

With a particular focus on electric vehicles, we analyze the market competitiveness of batteries in terms of economy, environment, and policy. Considering the large volumes of batteries soon to be retired, we comprehensively evaluate battery utility utilization and recycling from the perspectives of economic feasibility, environmental impact, technology, and safety. Batteries sustainability is discussed with respect to life cycle assessment and analyze from the perspectives of strategic resources and economic demand.

Key Words: Battery recycling, lithium-ion batteries, supercapacitors, electrolytes.

ΠΕΡΙΛΗΨΗ

Καταβάλλονται τεράστιες προσπάθειες για την ανάπτυξη υλικών ηλεκτροδίων, ηλεκτρολυτών και διαχωριστών για συσκευές αποθήκευσης ενέργειας για την κάλυψη των αναγκών των αναδυόμενων τεχνολογιών, όπως τα ηλεκτρικά οχήματα, η ηλεκτρική ενέργεια και η ηλεκτροχημική αποθήκευση ενέργειας χωρίς τη χρήση κάρβουνου. Ωστόσο, οι ανησυχίες για τη βιωσιμότητα των μπαταριών ιόντων λιθίου (LIB) και των επαναφορτιζόμενων μπαταριών επόμενης γενιάς δεν έχουν προσεχθεί ιδιαίτερα.

Η ανακύκλωση διαδραματίζει σημαντικό ρόλο στη συνολική βιωσιμότητα των μελλοντικών μπαταριών και επηρεάζεται από τα χαρακτηριστικά των μπαταριών, συμπεριλαμβανομένων των περιβαλλοντικών κινδύνων και της αξίας των πόρων που τις αποτελούν. Επομένως, κατά την ανάπτυξη συστημάτων μπαταριών θα πρέπει να λαμβάνεται υπόψη η ανακύκλωση.

Στην εργασία μας θα επιδιώξουμε μια συστηματική επισκόπηση της βιωσιμότητας της επαναφορτιζόμενης μπαταρίας. Θα δώσουμε ιδιαίτερη έμφαση στα ηλεκτρικά οχήματα, και θα αναλύσουμε την ανταγωνιστικότητα των μπαταριών στην αγορά όσον αφορά την οικονομία, το περιβάλλον και την πολιτική. Λαμβάνοντας υπόψη τους μεγάλους όγκους μπαταριών που πρόκειται να αποσυρθούν σύντομα, θα αξιολογήσουμε διεξοδικά τη χρήση και την ανακύκλωση των μπαταριών από την άποψη της οικονομικής σκοπιμότητας, των περιβαλλοντικών επιπτώσεων, της τεχνολογίας και της ασφάλειας. Η βιωσιμότητα της μπαταρίας θα παρουσιαστεί (συζητηθεί) σε σχέση με την αξιολόγηση του κύκλου ζωής και θα αναλυθεί από την προοπτική των στρατηγικών πόρων και της οικονομικής ζήτησης.

Λέξεις κλειδιά: Ανακύκλωση μπαταριών, μπαταρίες ιόντων-λιθίου, υπερπυκνωτές, ηλεκτρολύτες

Contents

List of Figures

CHAPTER 1

1.1 Introduction

Energy is at the core of human civilization, fueling technological innovations and pushing society forward. Since time immemorial, harnessing different types of energy has had an enormous influence on both humanity and societies worldwide.

At its inception, early humans utilized energy from natural sources like sunlight and winds for basic needs like cooking and heating. Fire marked an incredible breakthrough in human evolution - revolutionizing hunting techniques, defense mechanisms, social bonding mechanisms and much more. As human societies developed so did their methods for harnessing energy. Water wheels harnessed river currents for grinding grain while powering early industries before coal became an energy source dominating agriculture, manufacturing and transportation processes through steam engines in the Industrial Revolution.

Electricity emerged as a revolutionary transformative force during the 20th century, providing unprecedented convenience and connectivity. Oil and natural gas discoveries revolutionized transportation and industry further while nuclear energy promised abundant clean power while creating complex challenges related to safety and waste disposal.

Energy's importance at the dawn of the 21st century cannot be overstated. Our modern world depends on an eclectic mixture of sources for its energy needs: fossil fuels, nuclear, hydroelectricity and renewable energies like solar and wind power all play their parts to meet population growth and economy expansion, keeping costs within reasonable bounds and simultaneously exerting pressure on finite resources and the environment.

Consequences associated with energy generation and consumption have become ever more obvious, particularly their effect on the environment. Conventional sources like fossil fuels can greatly contribute to climate change and environmental degradation while creating numerous hazards. As a result, renewable energies such as wind power have been widely adopted to lower carbon emissions while mitigating global impact of consumption.

Renewable energy sources have become key players in this global shift towards greener solutions. Solar panels harness sunlight's rays, wind turbines harness wind power, hydroelectric plants utilize flowing water, all combine to generate electricity potentially revolutionizing our energy landscape by decreasing greenhouse gas emissions and alleviating climate change effects, while at the same time mitigating its adverse effects. However, transitioning toward renewables does come with its own set of challenges that must be faced along this journey.

Renewable energy sources such as renewable photovoltaic panels present one key challenge when it comes to energy storage: their intermittent nature means their availability varies over time, necessitating effective storage systems in order to guarantee reliable supply. Lithium-ion (Li-Ion) batteries have quickly emerged as promising options thanks to their high energy density, long lifespan and lightweight properties; Li-Ions find applications not only in portable electronics devices such as cameras but also electric vehicles and renewable energy systems.

Li-Ion batteries have played an essential part in helping transition towards renewable energy sources. However, their production, usage and end of life management present significant environmental concerns. Mining for raw materials used for making Li-Ion batteries often uses environmentally damaging mining practices while improper disposal can release potentially toxic substances and endanger ecosystems and humans alike.

Given the rapid adoption and environmental impacts associated with Li-Ion batteries, sustainable recycling technology is becoming an urgent requirement. Sustainable recycling seeks to recover valuable materials from spent batteries while simultaneously mitigating any environmental burden caused by production or disposal processes; this involves sorting, dismantling and recovering metals or valuable components for reuse, thus cutting back reliance on virgin materials while at the same time helping protect natural resources and prevent pollution.

As our world moves toward renewable energy sources, the sustainable recycling of Li-Ion batteries becomes of increasing significance. Addressing challenges related to their production and disposal is vital in upholding renewable technologies' positive environmental benefits without jeopardy to society or ecosystem. This thesis sheds light on opportunities and barriers involved with sustainable Li-Ion recycling for researchers, policymakers, industry professionals working towards an eco-friendly future.

CHAPTER 2

2.1 Electrochemistry basics

Electrochemistry is the branch of chemistry that studies the association between electricity and chemical change and more specific the comprehension of the chemical procedure that causes electron movement.

Electrochemistry principles are fundamental nowadays and essential for the design of innovative devices with the main pursuit the independence from the fossil fuels and the reduction of CO_2 residues in the atmosphere.

An electrochemical cell is a device that either converts chemical energy into electrical, through inner chemical reactions, or exploits electrical energy to produce chemical. More precisely, the structure of these cells typically composed of two electrode, anode and cathode, and electrolyte through which ion carried. The working principle of a cell is based on oxidation-reduction reactions that allow ion and electron movement and thus production of electricity. Oxidation-reduction reactions, known as redox, are the chemical reactions where the oxidation number of the substrate change, depending on the gain or loss of electron. Redox essentially divide in two-half reactions that always occur together inside the cell. The one half substrate gains electrons (decrease of its oxidation state) and thus named oxidizing agent or oxidant and simultaneously oxidizes the other species. The other half, gives electrons, (increase of its oxidation state) reduces the other part and so-called reducing agent or reductant [1].

$$\text{Oxidation:} \quad Reductant\ agent \longrightarrow Ox.Product + e^- \tag{2.1}$$

$$\text{Reduction:} \quad Oxidant\ agent + e^- \longrightarrow Red.Product \tag{2.2}$$

$$\text{Redox:} \quad \begin{aligned} &Reductant\ agent + Oxidant\ agent \\ &\qquad \longrightarrow Ox.Product + Red.Product \end{aligned} \tag{2.3}$$

Despite the fact that electrochemical cells obey the same working principle, however they are classified in two main categories, galvanic and electrolytic, that achieve totally opposite outcome. Galvanic or voltaic cell converts the chemical energy into electrical, with main representatives batteries and fuel cells. In a galvanic cell, the negative electrode where the oxidation takes place is the anode, while the positive one, where the reduction occurs is the cathode. During the simultaneous operation of this kind of cell, the system releases energy to an external circuit [2].

On the other hand, electrolytic cell exploits the energy of an external source to produce chemical species. Water electrolysis for example, into hydrogen and oxygen achieved through an electrolytic cell. In this occasion, in the positive electrode, which is the anode, the oxidation reaction is held, while the reduction occurs in the cathode which is the negative electrode as is illustrated in **figure 1**. It is worth mentioned that an electrolytic cell, represents non-spontaneous reaction, in contrast with galvanic [3].

***Figure 1**. Anode and Cathode in a galvanic an in an electrolytic cell [5]*

2.2 History of electrochemistry

However, the investigation of the electrochemical processes mechanisms is a topic that attracts the scientific interest since the 18th century. Remarkable achievements during this period are highlighted above.

The Italian physician and anatomist, Luigi Galvani, after extensive and rigorous experiments published his results in 1791, where concluded that animal tissues could store electricity as Leyden jars, able to obtain it if two metals placed between two points. The term electricity is referred for the first time and despite the fact that was not absolutely insightful, the raised questions forced the next generation for further research, following this milestone.

Alessandro Volta, Galvani’s colleague, refuted the theory of ‘’animal electricity’’ that Galvani unveiled and accomplished a variety of experiments that lead to revealing conclusions in the field of metal classification. In 1800 he introduced the first working battery at the institute de France and gained a gold medal award from Napoleon Bonaparte. This battery, constructed from Zinc and Cooper piles, was able to provide continuous current.

At the same time, W. Nicholson and J. W. Ritter exploited Volta's battery and achieved the first electrolysis experiments decomposing water into oxygen and hydrogen [4].

A few years later, in 1807, H. Davy obtained elemental potassium after the electrolysis of elemental potash. Relied on this development, and on the comprehension of the reactions that take place at the electrodes and the electrolyte, he later accomplished same experiments for sodium and calcium.

Davy influenced his student Farraday, who was dedicated on this work and observed a significant contribution on the history of science by establishing the electrochemistry vocabulary (ion, anion, cation) between 1832 – 1834.

In 1839, William Robert Grove, a British physicist, demonstrated the first fuel cell using Pt electrodes and sulfuric acid electrolyte. He also focused on the reversibility principles of the electrolysis reaction and proposed fundamental properties for the electrochemistry, such as current density and three phase boundary that are common today.

Walther Nerst, in 1881, established a theory for electromotive forces of voltaic cells and formulated an equation that allows the calculation of the cell potential of redox reaction that is widely used even in our days [2, 5, 6].

In 1941 Jaroslav Heyrovsky, a Czech chemist, in his lecture ''use of oscillograph in polarography'' launched the polarography with controlled alternating current, after experiments on mercury electrodes [7].

By the years 1924 – 1930, another significant contribution to the electrochemical theory and more specifically the electron transfer at an electrode, was the foundation of an empirical relation between electrode potential and current density that reflects electrode kinetics, by Butler and Volmer [8].

After reviewing the fundamental principles and history of electrochemistry, attention will now turn towards its practical applications. Electrochemistry reveals an interrelation between electricity and chemical processes that has given way to an array of Energy Conversion and Storage Devices. These cutting-edge technologies harness principles such as redox reactions, ion movement and electron transfer to usher in an age of sustainable energy solutions. In the following chapter we'll dive deep into energy storage and conversion technologies like batteries and fuel cells that are shaping tomorrow's use of clean energy sources.

2.3 Energy Conversion and Storage Devices

Today's global challenges of depleting fossil fuel reserves, climate change and rising energy demands has necessitated innovative energy storage and conversion technologies that provide greater efficiency and sustainability. Out of the spectrum of potential solutions that encompass mechanical, magnetic, and thermal methods, electrochemical devices stand out as particularly promising avenues due to their ease of use, environmental sustainability and reliability, three aspects essential in any successful device. Examples include fuel cells, batteries, supercapacitors, and electrolyzers which play vital roles across industries. However, their adoption can present hurdles, such as cost-effectiveness and safety concerns can thwart full integration. Therefore, this chapter undertakes an in-depth investigation of electrochemical devices to better understand them as well as provide enhancements that would aid their seamless incorporation into novel applications.

2.3.1 Fuel cells

Fuel cells are electrochemical devices which directly convert chemical energy found in fuels into electrical power, unlike traditional power generation methods, which involve intermediate steps like chemical heat or mechanical work. They bypass all such constraints while simultaneously circumventing Carnot efficiency's thermodynamic limitations for maximum environmental sustainability and cost efficiency. As such, their unique design lends them well as green power generators.

Fuel cells also demonstrate versatility by processing different types of fuel and oxidants. While most media attention currently focuses on commonly-used natural gas and hydrogen as fuel sources with air serving as an oxidant source, their operation allows for processing various sources.

Conceptually, visualizing a fuel cell as a factory provides an accurate representation of its purpose. Much like manufacturing plants, fuel cells operate for as long as their supply of fuel remains. Although both technologies use electrochemistry in electricity generation processes, only fuel cells remain intact while promoting conversion of chemical energy from fuel into usable electrical power.

Over the decades, fuel cells have earned recognition as highly efficient energy converters with minimal environmental impacts. Their position as renewable power generation mechanisms solidified them as effective electrical power production alternatives that uphold sustainability principles. Fuel cells have quickly gained recognition as sources of clean energy. Their capacity to convert various sources into electricity solidifies their place as renewable power generators, with fuel cells serving as prime examples of devices which combine innovation with environmental sustainability. The fundamental operation of a fuel cell revolves around continuous fuel supply to the anode (negative electrode) and the continuous introduction of an oxidant, often oxygen from the air, to the cathode (positive electrode). Within this system, electrochemical reactions occur at the electrodes, electrolyte serves as ion conduction mean and simultaneously electric current produces useful work on an external load [9-19].

At the anode of the fuel cell, typically composed of hydrogen gas, a process of ionization occurs, releasing electrons and forming H^+ ions (protons). This ionization reaction releases energy as a result. On the other hand, at the cathode, oxygen combines with the protons and electrons provided by the anode to create water. The movement of electrons, carrying a negative charge, transpires from the anode to the cathode through an external circuit, contributing to the generation of electric current, while the H^+ ions migrate through the electrolyte [20].

Critical to the operation of a fuel cell is the selection of an appropriate electrolyte. The electrolyte facilitates the passage of ions (charged atoms) while preventing the flow of electrons. This segregation ensures that the electrons are directed through the external circuit, generating a flow of electric current that can perform work before they ultimately partake in the reaction at the cathode [21].

$$H_2 \leftrightharpoons 2H^+ + 2e^- \tag{2.4}$$

$$O_2 + 4H^+ + 4e^- \rightarrow 2H_2O \tag{2.5}$$

Fuel cell operation relies heavily on spatial separation. By splitting hydrogen combustion reactions into two electrochemical half reactions separated by an electrolyte barrier, electrons derived from fuel are forced outward before engaging with their final reaction. For this division to work effectively requires at least two electrodes, where individual reactions take place, separated by an electrolyte barrier, but this method also necessitates at least two electrodes because half reactions take place at once.

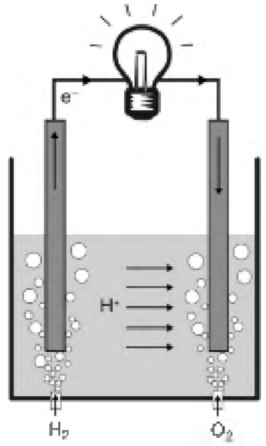


Figure 2. *A simple fuel cell [2]*

An H_2-O_2 fuel cell, represented by platinum electrodes immersed in sulfuric acid as an acid electrolyte, operates by dissecting hydrogen gas into protons and electrons at its left electrode, with protons free to traverse through the electrolyte but electrons restricted from doing so. Electrons then travel along an external connecting wire between them until reaching their right-side electrode, where they combine back with protons and oxygen gas to form water. The electron flow, would provide power supply that illuminates such a light bulb, thus signaling how this type of fuel cell produces electricity [9, 20, 22-32]. A simple illustration is given in **figure 2**.

Hydrogen-based proton exchange membrane fuel cells (H_2-PEMFCs) perform best when fed pure hydrogen, however, large-scale production remains prohibitively expensive. Only a fraction of global hydrogen production comes from water electrolysis. Solid oxide fuel cells may use different sources for power generation such as methane, methanol, ethanol or gasoline that undergo external steam reforming to produce fuels that contribute electrochemical combustion with hydrogen (H_2) being the major contributor.

Catalysts are employed in order to accelerate the slow-moving electrocatalytic reactions. Pt-based catalysts represent the most common used and promising competitor to affect the speed of both the oxygen reduction reaction (ORR) and anode methanol oxidation reaction (MOR) in the fuel cells. Over the last years, the research interest is turned into the development of facile Pt-based catalysts, in terms of shape and morphology, including nanotubes, concave cubes, nanoflowers and nanodendrites. In recent experiments, a number of novel tri-functional nanoflower catalysts were developed with a number of nanodendrites (Pt_3NiRh, Pt_3NiRu, Pt_3NiPd, Pt_3Ni and Pt_2Ni_2Rh nanoflowers), achieving great impact in the acceleration of the fuel cell kinetics. Au@PtNiAu concave octahedral core-shell nanocatalyst, represent another tremendous investigation, that is based in the production of numerous step atoms and thus the enhancement of the reaction speed [10, 14, 16].

Fuel Cell Efficiency (FCE) should always be factored into any evaluation of fuel options for a specific application, with FCE defined as the ratio between electrical power produced by the fuel cell and total chemical energy contained within its composition. Therefore, when selecting appropriate fuel, it is essential to factor into FCE, in order to optimize performance while simultaneously minimizing greenhouse gas emissions in pursuit of effective energy conversion. In fact, there exist multiple fuel cell technologies in the market, each characterized by its unique operating temperature range, compatible fuels and type of catalyst employed, suitable for distinct applications [20, 25, 30, 33-38].

1. Proton Exchange Membrane Fuel Cells (PEMFCs)

Proton Exchange Membrane Fuel Cells PEMFCs, known also as Polymer electrolyte fuel cell, are devices that powered by hydrogen as fuel and consist of a polymer membrane, usually Nafion and electrodes made of catalyst (Pt) supported carbon metals. During the operation, the Platinum-based catalyst existing in the anode, effects in the splitting of the hydrogen fuel into protons H^+ and electrons e^-. Subsequently, protons migrate through the ion-conductive membrane to the cathode, while electrons pass through an external circuit, in order to produce electric current. Then, at the cathode side of the cell the protons and electrons interact together with the supplied oxygen and form water, as the only process byproduct. A schematical representation of the PEMFCs working principle is shown in **figure 3** and the reactions that occur in each electrode are described from the following equations:

$$\textit{Anode:} \qquad H_2(g) \longrightarrow \ 2H + 2e^- \qquad (2.6)$$

Cathode: $$^{1}/_{2}\, O_2\,(g) + 2H + 2e^- \longrightarrow H_2O\,(l) \qquad (2.7)$$

Overall reaction: $$H_2\,(g) + {^{1}/_{2}}\, O_2\,(g) \longrightarrow H_2O\,(l) \qquad (2.8)$$

PEMCs operate at relative low temperatures, 60-100°C, which allows fast start-up times and efficient power production up to 250kW, with efficiency rates 40-70%. Thus, common PEMFC applications are portable electronics, transportation (hydrogen fuel cell vehicles) and stationary power generation. PEM fuel cells require inconsiderable maintenance owing to the absence of moving parts, thus considered the successor of the dated internal combustion engines ICE applied in the passenger vehicles, unfortunately the high initial production cost hinders their commercialization. Another drawback that struggles its industrial expansion, remain the degradation effect to the cell of the existing CO inside the H_2 fuel. Thus, researchers focus to exploration of novel both stable and CO-tolerant electrocatalysts [13, 27, 39-41].

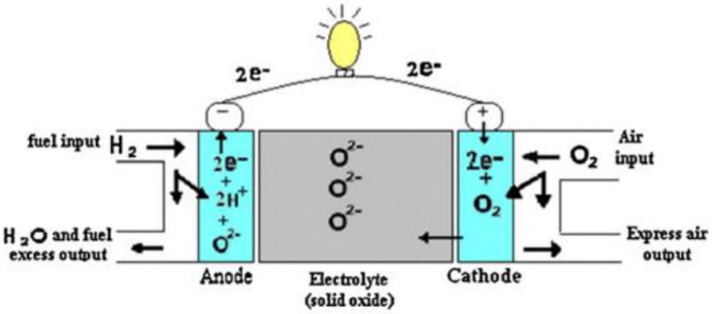


***Figure 3**. Proton exchange membrane fuel cell (PEMFC) [11]*

2. Solid Oxide Fuel Cells (SOFCs)

Solid Oxide fuel cells SOFCs are high temperature, clean, pollution free electrochemical cells that operate at 800-1000°C, the highest over all the types, to generate direct current-electricity. At the fuel electrode (anode), the fuel is oxidized and releases electrons through an external circuit, while at the cathode, where oxidant is fed, an oxidation reaction occurs in presence of the electrons as is illustrated in **figure 4** and described in the following equations:

Anode (Reduction): $$O_2^-\,(s) + H_2(g) \longrightarrow H_2O\,(g) + 2e^- \qquad (2.9)$$

Cathode (Oxidation): $$^{1}/_{2}\, O_2\,(g) + 2e^- \longrightarrow O_2^-\,(s) \qquad (2.10)$$

Common SOFC designs include solid Yttria Stabilized Zirconia YSZ electrolyte, sandwiched between Nickel-YSZ porous anode and ceramics with perovskite structure such as Strontium-doped lanthanum manganite (LSM) cathode. This cell design provides high electrical efficiency 60-70% and even more is possible in pressurized environments, with the additional benefit of fuel flexibility such as hydrogen, methane, methanol and ethanol. Bearing in mind these benefits, SOFCs considered to match with wide range of applications and ideally for stationary power plants that already utilize natural gas infrastructure [39, 40, 42, 43].

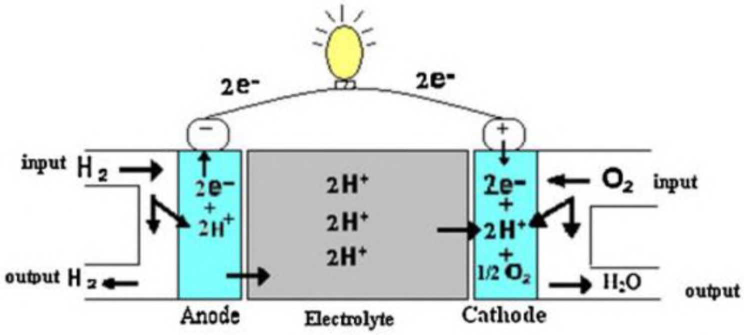


Figure 4. *Solid oxide fuel cell (SOFC) [11]*

3. Molten Carbonate Fuel Cells (MCFCs)

Molten carbonate fuel cells MCFC demonstrate a well-established technology system, adopted mainly in industrial power generation applications, due to their decent efficiency rates 55 – 65% and their negligible environmental pollution. This structure is composed of a liquid alkali carbonate mixture (Li_2CO_3, Na_2CO_3, K_2CO_3) suspended in lithium aluminate ($LiAlO_2$) as electrolyte, while Nickel Chromium (NiCr) and Lithiated nickel oxide (NiO) can serve as anode and cathode materials respectively. This system can operate at temperatures between 600-700^{0}C producing power ranging from 30kW up to hundreds kW in large power plants. As described from the following equations, MCFC employ CO_3^{2-} oxides that exist in the electrolyte to produce carbon dioxide CO_2, water H_2O and electrons at the anode, while new particles produced at the cathode as a product of the reaction between the air oxygen O_2, CO_2 and the electrons e^- from the circuit. As is shown in **figure 5**, the supplied fuel hydrogen H_2 in the anode originates from CH_4 after a process assisted by a catalyst inside the cell, knowing as reforming. Thus, this cell design provides fuel flexibility without carbon monoxide poisoning concern [39, 40].

Anode: $H_2 + CO_3^{2-} \longrightarrow H_2O + CO_2 + 2e^-$ (2.11)

Cathode: ${}^{1}/_{2}\,O_2 + CO_2 + 2e^- \longrightarrow CO_3^{2-}$ (2.12)

Reform 1: $CO + H_2O \longrightarrow CO_2 + H_2$ (2.13)

Reform 2: $CH_4 + H_2O \rightarrow CO + 3H_2$ (2.14)

Despite the enticing properties of MCFC, there are a number of concerns to overcome, such as slow start up and electrolyte and metallic parts corrosion, to make a MCFC power plant a commercial product [44, 45].

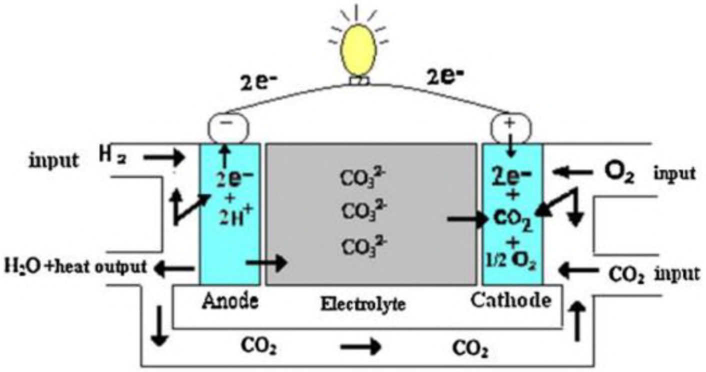


Figure 5*. Molten carbonate fuel cell (MCFC) [11]*

4. Phosphoric Acid Fuel Cells (PAFCs)

Phosphoric acid fuel cells PAFCs represent a mature widely used technology since 1970, that provide high reliability and easy construction. This type of cell typically operates at temperatures approximately 160-220°C, producing power, with relatively low electrical efficiency 35-45%, starting from 50kW and reaching some MW. The 11MW PAFC power plant in Japan from Tokyo Electric Power Co. is a remarkable example. PAFC's conformation, consist of a high concentrated liquid phosphoric acid (H_3PO_4) in thin (0,1-0,2mm) silicon carbide (SiC) matrix and a pair of surrounding porous electrodes, usually made of Platinum supported on carbon and follow similar working operation with the aforementioned PEMFCs as described from the following equations:

Anode: $2H_2 \longrightarrow 4H^+ + 4e^-$ (2.15)

Cathode: $O_2 + 4H^+ + 4e^- \longrightarrow 2H_2O$ (2.16)

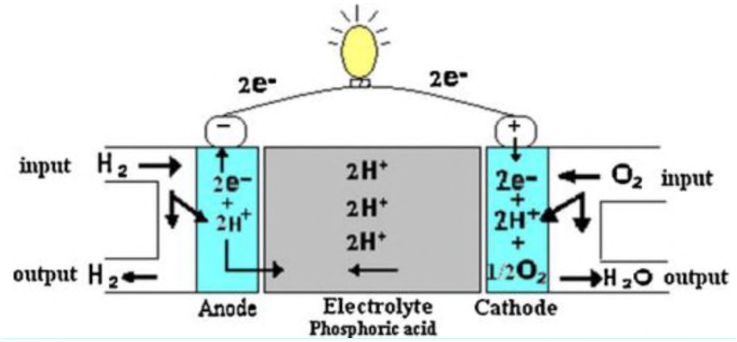


***Figure 6**. Phosphoric acid fuel cell (PAFC) [11]*

Figure 6 provides a simple description of phosphoric acid fuel cell. Unlike in AFC, in PAFCs, CO_2 does not affect the electrolyte, thus reformed gas derived from fossil fuels can be utilized in accordance with the Pt catalyst. However, major drawbacks of this technology retain the slow system start up, due to the solidity of the H_3PO_4 electrolyte in low temperatures near 40°C and the increasing cost from the expensive catalysts [39, 40, 46].

5. Alkaline Fuel Cells (AFCs)

Alkaline fuel cell AFC is a low temperature and low-cost device with no moving parts and high reliability and also the first practical implementation of electricity generation from hydrogen, adopted initially for space applications. During the operation, at the cathode the oxygen reacts with water producing negatively charged hydroxyl ions (OH^-). The ions travel to the anode through the electrolyte and a second reaction takes place between the hydrogen fuel and the hydroxyl molecules as is shown in **figure 7**.

Anode: $$2H_2 + 4OH^- \longrightarrow 4H_2O + 4e^- \tag{2.17}$$

Cathode: $$O_2 + 2H_2O + 4e^- \longrightarrow 4OH^- \tag{2.18}$$

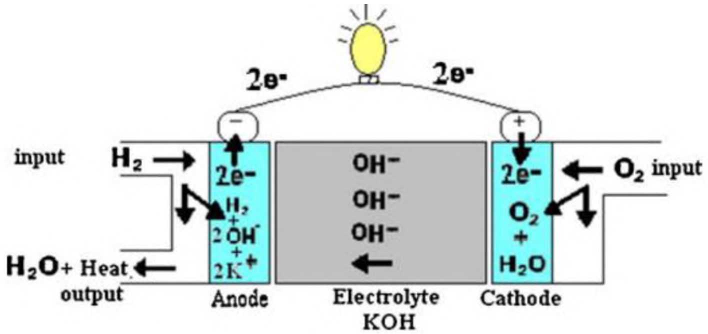


***Figure 7**. Alkaline fuel cell (AFC) [11]*

AFC structure typically utilize a potassium hydroxide (KOH) water solution, in concentrations about 30%, as an electrolyte, while nickel and silver catalyst supported carbon are possible versions for anode and cathode electrodes respectively. Furthermore, they provide 60-70% electrical efficiency in working temperatures lower than 100°C and achieve power production up to some tens of kW. In general terms, AFCs feature an advantageous inexpensive highly efficient technology, however a serious concern remain the sensitivity of the electrolyte to the CO_2 contaminants, that poison the KOH forming potassium carbonate K_2CO_3 [39, 40, 47, 48].

Advantages-Disadvantages

Each type of fuel cell offers unique advantages and limitations that determine its suitability for different applications based on factors like temperature range, availability of fuel sources, efficiency and cost. As research and development into fuel cell technology progresses further, these systems hold out hope as cleaner and more sustainable energy solutions for a wide variety of sectors ranging from transportation to stationary power generation [49-53].

Fuel cells exploit basic electrochemical principles and through oxidation-reduction reactions convert directly chemical energy into electrical, unlike traditional combustion engines, that turn into waste significant proportion of energy as heat. However, they share the same merit with the internal combustion engines ICE of the continuous power production. Fuel cells achieve exceptional efficiency rates, higher than ICE and can attain over 80% if co-generation process is employed, mainly in SOFCs and MCFCs, which operate at very high temperatures, despite the fact that renewable-based hydrogen electrolysis is preferred due to minimum environmental footprint. SOFCs also boast energy diversity by being capable of using different fuel types such as natural gas and biogas, which makes them adaptable for different energy scenarios.

Furthermore, the beneficial fossil fuel reformation process for producing H2 surprisingly is not such energy effective, proving that the energy content of the consumed fossil fuel is more than that of the produced H_2 and simultaneously less environmentally friendly due to hazardous emissions. Another major benefit of the fuel cells is the absence of moving structural parts, which entail maintenance disengagement, less additional costs and of course quiet operation. An additional distinct attribute that fuel cells provide is the modularity and power scalability. In particular, efficiency does not be affected by parameters like system size or load factor and thus small cells perform same efficiency rate with the bigger one. This allows better and easier control and system design in terms of fuel consumption or power output, depending on the requirement of the application. It is worth mentioning that hydrogen fuel can store about 2,6 times more energy per unit mass than gasoline, however requires approximately 4 times more volume than gasoline for storage. Hydrogen also may be abundant, however the pure form of it, applicable for fuel cells, requires challenging production, storing and delivery infrastructure, considering that a safe storage technique is the liquification of hydrogen at -253°C, which is energy and time consuming. Yet there is not a stable hydrogen distribution system around the world, able to cope with the emerging commercialization. Significant barrier moreover remains the high production costs associated with certain forms of fuel cells using noble catalysts like Pt and Ru, such as those seen in DMFCs and PEMFCs primarily because of materials required.

In conclusion fuel cells offer many advantages that make them attractive solutions in power generation. However, they still face numerous barriers which must be overcome for widespread adoption. As promising energy technologies go forward with full integration it will be imperative that fuel cells face challenges related to cost, catalyst availability, temperature sensitivity and kinetics issues to realize full integration within our energy landscape [54, 55].

2.3.2 Electrolyzers

Electrolyzers are devices designed to aid the process of water splitting by electrolysis. This essential process involves the separation of water molecules into their constituent elements, hydrogen and oxygen, by means of electric current. Water splitting has two separate half-reactions that take place. Hydrogen evolution reaction (HER) takes place at the cathode while oxygen evolution reaction (OER) happens at the anode [56-59].

$$H_2O(liquid) + Energy \leftrightharpoons H_2(g) + {}^{1}/_{2}\, O_2 \qquad (2.19)$$

At the cathode, the hydrogen evolution reaction involves the reduction of protons (H^+) from the water molecule to generate molecular hydrogen (H_2). On the other hand, at the anode, the oxygen evolution reaction involves the oxidation of water molecules to produce molecular oxygen (O_2) along with protons and electrons. Theoretical voltages of 0 V and 1.23 V are associated with the hydrogen and oxygen evolution reactions, respectively, indicating the energy input required to drive these processes [59-72].

However, the practical application of water splitting faces challenges, particularly in terms of energy efficiency and reaction kinetics. Preparing hydrogen in large quantities with high purity is hindered by the substantial overpotential and onset potential required for the reaction. The oxygen evolution reaction poses a more significant hurdle due to its sluggish kinetics, making it the most energy-consuming half-reaction. This reaction involves a complex four-proton and four-electron transfer mechanism, particularly notable in alkaline conditions, where high overpotential values are necessary to overcome the activation barrier.

To overcome these challenges, catalysts play an instrumental role. They help reduce activation energy consumption, speed reaction rates and limit wasteful overpotential. Catalysts such as transition-metal carbides, sulfides, phosphides, nitrides, selenides and oxides are used as oxygen evolution catalysts. For the oxygen evolution reaction their impact mainly relies on the mitigation of energy losses. These bifunctional electrocatalysts excel under either acidic or alkaline environments, creating environmental concerns related to corrosion issues as well as costly membranes or separators being necessary in their optimal performance environments. Ruthenium (Ru) is considered promising for alkaline HER, due to it's high bond intensity with hydrogen and the insignificant energy barrier for the water separation in alkaline media. Based on this principle, $RuMoO_{3-x}$ Ni foam and Fe_3O_4-NiFe layered double hydroxide (LDH) electrocatalysts demonstrated and exhibited low OER overpotential and decent stability. Another significant experiment, suggested worm-like S-doped RhNi alloy in a three-dimensional conformation, as a sufficient electrocatalyst for HER [59, 67].

Researchers have recently become interested in electrolyzers operating with neutral or near-neutral pH electrolytes. This approach holds promise for using natural water sources like oceans, lakes and rivers without using environmentally harmful components, aligning with sustainable energy production goals, while simultaneously minimizing overall costs associated with electrochemical systems. Researchers also are taking steps towards more eco-friendly electrolysis techniques by tackling challenges associated with reaction kinetics and catalyst efficiency and thus helping advance renewable energy technologies. Electrolyzers are categorized into the following fundamental groups according to the type of electrolyte that is used.

1. Alkaline Water (AWE) Electrolyzers.

2. Electrolyzers using Proton Exchange Membrane or Polymeric Membrane (PEM).

3. Solid Oxide (SOE) Electrolyzers.

Alkaline Water Electrolyzer (AWE)

An Alkaline Water Electrolyzer (AWE) is a device used to produce hydrogen gas (H_2) through the process of alkaline water electrolysis. This technology has been known since the late 18th century and has undergone various developments to improve its efficiency and feasibility for hydrogen production. AWE is particularly appealing for its potential to generate clean energy and contribute to the reduction of carbon emissions when combined with renewable energy sources.

The fundamental principle of alkaline water electrolysis involves the use of an electrolytic cell with an anode and a cathode immersed in an alkaline electrolyte solution, typically containing either potassium hydroxide (KOH) or sodium hydroxide (NaOH). When a direct current (DC) is applied to the cell through an external power supply, electrochemical reactions take place at the anode and cathode, resulting in the separation of water into hydrogen and oxygen gases [73].

At the cathode, a reduction reaction occurs where water molecules (H_2O) are reduced to produce hydrogen gas (H_2) and hydroxide ions (OH^-):

$$\text{Cathode:} \qquad 2H_2O + 2e^- \rightarrow H_2 + 2OH^- \qquad (2.20)$$

Meanwhile, at the anode, an oxidation reaction takes place, involving the conversion of hydroxide ions into oxygen gas (O_2), water molecules, and electrons:

$$\text{Anode:} \qquad 2OH^- \rightarrow {}^{1}\!/_{2}\, O_2 + H_2O + 2e^- \qquad (2.21)$$

The overall reaction of alkaline water electrolysis is the same as conventional water electrolysis:

$$\text{Overall:} \qquad H_2O \rightarrow H_2 + {}^{1}\!/_{2}\, O_2 \qquad (2.22)$$

In order to facilitate these reactions and ensure efficient separation of the products, an electrolyte solution and a diaphragm are employed. The diaphragm, which separates the anode and cathode compartments, prevents the mixing of the produced gases and allows the hydroxide ions to migrate from the cathode to the anode [74].

The components of an AWE system are essential to its functionality and efficiency:

1. Diaphragm: Traditionally, asbestos was used, but due to health concerns, modern diaphragms are often composed of materials like ceramic-based composites. The diaphragm ensures the separation of the two compartments and the proper migration of ions.

2. Electrodes: The cathode and anode are crucial components where the reduction and oxidation reactions take place, respectively. Nickel and its alloys are commonly used materials for both cathodes and anodes.

3. Electrocatalysts: These materials enhance the efficiency of the electrochemical reactions by lowering the activation energy required. Various combinations of metals and oxides have been studied as potential electrocatalysts to improve the kinetics of both hydrogen evolution and oxygen evolution reactions.

4. Electrolyte: The electrolyte, usually composed of KOH or NaOH, facilitates the movement of ions between the anode and cathode. Additives can be used to increase the ionic conductivity and reduce the corrosive nature of the electrolyte.

Alkaline water electrolysis (AWE) is an established technology and could become an efficient method for producing hydrogen when powered by renewable or nuclear sources without producing CO_2, particularly renewables or nuclear. Whilst its simplicity and suitability for hydrogen production remain advantageous, several challenges still persist such as energy consumption issues, installation costs, maintenance fees and durability issues - research is currently ongoing to overcome such hurdles and optimize alkaline water electrolysis systems more efficiently [75].

Proton Exchange Membrane Electrolyzer (PEM)

A Proton Exchange Membrane Electrolyzer (PEMWE) or Polymeric Membrane Electrolyzer is an electrochemical device introduced in 1959 by Grubb and further developed by the General Electric Company in 1966 to address challenges associated with water electrolysis for hydrogen production. This process has become a pivotal method due to its benefits and potential for sustainable hydrogen generation. As is depicted in **figure 8** he PEMWE shares similarities with Proton Exchange Membrane Fuel Cells (PEMFC) in terms of the solid electrolyte used, which is composed of polysulfonated membranes like Fumapem and Nafion [73].

The core principle of a PEM electrolyzer involves using an external direct current (DC) voltage to split water (H_2O) into its constituent elements, hydrogen (H_2) and oxygen (O_2), through electrochemical reactions. The process takes place within a specialized membrane electrode assembly (MEA), which consists of a thin, proton-conducting and electron-insulating proton exchange membrane (PEM) at its center. The MEA is flanked by porous catalyst layers where the electrochemical reactions occur. The

PEM separates the anode and cathode sides of the cell, allowing the migration of hydrogen protons (H^+) through the membrane, while electrons (e^-) flow through an external circuit [76, 77].

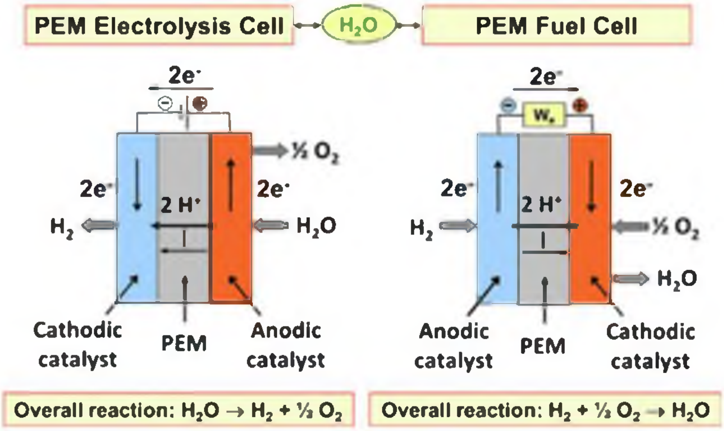


***Figure 8**. Schematic representation of PEM EL and PEM FC [9]*

For the electrochemical reactions to occur, an external DC power source is connected to the anode and cathode electrodes. The applied voltage must be higher than the thermodynamic reversible potential to initiate the water splitting. The energy required for the reaction to proceed (enthalpy change, ΔH_0R) is delivered through the electrical energy from the applied voltage.

However, due to various losses within the cell, the actual voltage required is higher than the thermodynamic reversible potential. These losses are categorized as Faradaic losses (activation losses) and non-Faradaic losses (ohmic and mass transfer losses). Activation losses result from the electrochemical reaction activation, causing a shift from thermodynamic equilibrium and slowing down the reactions. Non-Faradaic losses stem from ohmic resistance and mass transfer limitations.

PEM electrolyzers stand out for their compactness and simplicity, making them suitable for many different applications. PEMs provide high purity hydrogen production at efficient current densities. Furthermore, inexpensive membranes may allow low-cost mass production. Furthermore, with minor modifications PEM electrolyzers may even serve as fuel cells by producing electricity directly from hydrogen and oxygen.

Solid Oxide Electrolyzer (SOE)

Donitz and Erdle first proposed the concept of solid oxide electrolysis back in the 1980s, and since then there has been considerable research and development effort around this method of solid-oxide electrodeposition [73].

Solid Oxide Electrolyzers operate in high-pressure and high-temperature environments (typically 500-850°C) by employing steam (H_2O) and oxygen ions (O_2^-) as conductors, using steam as H_2O and O_2^- ions as conductors. They offer several advantages over conventional electrolysis methods, notably operating at higher temperature ranges than most others; this elevated temperature range helps increase efficiency when water splitting occurs. Key components of a Solid Oxide Electrolyzer include its dense ionic conducting electrolyte layer, a porous hydrogen electrode (cathode), and porous oxygen electrode (anode) as is shown in **figure 9**. For use within multiple cells stacks, interconnector layers are used between adjacent cells that act both current collectors and physical barriers between the cells to create physical separation.

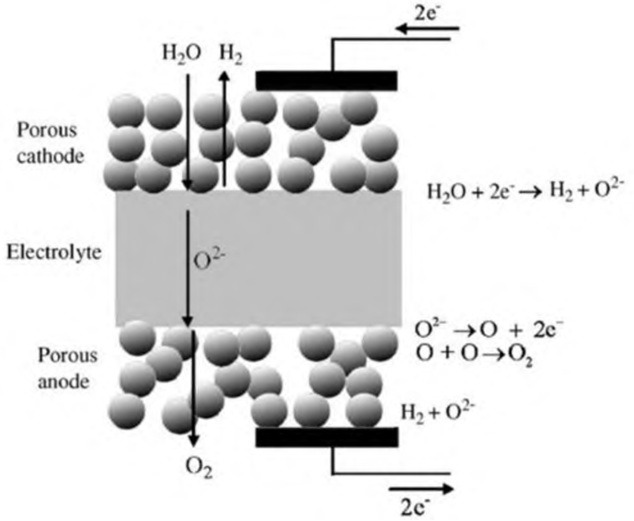


Figure 9. *Schematic illustration of SOEC hydrogen production [78]*

The electrolyte layer is pivotal to the SOE's functionality. It must possess high ionic conductivity for oxygen ions while remaining electrically insulating. This layer prevents gas transport between the electrodes and maintains structural integrity. Yttria-stabilized zirconia (YSZ) and 8 mol% yttria-doped zirconia (8YSZ) are commonly employed electrolyte materials due to their stability, ionic conductivity, and thermal properties.

The hydrogen electrode (cathode) facilitates the electrochemical reduction of steam into hydrogen gas and oxygen ions. A ceramic-metal (cermet) material called Ni-YSZ (nickel-yttria-stabilized zirconia) is often used for its electronic conductivity and catalytic properties. The oxygen electrode (anode), on the other hand, is responsible for oxidizing oxygen ions to produce oxygen gas. This electrode requires a material with high ionic-electronic conductivity and suitable electrocatalytic activity. Perovskite-based materials such as (La, Sr)(Co, Fe)O_3 and $La_{0.8}Sr_{0.2}MnO_{3-\delta}$ are used for this purpose [79].

The intermediate layer, situated between the oxygen electrode and the electrolyte, serves as a transition layer to address the compatibility issues between the two materials. Gadolinium-doped ceria (CGO) and yttrium-doped cerium (YDC) are commonly employed as intermediate layers. Alternatively, a composite material that includes both the electrode and electrolyte materials can be used to eliminate the need for an intermediate layer.

The interconnector, a metallic layer, connects individual cells within a stack and acts as a current collector and physical barrier. It must possess high electrical and thermal conductivity, stability at elevated temperatures, and a similar thermal expansion coefficient as the cells.

The total energy demand for hydrogen production using SOE technology depends on both electrical energy demand (ΔG) and thermal energy demand ($T\Delta S$), where T is temperature and ΔS is entropy change. Operating at higher temperatures can reduce electrical energy demand, while increasing thermal energy demand. This temperature-dependent energy demand allows for the efficient utilization of waste heat, making SOE advantageous [78].

SOE technology holds much promise but also faces several hurdles that must be surmounted, including material compatibility issues, degradation and lifespan restrictions. Research efforts continue in an attempt to overcome these challenges and bring Solid Oxide Electrolyzers closer to commercial viability, revolutionizing high-purity hydrogen production through efficient and sustainable methods.

2.3.3 Supercapacitors

A supercapacitor (also referred to as an electric double-layer capacitor or ultracapacitor) is an advanced energy storage device with its own distinct operating principle for efficiently storing and discharging energy. Comprised of aluminum current collectors, electrodes, an electrolyte solution and separator as is depicted in **figure 10**. Its core function resides in its ability to manage ionic distribution near its electrode surfaces resulting in an electric double layer EDL region with space charge zones.

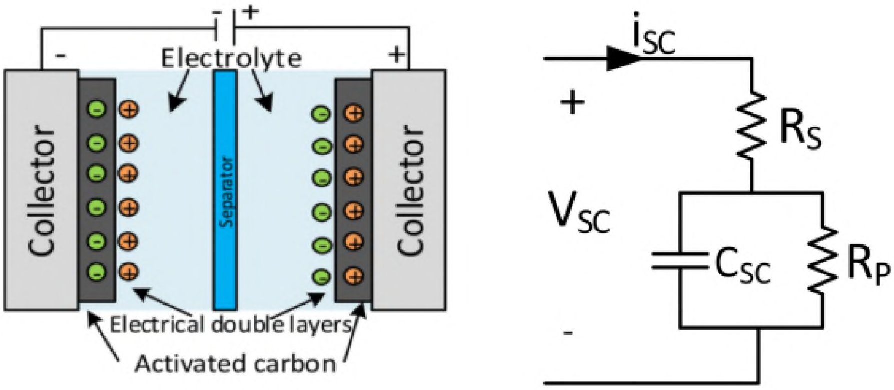


Figure 10. Structure of Supercapacitor and equivalent circuit model of SC [80]

Supercapacitors differ from batteries in that they do not rely on traditional electrochemical reactions for storage, rather they utilize electrostatic interactions instead to store charges without charge transference occurring between electrodes. As soon as an external voltage is applied to a supercapacitor's terminals, an electric field forms within its electrolyte. This causes polarization to take place, forcing ions through dielectric medium towards porous electrodes with opposite charges for migration. This ion movement leads to the formation of electric double layers at each electrode, effectively closing any gaps between them while expanding their surface area. Moreover, this arrangement increases energy storage capacity significantly.

An essential factor in supercapacitor design is selecting an electrode material, as this has a direct bearing on its performance. Supercapacitors offer many advantages over other energy storage devices, including longevity, high power output, adaptability in packaging, temperature tolerance of between -40°C to 70°C), minimal maintenance requirements and their light profile compared to traditional storage technologies. These benefits, make them especially suitable for applications requiring quick load cycling with increased reliability. For instance, in forklifts, load cranes electric vehicles or power quality enhancement systems [80-85].

Supercapacitors differ significantly from batteries in that they offer impressive power density capabilities. While batteries may reach energy densities up to 150 Wh/kg, electrochemical capacitors typically achieve 1/10th that amount. On power density alone however, batteries lag behind considerably by reaching 200 W/kg compared to their electrochemical counterparts, which have the capacity of producing much higher results. Additionally, they suffer from vulnerabilities like rapid performance degradation during charge/discharge cycles, cold temperature susceptibility, high maintenance costs and limited lifespan.

One of the hallmarks of supercapacitors is their inherent safety. Unlike batteries, supercapacitors possess low internal resistance levels that help mitigate overheating and explosion risks. Furthermore, their lifespan greatly surpasses that of batteries; making them highly reliable in applications that demand frequent charging/discharging cycles. It should be noted however, that mishandling fully charged supercapacitors by shorting its terminals may result in rapid discharge and potential electrical arcing damage to itself or nearby devices.

Supercapacitors boast many outstanding attributes, such as low equivalent series resistance (ESR), minimal leakage current, extended lifecycles, wide operational temperature ranges and increased usable capacities. Their operating principle centers on the double layer that forms between activated carbon electrodes and organic electrolytes when voltage is applied; energy storage mainly relies on electrostatic mechanisms, while pseudocapacitive components may contribute to overall capacitance values between 1 F and 5000 F with voltage limits capped at around 3 V.

Supercapacitors sit between traditional capacitors and batteries, offering both energy and power densities with substantial variations between them. Their unique versatility makes them well suited to energy storage applications in portable devices, remote equipment, vehicles, electric/hybrid vehicles as short-term energy storage devices using regenerative braking energy to store short-term energy reserves. Furthermore, their footprint has expanded to encompass telecommunications such as cell phones or personal entertainment gadgets.

Unlike common capacitors that rely on dielectric materials, supercapacitors exploit the principles of double-layer capacitance and pseudocapacitance to store and release electrical energy efficiently. In a supercapacitor, the key lies in the separation of charges at the electrode/electrolyte interfaces. As voltage is applied, charges of opposite nature accumulate on the electrode surfaces. This separation is facilitated by the electrolyte, which creates an electric field and enables energy storage within the device. The fundamental parameter of capacitance (C) defines the energy storage capacity of a supercapacitor and is the ratio of the stored charge (Q) to the applied voltage (V):

$$C = {}^{Q}/_{V} \quad (Farad) \tag{2.23}$$

For supercapacitors, the capacitance can be influenced by various factors, including electrode surface area (A) and the properties of the electrolyte [86].

The energy stored (E) in a supercapacitor is directly proportional to its capacitance and the square of its voltage: $E = CV^2/2$ (Watt or Joule). This reveals that increasing either the capacitance or voltage can enhance energy storage capabilities. In practice, one significant aspect for optimizing supercapacitor performance is the electrode's surface area. The larger the electrode's surface area, the greater the potential for higher capacitance values.

The total capacitance (C) of a supercapacitor can be expressed by a simplified equation:

$$C = \varepsilon_0 \, \varepsilon_r \, A \, / \, d \tag{2.24}$$

where ε_0 is the vacuum permittivity constant and ε_r is the electrolyte's relative permittivity. This equation underscores the importance of the electrode's surface area exposed to the electrolyte [87]. The overall electrochemical supercapacitor can be thought of as two capacitors in series, with the total capacitance inversely proportional to the sum of the reciprocals of the individual electrode capacitances

$$\frac{1}{C_T} = \frac{1}{C_1} + \frac{1}{C_2} \tag{2.25}$$

In a symmetric supercapacitor, where both electrodes exhibit equal capacitances, the total capacitance is halved [88].

Supercapacitors are typically evaluated based on special capacitance (CTS), which normalizes total capacitance by their weight and increases as weight decreases. Raising CTS involves raising capacitance while simultaneously decreasing weight. Energy density (E) measures stored energy per unit mass while power density (P) characterizes energy release rate; both properties of which can be affected by factors like cell voltage (V), total special capacitance (CTS), equivalent series resistance (ESR), and weight of its components. Enhancing supercapacitor performance involves increasing V and CTS while simultaneously decreasing weight and ESR. A supercapacitor's maximum operating voltage is determined by its electrochemical Stable Potential Window (ESPW), or range within which its electrolyte remains stable.

Effective energy storage and delivery capabilities, high power density, and the potential for optimization make them ideal candidates for applications requiring rapid energy cycling with high power outputs.

Supercapacitors' success lies within their electrodes and electrolytes, both of which play vital roles in determining their energy storage capabilities.

Graphene is an incredible two-dimensional material with impressive properties that has quickly earned widespread praise as an ideal candidate for supercapacitor electrodes. High specific surface area, outstanding strength, superior electron conductivity (10 times that of graphite), low density, flexibility and ease of chemical processing make graphene suitable for electric double-layer capacitors (EDLCs). Their capacitive performance relies heavily on factors like surface area, pore size distribution, interlayer spacing distances, heteroatom doping levels, surface functionalities and conductivity which all contribute towards amplifying their capacitive behavior overall.

Carbon nanotubes (CNTs) have also been extensively explored for their potential as supercapacitor electrodes. These cylindrical nanostructures, available as both single-walled (SWCNT) and multi-walled (MWCNT), exhibit narrow size distributions within the nanometer range, high accessible surface areas, low resistance levels and outstanding stability. Due to their unique properties, SWCNTs and MWCNTs have long been considered viable supercapacitor electrodes. CNT/oxide composites represent an innovative breakthrough in supercapacitor development. Their combination with pseudocapacitive oxide phases provides improved percolation of active particles, efficient diffusion, resilience against volumetric changes during cycling as well as against volumetric fluctuations.

Polyaniline (PANI), a conducting polymer with tunable pseudocapacitive behavior, has found application both as a conducting agent and as an electroactive material in energy storage. Its morphology, which can be tailored during synthesis, plays a critical role in determining its supercapacitor performance. Adding certain additives during polymerization can enhance the specific capacitance and energy of PANI-based supercapacitors. Notably, PANI's initial doping is not essential for its electroactivity, as doped PANI can exhibit higher specific capacitance due to the presence of covalently attached dopants that do not impede electrochemical processes [89]. Polypyrrole (PPy) is another extensively researched conducting polymer for supercapacitor applications. Its affordability, high capacitance, stability, and solubility in aqueous environments make it a favorable candidate. PPy has been combined with carbon nanotubes to create hybrid electrode materials that effects both in EDLC and pseudocapacitance, resulting in improved electrochemical performance [90].

Electrolytes, vital components of supercapacitors, are responsible for transferring and balancing charges between electrodes. Aqueous electrolytes, which exhibit high conductivity, are commonly used due to their compatibility with various electrode materials. However, their limited electrochemical stability and energy density restrict their application range. Organic electrolytes and ionic liquids offer wider operating voltage windows, leading to higher energy densities, although their lower ionic conductivities can pose challenges.

Organic electrolytes dominate the commercial supercapacitor market due to their higher operating potential windows and compatibility with various electrode materials, while ionic liquids (ILs) have recently gained considerable interest as alternative electrolytes due to their thermal, chemical, and electrochemical stability as well as tunable properties. Their unique combination of cations and anions contributes to their low melting points which make ILs especially suitable for energy storage applications; yet due to their diverse properties and potential uses further investigation is warranted. Selecting an electrolyte suitable for use in a supercapacitor is crucial to its optimal performance. Key requirements of an ideal electrolyte include high conductivity, compatibility with electrode materials, electrochemical stability and thermal stability. Researchers are constantly working on creating electrolytes that meet these criteria while also meeting challenges like low conductivity organic electrolytes or solid-state electrolyte limitations [91].

Supercapacitors come in an assortment of configurations and energy storage methodologies tailored to specific applications. They can be divided into physical construction categories like flat, cylindrical and rectangular designs as well as energy storage mechanisms, which fall under three primary categories: EDLCs, pseudocapacitors (PCs) and hybrid supercapacitors (HSCs) [80, 82].

Electric Double-Layer Capacitors (EDLCs): As the foundational type, EDLCs rely on an electric double-layer mechanism. This involves forming an electric double layer at the electrode-electrolyte interface where ions accumulate into a compact layer resulting in significant increases in capacitance. Charge storage occurs via physical processes without faradic reactions leading to high power density with rapid charging and discharging rates [92].

Pseudocapacitors: Pseudocapacitors are a subclass of supercapacitors operating on the Faradaic charge process. This technique involves either irreversible or reversible redox reactions at the electrode-electrolyte interface, leading to enhanced capacitance compared to traditional EDLCs. Pseudocapacitive materials undergo fast, reversible redox processes at their electrode surface similar to battery batteries but with rapid rate characteristics similar to capacitors such as quasi-rectangular cyclic voltammograms (CVs) or quasi-triangular galvanostatic charge-discharge (GCD). These features distinguish these materials electrochemically from their traditional counterparts through electrochemical.

Subcategories of pseudocapacitors include surface-redox pseudocapacitors and intercalation pseudocapacitors. Surface-redox pseudocapacitors store charge via surface charge transfer between electrodes. Intercalation pseudocapacitors display rapid charge storage rates that rival or surpass traditional surface redox materials [93].

Hybrid Supercapacitors (HSCs): Hybrid supercapacitors (HSCs) combine the energy storage principles of both EDLCs and pseudocapacitors into one device, offering greater energy density with lower capacity limits than either alone could achieve. By combining their strengths, HSCs overcome individual component's shortcomings and achieve higher capacitance values than either could individually provide. HSCs come either symmetric or asymmetric in design with electrode combinations made up of various materials. Their synergy enhances electrochemical behavior, while key factors such as cycling stability and affordability are maintained. Asymmetric HSCs exhibit extended values in specific capacitance while higher rated voltage results in greater specific energy storage potential than either type [94, 95].

Notably, researchers have explored novel electrode configurations that utilize innovative materials and energy storage mechanisms, notably hybrid electrode systems featuring

EDLC/pseudocapacitive or EDLC/battery setups that further increase performance. Such designs exploit both the kinetics of EDLC materials as well as pseudocapacitive or battery electrode materials for increased electrochemical performance improvements. From the **figure 11** below, we can distinguish the prevalence of supercapacitor in terms of energy density against conventional capacitors while the opposite occurs in terms of power density of power density. Evidently, from this diagram it is clear that SCs fill the gap between batteries and capacitors.

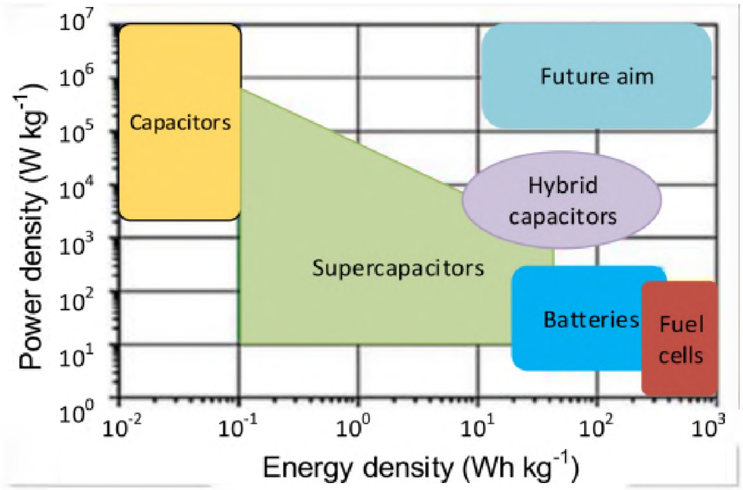


Figure 11. *Comparison of the energy and power density of storage devices [80]*

2.3.4 Electrochemical Sensors

Electrochemical sensors are innovative devices designed to detect and quantify various chemicals by converting their interactions into electrical signals that can be measured. Due to their accuracy, sensitivity, and versatility these sensors find application in fields ranging from environmental monitoring and healthcare processes all the way through industrial production lines.

Electrochemical sensors consist of three fundamental elements: an electrode, electrolyte and sensing material. Together these three components actuate a chain of reactions which enable detection of specific molecules or ions present in their environment through interaction between sensing material and target molecules.

The electrode is often constructed of metal, carbon or conductive polymers, which allow electrons to flow easily between sensing material and electrode. An electrolyte solution serves as a medium between them both and plays an essential part in maintaining electrochemical equilibrium necessary for accurate measurements.

At the center of a sensor's function lies its sensing material, which acts as a molecular gateway. This material, often composed of polymers or metal complexes, interacts with target molecules selectively. When they contact it, chemical reactions initiate that ultimately alter its electrical properties. Electrochemical sensors operate through an intricate combination of redox reactions and thus the exchange of electrons among molecules. When target molecules bind with sensing material and alter its redox state, this causes changes to current or voltage between electrodes in electrolyte solutions. When measured over time this change becomes an electrical signal which allows scientists and engineers to infer concentration levels for target molecules present in an environment [96-101]. A schematic representation of an ethylene electrochemical sensor is illustrated above in **figure 12**.

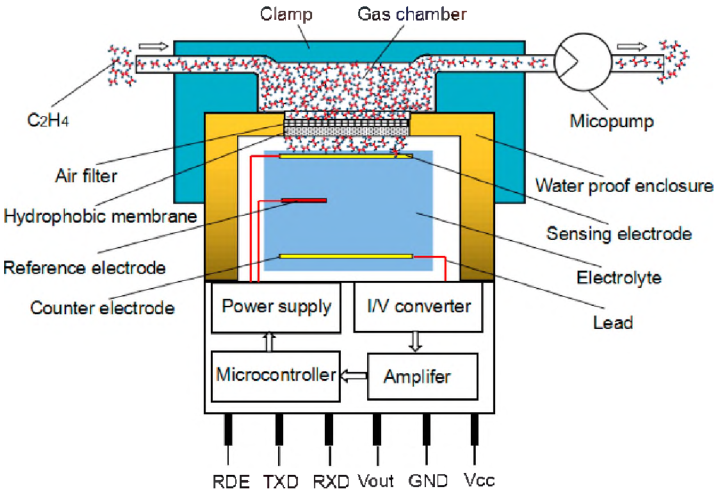


Figure 12. *Schematic diagram of a smart electrochemical ethylene sensor [102]*

Electrochemical sensors have many diverse applications. Gas sensors detect pollutants in the air while glucose sensors help track diabetes patients' blood sugar levels. Environmental monitoring, food safety management systems and industrial processes all benefit from electrochemical sensing technology's precision. Electrochemical sensors come in various types, each designed to detect specific analytes or target molecules. Here is a selection of some of the more popular varieties [96, 103-108].

Equilibrium Potentiometric Gas Sensors

Equilibrium potentiometric gas sensors rely on the establishment of an equilibrium potential at the sensing electrode (SE) based on the Nernst equation. These sensors consist of an electrolyte enclosed in a tube, with a reference electrode (RE) and a sensing electrode (SE) on either side. The potential at the SE depends on the concentration of the target gas. The Nernst equation governs this relationship, and the sensor operates as a concentration cell. Equilibrium potentiometric sensors are commonly used for gas analysis, and their accuracy depends on the known concentration of the reference atmosphere.

Mixed Potential Gas Sensors

Mixed potential sensors function by employing multiple reactions at the SE, leading to a mixed potential that provides information about the target gas. Unlike equilibrium, these sensors do not establish an equilibrium and exhibit non-Nernstian behavior. Mixed potential sensors detect gases like H_2, CO, CO_2, hydrocarbons, SO_2, NOx, NH_3, and H_2S. They measure the potential difference between the SE and RE, which is influenced by the kinetics of various reactions on the SE.

Amperometric Gas Sensors

Amperometric sensors work by applying an external voltage to drive specific reactions at the electrodes. These sensors are designed with gas diffusion limitations, where the gas must diffuse through a porous or capillary barrier to reach the electrode. Amperometric sensors have an advantage over potentiometric ones as they can operate without a reference atmosphere. The limiting current in amperometric sensors is linearly related to the gas concentration, making them precise for medium to high gas concentrations. These devices come in various designs and can sufficiently detect O_2, H_2, CO, NO_x, CHs and NH_3.

Combined Gas Sensors (Amperometric-Potentiometric)

Combined sensors integrate both amperometric and potentiometric cells. These sensors consist of two electrochemical cells that work synergistically to enhance reliability. One cell operates as an amperometric sensor to measure the limiting current, while the other functions as a potentiometric sensor to measure EMF. This combined approach provides more accurate and robust gas detection capabilities.

Impedance-Based Gas Sensors

Impedance-based sensors utilize sinusoidal voltage and current responses to measure impedance. These sensors have designs similar to mixed potential sensors and are applied to semiconductor-based and solid oxide-based systems. They offer an alternative approach to gas detection, and reports indicate successful detection of gases like steam (H_2O), NOx, and CO using impedance-based techniques.

Electrochemical sensors have found applications across various industries and scientific domains, illustrating their versatility and importance. When it comes to gas sensing, stabilized zirconia-based sensors have proven invaluable in transport, industry and research sectors - being especially adept at analyzing high temperature gas mixtures from heat power plants or dust-laden exhaust gases at elevated temperatures. With impressive accuracy, speed, wide oxygen concentration analyses without extensive sample prep required and impressive speed analysis these sensors contribute significantly towards emissions monitoring and process optimization.

Nitrous Oxide (N_2O), best known for its use as both an inhalation anesthetic and fuel enhancer, serves to showcase the versatility of electrochemical sensors. Medical professionals consider nitrous oxide one of the safest anesthetics without complications; when added to fuel mixtures for automotive and internal combustion engines it improves engine performance by lowering air temperature, increasing oxygen content, and improving combustion rates. Nitrous oxide-infused fuel also serves the food industry by acting as food additive, propellant, packaging gas while rocket engines incorporate it as an oxidizer highlighting its relevance for space exploration [104, 109-113].

Proton-conducting materials based on $BaCeO_3$ and $BaZrO_3$ play key roles in solid oxide fuel cells, electrolyzers and hydrogen permeation membranes and further contribute towards sustainable energy technologies by producing hydrogen for hydrogen production as well as ammonia synthesis, making these proton-conductor materials indispensable. It is proved that a combined potentiometric and amperometric sensor with $BaCe_{0.7}Zr_{0.1}O_{3-\delta}$ proton conducting electrolyte can sufficiently employed for hydrogen analysis at temperatures between 450-550°C [114-117].

Yttria-stabilized zirconia (YSZ) has long been considered an outstanding material for automotive sensors, counting more than four decades of use in gasoline vehicles and especially the structure with $0.9ZrO_2 + 0.1Y_2O_3$ (YSZ) and a ceramic diffusion barrier, which is designed for hydrogen and water vapor detection in the air. With excellent chemical stability, oxygen ion conductivity, adhesive properties, and chemical stability qualities it makes an attractive candidate for gas sensors of various kinds. Furthermore, this versatile material allows sensors to be made in both planar and tubular forms for optimized sensing characteristics and maximum sensing performance [118].

As the world attempted to address COVID-19's challenges, electrochemical biosensors offered tremendous promise as a detection method. Their advantages include accuracy, sensitivity, speed, and portability, complementing existing diagnostic tools perfectly. Recent advancements of SARS-CoV-2 electrochemical biosensors with Au-based and carbon/graphene transducer electrodes have revolutionized detection capabilities with rapid response times, exceptional sensitivity, comparable specificity with current methods and nanomaterial incorporation further improving performance, although synthesis methods or material combinations may influence outcomes further [23, 119].

Reviewers emphasize both Au-based and carbon/graphene electrodes' potential. Reducing graphene oxide (r-GO) with Au nanoparticles expand detection areas and enhance sensor characteristics. Doping or structural alteration techniques enhance graphene electrodes. Detection techniques like electrochemical impedance spectroscopy, amperometry and differential pulse voltammetry provide reliable insights into analyte concentrations. At the same time, fine-tuning operational parameters ensure optimal performance particularly in environments with variable virus concentrations [120].

2.3.5 Batteries

At the core of modern energy storage, batteries are intricate devices that exploit electrochemical reactions to store energy. These devices comprise two primary electrodes: an anode, or the negative electrode, and a cathode, the positive electrode as shown in **figure 13**. These components are separated by an electrolyte, which allows ions to flow while maintain electrical neutrality. As a battery discharges, a chemical reaction unfolds at the anode, liberating electrons. Simultaneously, a corresponding reaction occurs at the cathode, where electrons are accepted. This movement of electrons generates an electric current that can be employed to power an array of devices.

Batteries are broadly classified into two main categories: non-rechargeable and rechargeable. Non-rechargeable batteries, also known as primary batteries, undertake chemical reactions that are largely irreversible. For instance, the alkaline battery features an anode of zinc and a cathode of manganese dioxide. During discharge, the zinc anode oxidizes, liberating electrons, while manganese dioxide at the cathode gains electrons and protons. Since these reactions cannot be effectively reversed, primary batteries are not rechargeable and are discarded after their energy depletion [121].

In contrast, rechargeable batteries, or secondary batteries, operate via reversible chemical reactions. Lithium-ion batteries, a notable example, have an anode usually composed of graphite and a cathode containing compounds like lithium cobalt oxide. During discharge, lithium ions traverse from anode to cathode, producing an electron flow. Upon recharging, the movement of lithium ions is reversed. This reversibility allows rechargeable batteries to be repeatedly charged and discharged, making them a more sustainable energy storage solution for various applications.

Below are presented the most common battery types, categorized by their chemistry, materials and applications.

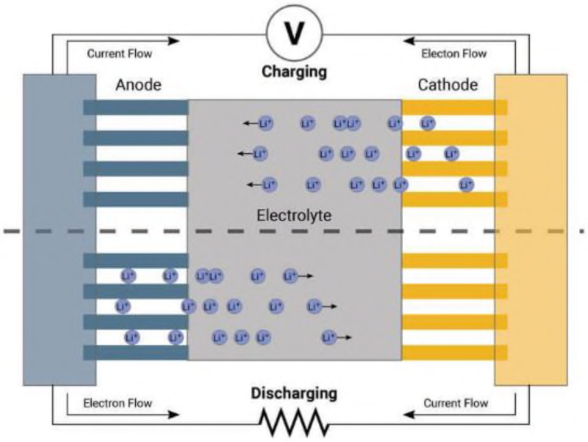


Figure 13. *Basic Battery depiction [122]*

<u>Alkaline batteries</u>

Alkaline batteries have played a central role in energy storage for over 100 years, dating back to Edison's nickel-iron accumulator and Jungner's nickel-cadmium battery system. These innovations paved the way for alkaline rechargeable electrochemical energy storage to be implemented across various markets. Alkaline batteries stand out with their unique anode (zinc) and cathode (manganese dioxide) materials that promote efficient electrochemical reactions necessary for their performance. Chemical interactions involving zinc-oxidation at the anode and reduction at the cathode result in an electric current flowing between them, powering everything from remote controls to hybrid electric vehicles (HEVs). Alkaline batteries offer particularly substantial charging and discharging capabilities - something particularly crucial in vehicular applications and emerging electric supply systems designed for power-intensive functions.

However, alkaline batteries do not come without challenges and prospects. While their high-power output and durability make them suitable for various applications, their implementation in all-electric vehicles remains limited by cost and limited driving range compared to alternatives like lithium-ion. Recent strides such as research into manganese-zinc rechargeable alkaline batteries (RABs) has aroused considerable interest due to their potential of mitigating these concerns by employing cost-effective materials with promising energy density (>500Wh kg^{-1}) and capacity (~308mAhg^{-1}) projections that could broaden alkaline batteries reach into new applications, ushering alkaline into an era of energy storage potential [123, 124].

Lead-acid batteries

Lead-acid batteries possess various key attributes which have contributed to their widespread adoption across different industries. Battery technology with cells immersed in dilute sulfuric acid electrolyte offers unparalleled float life of at least 70 years and over 1,000 deep discharge cycles. Their specific energy, typically 40 to 50 Wh kg^{-1}, and power output between 150-200 Wkg^{-1} provide the optimum combination of energy density and power capability. Battery functionality depends upon electrochemical reactions at both anodes and cathodes. Lead dioxide (PbO_2) binds with sulfuric acid at anode for reaction that results in lead sulfate ($PbSO_4$) production while simultaneously liberating electrons. At the cathode, pure lead (Pb) reacts with sulfuric acid to form lead sulfate and liberate electrons. This provides sufficient electron flow for creating electric current, making lead-acid batteries an increasingly popular and affordable solution.

Lead-acid batteries offer numerous advantages. However, their specific energy is relatively lower when compared with newer battery technologies and thus limit their use in applications requiring higher energy densities. Battery packs are particularly susceptible to sulfation, the accumulation of lead sulfate crystals over time which reduces performance and lifespan, with lasting consequences to performance as well as lifespan. Lead-acid batteries also remain relevant in industries requiring reliable yet cost-effective energy storage solutions, such as automotive starting systems and backup power supplies. Their historical significance, coupled with current developments, further demonstrate lead-acid batteries' longevity within modern energy landscape [125, 126].

Nickel-Cadmium batteries

NiCd batteries were first invented in 1899 and have seen numerous refinements ever since, representing an essential advancement in battery technology. At first, active materials were deposited onto porous nickel-plated electrodes. Later innovations included absorption of gases during charging to create modern sealed NiCd batteries which found widespread applications such as two-way radios, medical equipment, video cameras and power tools. Ultra-high capacity NiCds introduced in late 1980s increased their potential by 60% despite higher internal resistance and decreased cycle durability issues.

NiCd batteries offer numerous advantages. Their resilience allows for high cycle counts with proper care, their rapid charging being hassle-free, their load performance being good under abusive conditions and their long shelf life making storage and transport convenient as well as their reliability in low temperatures are among their many strengths. Furthermore, economic pricing makes these batteries an invaluable addition to your product ranges and selection.

However, NiCd batteries also have limitations that must be considered before making a decision about them. Their specific energy lags behind newer systems and memory effects require regular full discharge cycles for optimal function. Their toxic presence necessitates careful disposal practices while their high self-discharge rates require frequent recharge after storage. Yet these characteristics continue to find applications across industries due to their enduring benefits and dependability [127].

Lithium batteries

Lithium batteries are primary cells; thus, recharging is not indicated if gets empty once, that are characterized by lightweight structure, high energy density capabilities both gravimetric and volumetric and relatively long self-life (5 – 10 years). Each cell composed of metallic lithium anode whereas as cathode various materials can be employed such as manganese dioxide, poly(carbon monofluoride) and vanadium pentoxide, often combined with lithium cobalt dioxide ($LiCoO_2$) intercalation ingredients. This composition provides voltage 1,5 – 3,7V with low self-discharge rate, suitable for common portable applications like cameras, watches, remote controls etc.

Unfortunately, these batteries include highly flammable solvents and hazardous components that can lead to thermal runaway and explosion above specific temperature limit. In particular, if unexpectedly lithium metal gets in contact with water, then flammable hydrogen gas may release with a consequent ignition. Additionally, in defined lithium battery chemistries, such as thionyl chloride-based, if safety management device does not exist, high runaway activity is reported above a specific temperature [128, 129].

Nickel-metal hydride batteries (NiMH)

NiMH batteries, often classified as secondary batteries, stand out by being rechargeable due to certain chemical compounds found within their composition and thus being capable of being charged over their designated lifespan. This distinguishing factor allows NiMHs to remain cost effective solutions. NiMH batteries boast nearly twice the energy density of Nickel Cadmium (Ni-CD) cells at equivalent voltage, making them an excellent option for charging portable electronics and electric vehicles. NiMH batteries have long been favored as reliable power solutions due to their impressive cycle life and energy density, often exceeding hundreds of recharge cycles within five years of purchase. Their adaptable size range from milliamp-hours to ampere-hours contributes greatly to their utility and versatility.

NiMH batteries consist of two elements separated by a separator to prevent short circuiting: a nickel oxy-hydroxide and metal hydride electrodes, sandwiching an electrolytic separator between them to protect from short-circuiting. A battery employs an alkaline electrolyte such as potassium hydroxide (KOH) for optimal ion diffusion during charge and discharge cycles, with a current collector providing enhanced conductivity that maximizes battery capacity. NiMH batteries feature self-sealing safety vents to release excess gases during overcharging or other exceptional events, further increasing their safety profile and making these batteries suitable for power tools and hybrid vehicles. NiMH batteries may offer numerous advantages, yet they still present certain limitations: intricate charging processes require precise timed charges in addition to having significant self-discharge rates. Over time however, research and alloy enhancement have improved NiMH battery stability and energy retention, further solidifying them as reliable energy storage solutions suitable for various applications [130, 131].

CHAPTER 3

3.1 Introduction to Li-Ion Batteries

Li-Ion batteries have quickly earned immense recognition and acceptance across numerous applications due to their unique properties. LIB technology replaced bulky lead acid and Ni-MH batteries previously dominating global markets with sleeker, more efficient energy storage solutions across different industries. Here is a summary of their utilization:

Li-Ion Batteries Are Essential to Portable Electronics: Li-Ion batteries have become indispensable components in portable electronic devices like smartphones, laptops, tablets and wearable devices. Their high energy density enables compact designs with extended battery lives, giving smartphones, laptops, tablets and wearable devices longer periods between charges while their lightweight nature enables on-the-go use for convenience and mobility for their users.

Electric Vehicles (EVs): Li-Ion batteries have transformed the EV industry through their high energy density and sustained power delivery capacity, enabling longer driving ranges on one single charge while decreasing our dependence on fossil fuels while supporting sustainable transport initiatives. Fast charging technologies further facilitate practicality by speeding up charging times while improving driver convenience. Depending on the customer's needs, electric mobility nowadays adopts battery technology in multiple versions. Thus, an electric vehicle may be battery electric vehicle (BEV) powered by electric motor only, or hybrid electric and plug-in hybrid electric that combine both electric and combustion engine.

Energy Storage Systems (ESS): Li-ion batteries play an integral part in energy storage systems that utilize renewable energies, such as solar and wind power for renewable energy storage purposes. Their intermittent nature of renewable generation requires them to store extra power during periods of low demand before releasing it during periods of peak need, guaranteeing reliable supply at all times and supporting cleaner, more sustainable energy for our future. The ability to store the excess produced energy into li-ion batteries, motivated the development of energy storage parks in places with insufficient existing electrical supply infrastructure.

Li-Ion batteries have become essential parts of aerospace and defense applications. Their high energy density and lightweight properties make them invaluable tools in powering satellites, spacecraft, unmanned aerial vehicles (UAVs) and portable communication devices such as remote sensing equipment or unmanned systems in challenging environments.

Medical Devices: Li-Ion batteries play an essential part in powering medical devices, both implantable and portable, including pacemakers and neurostimulators, with long-term battery power support to replace infrequent replacement needs. Portable medical equipment like insulin pumps and diagnostic equipment depend on these battery packs due to their compact size, high energy density, rechargeability capabilities, ultimately improving patient care and quality of life.

Li-Ion batteries have made significant strides forward across various industries, fostering technological progress while supporting environmentally responsible practices and enriching individuals' quality of life worldwide. Through ongoing research and development initiatives geared at optimizing performance, safety, and environmental stewardship efforts aimed at optimizing these batteries further advancement is made.

Furthermore, they have quickly become one of the go-to choices across numerous applications due to their many advantages, primarily their impressive energy density. Li-Ions boast one of the highest densities among rechargeable battery technologies allowing efficient powering for portable electronics and electric vehicle while prolonging usage times without needing frequent recharge sessions.

Except from the greater energy density, they offer than other rechargeables, they also feature higher nominal voltage output than their competitors. Nominal voltage refers to the potential difference between positive and negative terminals of their cells. Li-Ion typically provides between 3.6-3.7V per cell, while NiCd or NiMH batteries offer 1.34-3.2V output per cell. Li-Ion's higher voltage output enables it to supply more power while increasing device efficiency; especially useful when applied in electric vehicle acceleration rapidly with sustained speeds.

They also offer another great benefit in terms of cycle life. This refers to how many charge/discharge cycles they can withstand before showing signs of capacity degradation, with most models lasting hundreds to thousands depending on chemistry and use conditions. Their extended cycle life (-10years) makes Li-Ion ideal for portable electronics or electric vehicle batteries, which need frequent charging/discharging cycles before needing replacement, thus renders them ideal candidates for long term durability while saving cost! With multiple charging cycles until replacement becomes necessary.

Researchers, engineers and innovators continue to leverage Li-Ion batteries' advantages as energy storage tools. They specifically seek ways to enhance performance, safety and sustainability of this cutting-edge battery technology. Furthermore, advancements in Li-Ion hold great promise to revolutionize how devices are powered, while supporting transition to cleaner sources of power that enable a sustainable future. Since their first introduction in 1991 by Sony Corporation admiral efforts have been held in the development of a variety of shapes, chemical compositions, material selection etc., that totally affect the overall battery efficiency. Now main researcher’s pursuit is to exceed problems such as battery degradation and battery aging mechanisms that lower the battery yield and are affected by various mechanisms such as electrode material size, porosity, cell configuration etc. Moreover, global targets and predictions for future demands and reduced costs, related with material scarcity, cause serious concerns and the necessity for the exploration of new technologies, also known as ‘Beyond-Li-ion’ technologies. There is a list of prospective types, that belong in the category of ‘Beyond-Li-ion’ technologies, on the academic bench and each one features unique properties and unwanted obstacles that need urgently surpassed.

3.2 Anode and Cathode of Li-Ion Batteries

A typical LIB cells consists of 15 – 30% anode, 25 – 30% cathode, 10 -15% electrolyte, 3-4% separator, 18 – 20% casing and 10% other components [132]. A simple depiction of the li ion battery cell structure is given in the **Figure 14**.

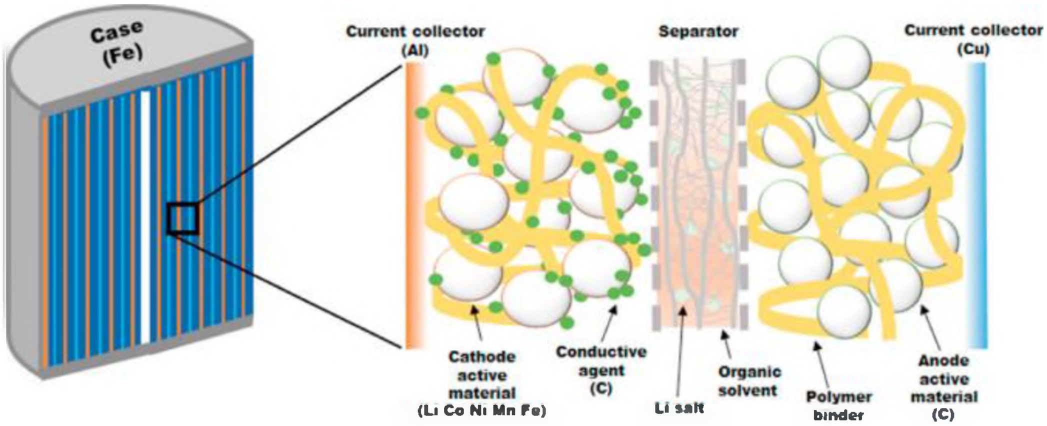


***Figure 14**. Schematic representation of a LIB cell [133]*

Anode and cathode present the most expensive materials of the battery and play a critical role in ensuring battery performance and efficiency. We will explore various materials used as anodes and cathodes, such as graphite, lithium iron phosphate (LFP), lithium cobalt oxide (LCO) and lithium nickel manganese cobalt oxide (NMC), to understand their electrochemical properties as well as their impact on battery performance.

Anode Materials

Anode is the negative electrode where oxidation reactions take place during battery discharge, thus conducts the electrons and allows the li ions to pass through the structure. Lithium-ion storage works through intercalation: as lithium ions enter and leave its structure during charging and discharge respectively allowing reversible lithium storage [134-137]. The most common anode composition is a combination of a Cu current collector, an organic binder (PVDF) and the active material made up of graphite due to its superior cycling stability, high capacity, low cost and abundant availability. The 50% of the global synthetic graphite over the last years originate from China, however due to geopolitical concerns and the necessity for a stable supply chain, further extraction investigation move forward, especially in Africa [138]. Although graphite dominates the global li ion battery industry, new material technologies and applications, implies more challenging specifications in terms of performance and energy density where abode's seem to be limiting [136]. A next generation of anode explored is Lithium Titanium Oxide, which exhibits competitive properties such as high capacity and longer lifespan, however the ''severe gassing'' produced from the reaction between the electrolyte and the LTO material and the higher production costs are two main drawbacks that delay its commercialization [137, 139, 140].

Cathode Materials

The cathode is the positive electrode where reduction reactions take place during battery discharge, theoretically the source of the Li ions, therefore determines the voltage and the capacity of the cell. Similarly with the anode, cathode consists of an Al current collector, an organic binder (PVDF) and the cathode active material in a layered, spinel or polyanionic crystal structure [136]. The spinel structure is represented from the AB_2O_4 formula such as $LiMn_2O_4$ and the polyanionic described from the (XO_4) n- formulation using phosphates, silicates and sulfates.

Despite the fact that the most commercially used cathode is the layered lithium iron phosphate cathode, different materials can be used depending on desired performance characteristics and cost [137, 141-143]. A more comprehensive presentation of current LIB cathodes accomplished in following steps.

Electrochemical Properties and Battery Performance

Electrochemical properties of anode and cathode materials directly influence battery performance in terms of capacity, voltage, cycle life, rate capability and safety parameters. LIB identification and assessment prior to utilization or recycling rely heavily on these parameters.

- Capacity refers to the amount of charge a battery can store, determined by its specific capacity materials. With higher specific capacities come higher charge-storage potential per mass or volume unit and therefore lead to an increase in energy density.
- Voltage can be defined as the electrochemical potential difference between anode and cathode electrodes, with various combinations producing distinct voltage levels that affect overall battery voltage as well as compatibility with electronic devices.
- Lifespan refers to the total number of charge/discharge cycles a battery can withstand before significant degradation sets in. Anode and cathode materials with superior cycling stability and minimal side reactions help extend its cycle life.
- Rate capability describes a battery's ability to provide or accept rapid charges and discharges, making them ideal for high-power applications that demand fast charging processes or applications requiring high power levels. Materials with superior ionic and electronic conductivity facilitate rapid charge/discharge cycles needed for fast charging processes or applications that demand higher levels of energy output.
- When designing batteries, safety must always come first. Choosing anode and cathode materials that offer strong thermal stability, low reactivity, and reduced risk of thermal runaway are crucial in order to produce safe batteries, helping prevent accidents or cell failures from happening [139].

Selection of suitable anode and cathode materials is central to creating high-performance batteries, with materials like graphite, LFP, LCO and NMC offering their own set of advantages and drawbacks when applied to energy storage systems. Understanding their electrochemical properties as they relate to battery performance is vital when developing advanced energy storage systems. Research efforts strive to optimize capacity, cycle life, rate capability and safety features so as to meet future requirements.

3.3 Electrolyte and Separator

Apart from the positive and the negative electrode that are the core of LIB cells, electrolyte and separator own a significant role for the battery operation. Electrolyte and separator components which work together for efficient ion transport while also helping avoid short circuits.

LIBs' electrolytes serve as an essential conductor of lithium ions (Li^+) during their charge and discharge processes, acting as a conduit between cathode and anodes to facilitate movement of Li^+ ions from charge to discharge stages while electrons flow through the external circuit for current generation. Their high conductivity guarantees efficient ionic transport that maximizes battery energy storage capabilities as well as power delivery capacities [135, 136].

LIBs employ various types of electrolytes, including both liquid and solid-state types. Liquid electrolytes have been favored for commercial battery applications due to their excellent conductivity, often consisting of lithium salts such as $LiPF_6$, $LiClO_4$, $LiCF_3SO_3$, $LiBF_4$, $LiASF_6$, PVDF and N-methyl-2-pyrolidone NMP, dissolved in organic solvents such as dimethyl carbonate (DMC), diethyl carbonate (DEC), ethylene carbonate (EC) or propylene carbonate (PC). These solvents offer good ionic transport within batteries while offering high conductivity across ionic gradients, however flammability could pose safety issues in high temperature environments or when a malfunction occur [139].

Researchers are taking proactive measures to address safety and stability concerns associated with liquid electrolytes by exploring solid-state electrolytes as an alternative solution. Solid-state electrolytes offer numerous advantages in contrast with the liquid, including greater energy storage capacity, enhanced safety features and reduced dendrite formation risk. Dendrites are needle-like structures that form during repeated charge and discharge cycles, potentially penetrating the separator and short circuiting it - endangering battery safety and longevity. Solid-state electrolyte materials that show promising properties include ceramics, polymers and composites such as lithium garnets, sulfides, phosphates (polyethylene oxide) PEO, (polypropylene oxide) PPO, (polyacrylonitrile) PAN and (poly methylacrylate) PMMA. Unfortunately, significant challenges remain regarding fabrication costs, room temperature conductivity limitations and limited ionic conductivity issues for widespread commercial adoption of these promising electrolyte materials [141, 142].

Electrolytes help facilitate ion transport while separators prevent direct contact between cathode and anode electrodes, often by acting as thin, porous membranes that serve as physical barriers between them, permitting Li^+ ions to pass while protecting electrodes from touching each other or creating short circuits. Separators typically incorporate microporous materials like polyethylene (PE) and polypropylene (PP), with their high mechanical strength, thermal stability, and electrolyte absorption capacities.

Separators should be tailored to match the size and concentration of Li+ ions for efficient transport through the battery, while their low electrical conductivity must prevent self-discharge or energy loss within [135, 139]. The selection of separator material, thickness, and porosity has an enormous influence on battery performance and safety. Thinner separators reduce ionic resistance for increased power output while thicker ones help increase storage capacity. Furthermore, porosity affects electrolyte absorption and distribution affecting mobility as well as overall battery performance - so manufacturers often employ wetting agents or coatings to optimize properties that improve its performance under varying operating conditions [141, 142].

LIBs contain electrolyte and separator components which work closely together to facilitate efficient ion transport while simultaneously protecting against short circuits that could result in battery failure. Electrolytes act to transport lithium ions between electrodes while separators serve as physical barriers that separate cathode and anode electrodes. When selecting an electrolyte type - liquid or solid state - for use, considerations such as performance, safety and cost must be carefully taken into account. Separator materials thickness and porosity have direct ramifications on power density, safety, and overall battery performance, with continued advances in electrolyte and separator technologies becoming ever more essential to optimizing lithium-ion systems for various uses.

3.4 Binders and Battery Types

Batteries are indispensable energy storage devices that power numerous electronic devices, electric vehicles and renewable energy systems. Their performance and efficiency rely heavily on fabrication of electrodes; with polymeric binder molecules playing an essential part in binding active material particles within electrode structures together while aiding electron and ion transport. In this chapter we consider their significance in electrode fabrication while exploring their influence on performance using different battery types as examples.

Binders play an indispensable role in electrode fabrication, providing mechanical integrity by holding active materials, conductive additives and other components together and adhering them securely. Furthermore, binders allow electrodes to form porous structures for efficient diffusion of ions and penetration of electrolytes. Binder materials and their characteristics have an enormous effect on battery performance:

- Capacity: Selecting an effective binder ensures efficient utilization of active material, impacting battery capacity. Select binder with wetting properties and low viscosities that facilitate electrolyte infiltration to maximize contact between active material particles and electrolyte molecules; this increases capacity and energy density while simultaneously increasing capacity.
- Cycling Stability: Binder materials play an essential role in maintaining mechanical stability during charge-discharge cycles, with strong adhesion between electrode components and flexible binder materials helping prevent cracks, delamination and loss of electrical contact, thus increasing cycling stability of batteries to maintain sustained capacity over time.
- Rate Capability: Battery conductivity and compatibility have a dramatic impact on its rate capability, which ultimately determines its ability to deliver power efficiently. High-performing binders with excellent conductivity allow fast charge transfer and ion transport, giving batteries superior power capacity.
- Binder Degradation: Battery binder materials may undergo chemical and electrochemical degradation during cycling, adversely impacting battery performance. Degradation products can form insulating layers which impede ion transport and decrease capacity;

materials with excellent chemical stability reduce degradation rates to ensure long-term battery performance.

- Porosity and Electrolyte Uptake: Binders play an essential role in shaping electrode porosity and electrolyte uptake. Binder materials with suitable rheological properties facilitate well-defined porous structures for efficient electrolyte infiltration, leading to enhanced diffusion rates that lead to improved electrochemical performance.

Binder materials like polyvinylidene fluoride (PVDF), polyacrylic acid (PAA), carboxymethyl cellulose (CMC), sodium alginate and styrene-butadiene rubber (SBR) have become essential components in electrode fabrication processes, each offering specific advantages tailored to battery chemistries or applications [135].

Lithium-ion, lead-acid, nickel metal hydride and solid-state batteries all utilize specific electrode configurations and binder materials in order to maximize performance and efficiency. An analysis of binder selection's effect on performance across these battery types illustrates its relevance for optimal battery performance and efficiency.

Understanding the roles and effects of binders on electrode fabrication and battery performance allows us to advance battery technologies, optimize energy storage systems for specific uses, and increase overall sustainability in energy use. Extending research and development efforts on binder materials will only advance performance, durability and reliability - thus contributing to creating an energy future that benefits everyone.

3.4.1 Battery types based on cathode material

Lithium-ion (Li-ion) batteries have quickly become popular choice across an array of applications, from portable electronics and electric vehicles to energy storage solutions and solar panel energy harvesting, due to their high energy density and rechargeable nature. Offering various chemistries and geometries depending on each application's individual specifications.

Based on the material of the cathode, LIBs are categorized in the following different types.

Lithium Iron Phosphate ($LiFePO_4$)

Lithium Iron Phosphate (LFP) Batteries, also known as ''lithium Ferrophosphate'', consists of a Lithium Iron Phosphate cathode, that was first introduced in 1996, and a graphitic anode material. This is the most widely used technology nowadays on the battery market and this success is owing to the excellent nontoxic and high stability properties of this cathode composition. The absence of Mercury and Cadmium and the replacement of Nickel and Cobalt with iron and Phosphate renders the LFP chemistry both cheaper and nontoxic in comparison with other types, despite the fact that the electrolytes, organic chemicals and the metals can cause serious environmental problems if not properly handled after the end of life. A LFP cell supply 3.2 nominal voltage allows 98-100% discharge without damaging and can operate in high temperatures without explosion or thermal runaway risk. Furthermore, it is proved that LFP batteries can last 3-5 times more than others (approx. 2.000 cycles lifespan). However, they provide a relatively low specific energy 90 – 120 Wh/Kg, thus being suitable for standard versions of electric vehicles. In general terms, this type of battery provides ''stability'' and ''durability'' even in fully charged mode and that's why is well established in a variety of applications such as in electric vehicles, renewable energy storage systems and power tools [134, 135, 141].

Lithium Manganese Oxide ($LiMn_2O_4$)

Lithium Manganese Oxide (LMO) batteries provide superior power capabilities and offer greater thermal stability, making them suitable for applications requiring high power output. Their nominal voltage per cell stands at 3.7 V for optimal operation. LMO technology uses lithium manganese oxide as the cathode material, for enhanced li ion movement with low resistance, and high current delivery. LMO batteries can be found in power tools, medical devices, electric bikes and other high-power applications. They come in cylindrical, prismatic or pouch geometries for easier installation. Lithium Manganese Oxide (LMO) batteries offer superior specific energy (100 WK/kg – 150Wh/Kg), thermal stability, energy density and safety, at the expense of relative short lifespan (300 – 700 cycles) [135, 141, 144].

Lithium Cobalt Oxide ($LiCoO_2$)

$LiCoO_2$ batteries, commonly referred as LCO or Lithium-Ion Cobalt battery, released in 1991 and are known for their high energy density, making them ideal for portable electronics like smartphones and laptops with their nominal voltage of 3.7V per cell. LCO batteries utilize lithium cobalt oxide as the cathode material, offering lightweight and compact designs, however the low specific energy limits their adoption from high load applications like electric vehicles. Additionally tend to have shorter cycle lives compared to other Li-ion chemistries and are commonly found in cylindrical or pouch geometries. In general terms, Lithium Cobalt Oxide (LCO) batteries offer good cycling performance and specific energy, with a relatively shorter cycle life due to cobalt content safety concerns as well as limited thermal stability in high temperature environments [135, 141, 144].

Lithium Titanium Oxide (Li_2TiO_3)

Lithium Titanium Oxide batteries, more commonly referred as LTO, are distinguished by their exceptional lifespan, fast charging capabilities and wide temperature operating range. With a nominal voltage of 2.4V per cell these cells offer exceptional value. LTO batteries use lithium titanate as the anode material, instead of graphite, providing superior safety performance and being highly resistant to thermal runaway. Even at low temperature charging, considered one of the safest with no danger for platting formation and zero stain properties. LTO batteries are widely utilized in hybrid electric vehicles and energy storage systems requiring high power, long cycle life and robust performance in extreme temperature conditions. LTO batteries often take the form of cylindrical or prismatic geometries. Unfortunately, LTO batteries tend to have lower energy density and higher costs compared to some other types [135, 141].

Lithium Nickel Manganese Cobalt Oxide ($LiNiMnCoO_2$)

NMC cathode formulation is a combination of three major elements Ni, Mn and Co in a specific ratio depending on the requirements of the application. In particular, EV manufactures design different cathode stoichiometries ranging from low Ni content formulations, such as $LiNi_{0.33}Co_{0.33}Mn_{0.33}O_2$, with the name NMC111, to higher Ni excess, $LiNi_{0.6}Co_{0.2}Mn_{0.2}O_2$ named NMC622 and even higher content, $LiNi_{0.8}Co_{0.1}Mn_{0.1}O_2$ named NMC811. Thus, from the aforementioned is obvious that the NMC111 chemistry is composed of 1 part Ni, part Mn and another one of Co, and NMC622 composed of 60% Ni, 20% Mn and 20% Co respectively. The main purpose is to exploit the specific benefits from each element and to restrict the limitations that bring upon. Long range EV manufactures pursue batteries with a lot of Ni content in order to achieve increased specific energy, however Ni suffers from low stability and that's why Mn and Co are employed. Mn has the ability to form a spinel, which entails reduced internal resistance and thermal stability, with the drawback of a consequent specific energy decrease. Therefore, an estimated combination of these two distinct elements can lead to an enhanced structure, with unique properties. On the other side, Cobalt is a rare metal and thus regulates the total battery price, which fluctuates at the same rates with LFP. So NMC is a reasonable competitor of LFP, excepting the longer lifespan of the latter. NMC typical cells provide nominal voltage 3 – 4.2V, 150-220 KWh/Kg specific energy and extended lifespan about 1500 cycles. NMC also feature low self-heating rate and high thermal stability and rightly considered safer overall [134, 141, 144].

Lithium Nickel Cobalt Aluminum Oxide ($LiNi_xCo_yAl_zO_2$)

NCA is a Lithium Nickel Cobalt Aluminum oxide cathode-based battery that investigated in 1999.Similarly to NMC, NCA's technology rely on a combination of three major elements namely Ni, Co and Al in the position of Mn, shaping a representative chemical formula $LiNi_xCo_yAl_zO_2$, whereas x+y+z=1. In this cell structure Ni provides the amount of specific energy while Al is responsible for keeping the formation chemically stable and safe. Thus, NCA and NMC join some related properties, chiefly high specific energy, impressive specific power and descent lifespan. NCA battery cell typically feature cylindrical geometry and provide between 3.6-3.7V. Thus, module composed of numerous cells is able to deliver big amounts of current for extended periods, being suitable for sport EVs like Tesla. Lastly, these batteries ensure high energy density and perform well under high temperatures, offering long driving ranges for electric vehicles and excellent power delivery capabilities. Unfortunately, their shorter cycle life and higher costs due to cobalt use significantly limit their usefulness [135, 145]. A comprehensive comparison of the unique properties of each chemistry is given below in **figure 15**.

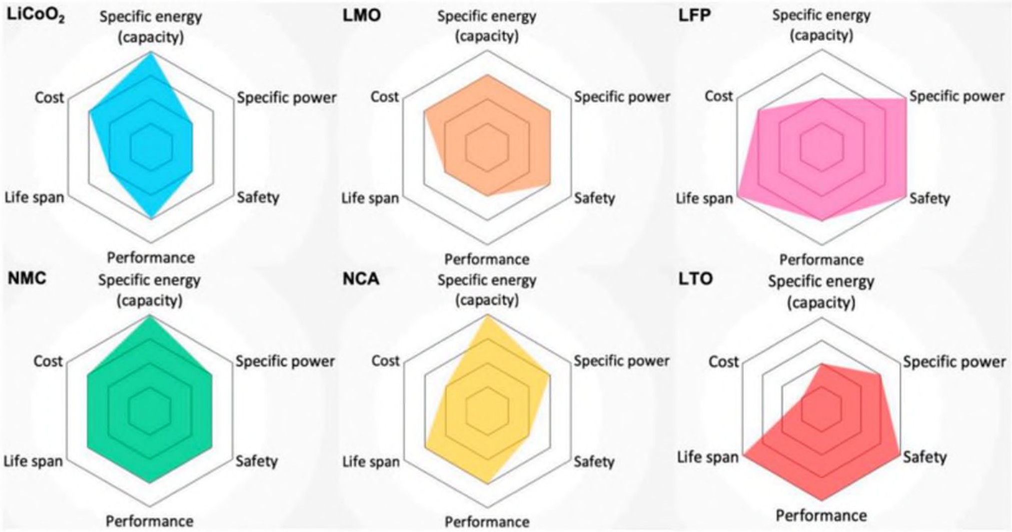


***Figure 15**. Comparison of different types of Li-ion batteries used in EVs from different perspectives [141]*

3.4.2 Battery types based on their shape

Apart from the basic classification of the Li-ion batteries that is based mainly on the cathode material, the shape-form is another important characteristic that classifies the batteries into three more categories. Prismatic, cylindrical and pouch. Each category presents individual properties, advantages and disadvantages, so each manufacturer adopts and develops different cell design accordingly with requirements of each product. So in general terms we cannot assume that is one shape that fits in every purpose.

Cylindrical

Cylindrical cells first released in 1991 by Sony and nowadays are the most popular choice for commercial use. As the name implies, the single repeating unit consists of anode, cathode and separator sheets and electrolyte that are twisted tightly and enclosed into a rigid cylindrical steel case. Their production is usually based on size standardization. 18650 for instance, a rechargeable li-ion battery that delivers 3.6V nominal voltage and up to 3600mAh and its name reveals its actual dimension. The first two digits (18) indicate the diameter millimeters, the next two (65) refer to battery length in millimeters and the last one (0) stands for the cylindrical shape. When bigger amount of energy required (EV), more cylindrical cells are employed in multiple rows to formulate a module. This time the arrestors lying in the opposite side and rigid spacers or spacer strips or special mounting brackets are used to join the cells each other and to deliver the total energy voltage. Despite the fact that cylindrical cells can reach lower gravimetric energy rates than prismatic ones, it is proved that they can deliver more power at once and thus ideal for high performance applications. The cylindrical cell shape establishes excellent mechanical stability and the best protection against thermal diffusion combined with competitive manufacturing costs due to the low production complexity.

Prismatic

The Prismatic cell jelly roll that contains anode, cathode and separator sheets in a ''sandwich'' form is wound in a rectangular area and compressed to fit in a hard plastic or a metallic housing. This geometry technology introduced in the early 1980, and since now still not exist a universal format. The electrode sheets inside the casing are either stacked if the main purpose is to achieve better performance (more energy at once) or rolled and flattened if more durability is desired.

Prismatic cells deliver approximately 400 – 2000 mAh/cell and they exhibit space utilization and flexible design, that can get even improved at the expense of manufacturing cost. So reasonably a very common application of them is the portable electronics (smartphones, laptops, etc.). They can also be part of the HEV and EV energy storage system. For this purpose, more than one cell is connected together in a single-row or two-row module with the arrestors having the same polarity. In comparison with the cylindrical cells, we notice that prismatic are usually more expensive but able to store more energy load.

Pouch

In 1995, scientists surprised the entire battery world with the pouch cell, an entrepreneurial battery design. Pouch cell comprises conductive foil tabs welded to the electrode and sealed in a heat-sealable laminated multilayer foil or plastic film for protection. This formulation presents a flexible lightweight construction that can be fitted in various shapes and better weight minimization compared to cylindrical and prismatic cells. The positive and negative terminals are located outside of the pouch and a technical cell standardization does not exist. In recent applications the nominal cell capacity may not be sufficient, so more cells can be connected in a row either by adhesive welding or with screws and busbars to create a module. A main drawback that researchers investigated is that during charge – discharge, excess gas generation may lead to battery swelling and bugling. This excess gas generation inside the bag produces a subsequent high-pressure environment that may occur a crack at the film layer or an undesirable external damage if not enough space reserved. In this way, researchers designed a supplementary gas bag that absorbs the redundant gases produced by the first charge – discharge cycle and this bag is cut off in refining process before is available in the market. Thus, considering that a small swelling percentage after long cycles is acceptable, mechanics should allocate extra space, prevent tight modules and create protection against sharp edges.

Each combination of chemistry and geometry offers its own set of distinct advantages that are tailored specifically to particular applications depending on energy density, power output, safety requirements, lifespan span and overall performance. **Figure 16** demonstrates a briefly comparison of fundamental properties between cylindrical, prismatic and pouch cell designs.

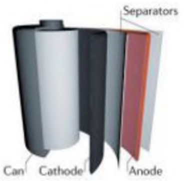
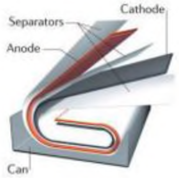
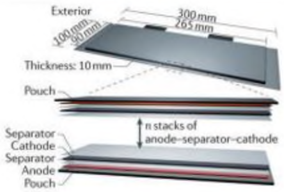
Shape	Cylindrical	Prismatic	Pouch
Diagram			
Electrode Arrangement	Wound	Wound	Stacked
Mechanical Strength	++	+	−
Heat Management	−	+	+
Specific Energy	+	+	++
Energy Density	+	++	+

Figure 16. *Basic properties of cylindrical, prismatic and pouch cell designs [18]*

3.5 Performance Evaluation of Li-Ion Batteries

Lithium-Ion batteries (Lithium-Ion batteries) have long been recognized as an integral energy storage technology, powering everything from smartphones and laptops to electric vehicles and renewable energy systems. Their performance is evaluated based on various metrics including capacity, voltage, energy efficiency and cycle life.

Capacity is a fundamental metric used to assess how much charge a battery can store; usually expressed in ampere-hours or milliampere-hours (mAh). It directly corresponds with how much energy can be provided in one discharge cycle. Higher capacity batteries store more energy, enabling devices to run for extended periods before needing recharged again. Please keep in mind that actual usable capacity may differ based on factors like discharge rate, temperature environment and age of battery used for charging purposes.

Voltage is another crucial metric that measures the electric potential difference between positive and negative terminals of a battery. Li-Ion batteries typically operate between 3.6 to 3.7 volts per cell, though chemistries and designs may cause slight variance. Multiple cells connected in series may achieve higher voltages. It must meet all functional requirements for its device or system before purchase to ensure optimal functioning.

Energy efficiency refers to the ratio between electrical energy output and input during charge and discharge cycles, and various factors affecting it during charge and discharge cycles. Internal resistance, self-discharge rate and the charging/discharging processes all have an effect on Li-Ion batteries' overall energy efficiency, by optimizing this metric it becomes possible to minimize energy losses while providing maximum usable energy at any given input. Maximizing it has direct bearing on overall device or system performance as this metric directly influences runtime efficiency.

Cycle life of Li-Ion batteries measures the number of charge/discharge cycles they can endure before their capacity significantly degrades, such as electric vehicles and renewable energy storage systems. Each charge/discharge cycle involves charging to its maximum capacity before discharging to reduce current and temperature requirements for discharging back to zero. Factors including discharge depth, current consumption during charging/discharging operations, temperature requirements for discharging operations, management practices as well as depth of discharge can all have an effect on its cycle life; longer lasting batteries indicate longer lasting batteries which is especially critical in applications where batteries must regularly charged/discharged such as electric vehicles and renewable energy storage systems, where frequent charge/discharge cycle life is essential to its functionality, such as renewable energy storage applications such as vehicles/storage systems/Batteries that utilize Li-ion technology such as this metric indicates.

Note that Li-Ion batteries' performance metrics are interdependent, with one impacting another. For instance, increasing capacity may decrease cycle life while optimizing energy efficiency requires tradeoffs between capacity and overall capacity. Battery manufacturers and researchers consistently work to improve these metrics so as to meet specific application needs.

Utilizing Li-Ion battery performance metrics helps users make informed decisions when selecting and utilizing these batteries, whether for smartphones, electric vehicles, renewable energy systems or renewable energy solutions. Assessing capacity, voltage, energy efficiency and cycle life helps ensure optimal performance, longevity and overall satisfaction with its performance.

Comparing different battery chemistries and types is vital when making comparisons between them, so here is a formal comparison between several commonly used battery chemistries:

I. Lithium Iron Phosphate ($LiFePO_4$ or LFP):
    - This technology exhibits superior safety and thermal stability
    - Exhibiting long cycle life that can withstand thousands of charge/discharge cycles.
    - Offering lower energy density when compared with other chemistries

- Ideal for applications that prioritize high power output and reliability, such as electric vehicles and renewable energy systems.

II. Lithium Manganese Oxide ($LiMn_2O_4$ or LMO) offers superior thermal stability and safety characteristics, along with moderate energy density and capacity, making it suitable for power tools, medical devices and consumer electronics applications.

III. Lithium Cobalt Oxide ($LiCoO_2$ or LCO):
   - Exhibiting high energy density and capacity, LiCoO2 has become popular in consumer electronics products due to its energy density and capacity; however, its cycle life and lower thermal stability limits make it unsuitable compared to other chemistries.
   - Primarily utilized in applications requiring high energy density, such as smartphones and laptops.

IV. Lithium Titanate ($Li_4Ti_5O_{12}$, or LTO):
   - Demonstrates an exceptionally long cycle life, capable of withstanding many thousands of cycles
   - Offers excellent high-temperature performance and safety characteristics
   - Features lower energy densities compared to other chemistries, yet excels in applications requiring rapid charging, high power output and wide temperature ranges such as electric buses and grid energy storage

V. Lithium Nickel Manganese Cobalt Oxide (LiNMC or NMC):
   - Achieves an ideal combination of energy density, capacity and cycle life for portable electronics and electric vehicles. Widely utilized.
   - Performance characteristics can be modified through changing ratios of nickel, manganese and cobalt.
   - In comparison with some other chemistries, however, this one incurs higher costs.

VI. Lithium Nickel Cobalt Aluminum Oxide ($LiNiCoAlO_2$ or NCA):
   - This chemical composition exhibits high energy density and capacity. Commonly found in electric vehicles due to its ability to provide high power output, it's often employed with these vehicles due to comparatively higher costs and slightly decreased stability compared to other chemistries.

- Demonstrates acceptable performance regarding energy density and specific power.

Selecting an ideal battery chemistry depends upon the requirements of a particular application. As important considerations when making this selection are energy density, capacity, cycle life, safety features, power capability and cost considerations.

Research and development projects continue to investigate various battery chemistries with the goal of increasing energy density, cycle life, safety and cost-effectiveness across a wide array of applications.

To properly evaluate Li-Ion batteries, various testing and characterization techniques must be utilized. These provide valuable insight into their behavior, performance parameters and overall health - these methods will be described further below.

Capacity testing involves charge-discharge cycling, which involves continuously charging and discharging a battery over time in order to assess any gradual reductions in capacity over time. Coulomb counting measures charge/discharge currents in order to provide a more precise calculation of its capacity.

Voltage and energy testing techniques utilize open circuit voltage (OCV) measurements that offer insight into a battery's state of charge and capacity; energy density measurements provide information on how much energy can be stored per volume/mass; this allows comparison across battery chemistries.

Impedance spectroscopy measures battery impedance at various frequencies to gain insight into its internal resistance, electrode kinetics, electrolyte conductivity and overall performance.

Cycle life testing utilizes full-cycle battery use, wherein repeated charging and discharging cycles until significant capacity loss is observed. Accelerated aging tests involve creating harsher operating environments by increasing temperature or current. They aim to accurately gauge an expected cycle life.

Rate capability testing measures how well a battery performs under various load conditions, using techniques such as pulse and step current testing and C-rate evaluation to assess its ability to supply current in response to different load demands.

Thermal testing assesses how a battery responds to heat and thermal cycling, helping assess its thermal stability and performance under various temperatures conditions.

Aging and calendar life testing seeks to understand a battery's behavior during storage and long-term aging, such as self-discharge rates, capacity retention levels, and degradation patterns over an extended period. This method also takes into account any self-discharge rates, capacity retention rates or degradation patterns observed over such tests.

Safety testing involves abuse testing, where a battery is exposed to extreme conditions like overcharging, over-discharging, short circuiting and mechanical abuse. Environmental testing evaluates its performance under various environmental factors like temperature, humidity and vibration.

Test and characterization techniques offer invaluable data for evaluating Li-Ion battery performance, reliability, and safety aspects. This data provides essential insight for optimizing battery designs, optimizing energy storage systems, and assuring safe operations of devices or applications that rely on Li-Ion technology.

3.6 Future Prospects and Challenges

Li-Ion battery technology has seen remarkable advances, with numerous innovations that indicate its promising future. Recent advancements include those designed to increase performance, safety and energy density of Li-Ion cells, opening new possibilities in applications.

One key area of research aims at increasing the energy density of Li-Ion batteries. By expanding energy storage capacities, this could extend run times for portable electronics, electric vehicles (EV) and renewable energy storage systems, such as those found on renewable power farms. Researchers are exploring novel electrode materials like silicon anodes, which have higher specific capacities compared to traditional graphite anodes. solid state electrolytes may lead to safer Li-Ion batteries with increased energy density.

Fast-charging technology has long been of keen interest. Li-Ion battery charging times can often become the source of great frustration among drivers. Researchers are working towards fast-charging solutions, which could significantly shorten charging time, while not negatively affecting battery lifespan or safety, something which would revolutionize EV ownership, making EVs more accessible than ever before.

Flexible Li-Ion batteries are currently being developed rapidly to allow direct integration of power storage directly into clothing, smartwatches, medical devices and other wearable technologies. Furthermore, flexible Li-Ion batteries may even be utilized in flexible displays or foldable electronics to enable innovative designs with flexible devices [146].

Safety research of Li-Ion batteries is also of great significance. Although Li-Ion batteries have made great strides forward when it comes to safety, incidents involving thermal runaway and fire still occasionally arise despite advances. Therefore, researchers are investigating advanced materials and designs which further bolster Li-Ion battery safety, including self-healing materials, solid state electrolytes and advanced thermal management systems to prevent thermal runaway.

Lithium-Ion batteries offer many exciting opportunities in future applications and prospects, playing an essential part in increasing renewable energy sources, such as solar and wind power. Large-scale Li-Ion energy storage systems can efficiently store excess power generated during periods of peak production before releasing it when demand spikes, thus ensuring grid stability while optimizing renewable energy utilization.

Li-Ion batteries will continue to play an essential role in powering the fast-growing market for electric vehicles (EVs), offering longer driving range, quicker charging rates and overall improved performance. As adoption for these EVs grows, so does demand for advanced Li-Ion battery technologies.

Li-Ion batteries could find applications in aerospace as power source for unmanned aerial vehicles (UAVs) and electric aircraft, providing extended flight times while decreasing fossil fuel dependency. Their high energy density and lightweight properties make Li-Ion ideal for aviation use, providing extended flight duration while decreasing fossil fuel dependence.

Solid-state Li-Ion batteries

Solid-state Li-Ion batteries have become one of the most exciting prospects within the batterie sector, offering revolutionary changes from conventional lithium-ion batteries (LIBs). Their main difference lies in how ions transport across their respective electrolytes. In typical LIBs Li^+ ions migrate through a liquid electrolyte between the electrodes, while in solid-state Li-Ions solid electrolytes are utilized as shown in **Figure 17**. This innovative approach opens new avenues for improved battery technology development.

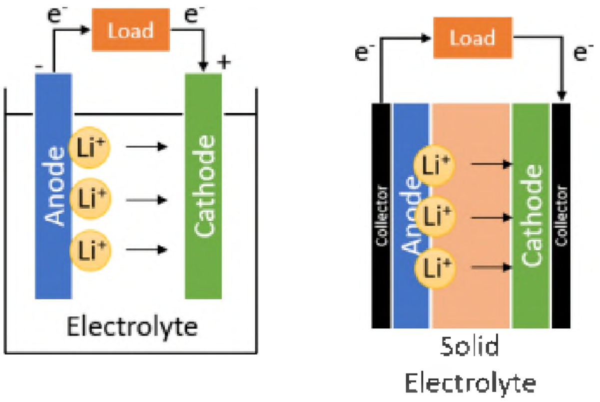


***Figure 17**. Schematic illustration of ion and electron transport of LIB and SSB [147]*

Solid-state Li-Ion batteries utilize the principle of lithium-ion diffusion across solid electrolytes, offering numerous advantages over their liquid electrolyte counterparts. Their revolutionary design eliminates flammable liquid electrolytes altogether, significantly improving safety standards, while offering higher energy density, extended lifespan, and improved thermal stability compared to their liquid electrolyte LIBs.

But switching from liquid electrolytes to solid poses difficulties, that need to surpass. Optimizing their ionic conductivity to match that of liquid ones, requires research efforts in developing solid electrolytes with elevated conductivity levels, that allow lithium ions to move smoothly around battery structures [147].

An equally intimidating challenge lies in managing the interface between solid electrolyte materials and electrode materials, a vital aspect of battery performance, efficiency and longevity. While traditional liquid-ion batteries (LIBs) feature seamless interaction between liquid electrolytes and their respective electrodes, solid-state batteries require careful engineering in order to establish and maintain effective electrode-electrolyte contact.

Innovative solutions have been pursued to address these difficulties. Solid oxide electrolytes such as NASICON-type, perovskite-type, garnet-type, γ-Li_3PO4 type and amorphous/glass type solid oxide electrolytes exhibit excellent chemical stability. Solid sulfide electrolytes also have shown promise due to their excellent ionic conduction capabilities, but due to chemical instability issues in air they must be handled under inert gas atmosphere conditions for safe handling.

Solid polymer electrolytes offer many advantages in terms of processability, flexibility, safety and intimate contact with electrodes. One such solid polymer electrolyte developed through radical copolymerization is known as Single Lithium-ion SLIC-SPEs electrolyte. It's conductivity measures prove it's worth alongside mechanical strength, thermal stability and wide electrochemical stability.

Lithium-Sulfur (Li-S) batteries

Lithium-Sulfur (Li-S) batteries have become one of the most compelling contenders in advanced battery technologies, offering promise to transform energy storage due to their outstanding theoretical energy density. Utilizing sulfur as the cathode material, one of the highest theoretical capacities among solid elements, measuring an impressive 1675 mAh*g^{-1} capacity, they offer greater storage capacity while being both cost-efficient and eco-friendly than their lithium counterparts (Li-Ion batteries).

Design of Li-S batteries involves creating a positive electrode comprised of an electronically conducting host that facilitates electron movement towards sulfur, one of the core elements that sets these batteries apart from others. At discharge time, lithium ions from the negative electrode migrate through electrolytes to combine electrons from lithium-ion sources in the electrolyte to reduce sulfur to Li_2S--thus contributing to theoretical energy densities of either 2,500 Wh*kg^{-1} or 2,800 Wh*L^{-1} depending on weight or volume considerations respectively. **Figure 18 a**) and **b**) demonstrate schematically the structure of a lithium sulfur cell as well as the charge and discharge mechanism.

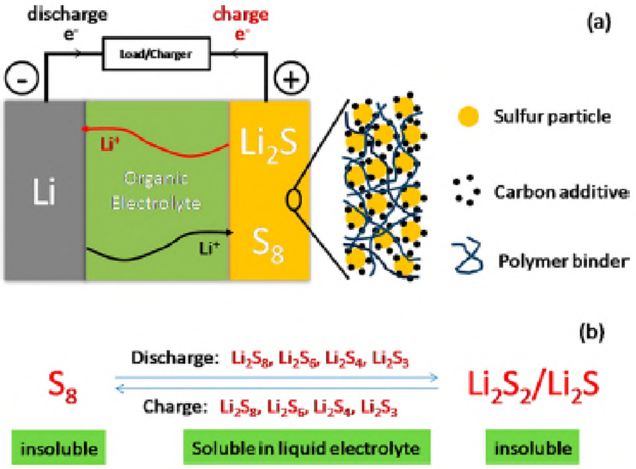


Figure 18. ***a****) Illustration of the charge (red)/discharge (black) process involved in a rechargeable LiS cell consisting of lithium metal anode, organic electrolyte, and sulfur composite cathode and* ***b****) charge/ discharge process involving the formation of soluble lithium polysulfides (Li_2S_8, Li_2S_6, Li2S$_4$, and Li_2S_3) and insoluble Li_2S_2/Li_2S [148]*

Li-S batteries' primary advantage lies in their potential to deliver unparalleled energy density, coupled with lower costs. Li-S batteries' theoretical energy density of between 400 to 600 $Wh*kg^{-1}$ is substantially higher than conventional Li-Ion batteries and opens the way to accomplishing goals such as 500 km driving range targets [148-151]. However, practical implementation of Li-S batteries does present numerous obstacles and hurdles to their adoption. The most important challenge remains the shuttle effect during the dissolution of polysulfide in organic liquid electrolyte. This phenomenon actuates among the electrodes a forward and backwards diffusion of the polysulfides that lead to poor cycling stability and anode corrosion. Another drawback is the lacking conductivity of S ($5x10^{-30}S/cm$) at $25^{o}C$, that consequently affects the reaction implementation of the active material. Furthermore, sulfurs cause about 80% expansion during Li_2S formation, posing serious destruction risk.

For this reason, recent advancements are based on the implementation of porous carbon as S hosts. That feature qualifying electrical conductivity. Their innovations aim at increasing Li-S battery stability and cycling performance for eventual incorporation in commercial products. However, concerns about the complex production process, high cost and low efficiency still exist. Various experiments proved that metal oxides, metal sulfides and metal nitrides can deal with the shuttle effect and offer satisfying cycle capacity. Metal oxides, such as TiS_2 were investigated as cathode materials and provided promising properties. Between metal nitrides (TiN, CrN, VN, ZrN, NbN) Vanadium Nitride offers $1,17x10^{6}$ S/m electrical conductivity, great catalytic properties and chemical accumulation strength for the polysulfides. In a recent work VN nanoribbon/Graphene (VN/G) cathode, demonstrated $1,461mAhg^{-1}$ specific capacity at 0.2C and almost 100% efficiency. Shengyu Jin and his coworkers synthesized a novel CoFe@NC/PPC chemistry, employing as raw materials Prussian blue analogues and biomass. This composition after injected with sulfur resulted in $447,4mAhg^{-1}$ after 500 cycles and the efficiency estimated 97,3%.

Li-S battery research has made significant strides forward. however, persistent challenges such as reduced practical specific energy, capacity decay during cycling and self-discharge rates continue to prevent their commercialization. Yet Li-S' inherent advantages - low cost, wide temperature range compatibility and potential long cycling lifecycles - continue to motivate innovation.

Lithium-air batteries

Lithium-air batteries have emerged as a promising frontier of energy storage technology, boasting the highest theoretical energy density of any type. Their innovative approach employs atmospheric oxygen as cathode material for ultrahigh energy densities - sparking interest among battery enthusiasts as they promise revolutionizing this sector. Unfortunately, Li-air batteries do present many obstacles which need to be surmounted in order to realize their full potential.

One of the primary challenges presented by Li-air batteries is the slowness of oxygen reduction and evolution reactions, which are essential to their operation. Furthermore, side reactions accumulate quickly, which compromise their reversibility and overall efficiency. To combat these obstacles effectively requires developing advanced catalysts, stable electrolytes, and compatible electrode materials that can boost performance and reliability of Li-air batteries [152-154].

An especially intriguing area in this realm is lithium-air batteries, commonly referred to as lithium/oxygen batteries (Li/O_2). They belong to the family of metal/air devices. Typically, the core components of a battery cell include an Li-metal anode, porous carbon cathode and electrolyte with dissolved lithium salt. During discharge of this cell, Li^+ ions and electrons, that flow through external circuit, produced from the oxidation of Li metal anode. Simultaneously, at the cathode Li^+ ions diffuse, due to an electrochemical potential gradient. The atmosphere oxygen undergoes reduction at the cathode to form lithium peroxide (Li_2O_2) and, eventually, lithium oxide (Li_2O).

Estimating the practical value of Li-air batteries can be challenging due to their complex reaction products during discharge, which make estimating their practical worth difficult. Recent estimates of specific energy values as high as 3582 $Wh*kg^{-1}$ have been proposed for non-aqueous and aqueous electrolytes respectively due to O_2 reduction reactions leading to lithium peroxide and lithium hydroxide formation.

Overcoming challenges related to electrolyte stability, cathode protection against moisture and CO_2, and Li_2O_2 oxidation overpotential reduction remain essential components of Li-air battery performance. Enhancing battery performance through improving electrolyte conductivity and decreasing interfacial contact resistance between components is also vital. Each compartment of Li-air batteries presents its own set of critical hurdles that must be carefully addressed for maximum cyclability and rechargeability.

Li-air battery technology has seen rapid advancement over time. Initial systems using non-aqueous electrolytes were first implemented in 1996 with Li-metal anodes and air cathodes as its core elements.

Considering that the cathode is the most functional component of the cell, where the electrochemical reaction of Li^+, e^- and O_2^- take place and thus the position where the discharge products accumulate, it is vital to design cathodes able both to carry sufficiently the products and simultaneously to enhance Li^+, e^- and O_2^- transfer. After extensive analysis researchers evidenced that a sufficient LiO_2 cathode must fulfill with high conductivity and optimizing channel design for smooth electrolyte and O_2 supply. Additionally, it is proved that a sufficient microporous-mesoporous hierarchically structure reveals active sites, whereas binder's absence avoids side reactions and establishes easier production. Shengyu Jing and his co-researchers demonstrated a three-dimensional cathode co-doped with Co and N derived from wood in molten salt medium and this positive electrode achieved satisfying specific capacity 9,44mAhcm^{-2} and high cycle stability 113 times working in low 0.5mAhcm^{-2} capacity. Huagen Liang and collaborators exploited the properties of Se (selenium) element and developed a 3D self-supported Co-CoSe@NSeC/bioC cathode. After evolution of Co-metal on biomass and a selenization process using Se powder to produce Co/CoSe, N and S doped into the carbon basis and N-C and Se-C bonds formatted. This conformation revealed high kinetic speeds, fast e^- transfer and high specific capacity 9.1 mAhcm^{-2} [155-162].

Zinc-air (Zn-air) batteries

Zinc-air (Zn-air) batteries stand as an enduring symbol of hope in today's ever-evolving energy storage landscape, providing superior safety, high energy density and affordability to be considered among leading contenders for next generation battery technology. Renowned for these qualities as well as for meeting other challenges associated with increasing energy storage capacities by being safer than its competition, they hold great promise as future energy storage solutions.

With an energy density of 1,218 Wh kg^{-1}, Zn-air batteries exhibit impressive energy density levels that indicate their potential to enable enhanced performance across many applications. Yet its significance goes far beyond energy metrics: its safety and cost-effectiveness make them attractive options for powering emerging energy-intensive technologies.

But, like any innovative technology, Zn-air batteries still present hurdles that must be surmounted for widespread adoption. At present, alkaline electrolytes dominate zinc-based batteries due to their balance between cost and ionic conductivity. Unfortunately, environmental conditions like CO_2 emissions or humidity poses risks that threaten their stability as an electrolyte solution. Zn-air batteries that rely on air electrode performance can become vulnerable to CO_2-induced K_2CO_3 production, impairing its integrity. Furthermore, batteries must contend with issues of electrolyte evaporation and water absorption from outside sources requiring innovative solutions in order to operate reliably under all environmental conditions [163].

An avenue of possible relief lies in using room temperature ionic liquids (RTILs) and solid electrolytes as potential solutions to electrolyte-related challenges, although their effectiveness has been severely hindered due to limitations related to conductivity and interface compatibility issues.

Electrolytes play an essential part in developing Zn-air batteries. Alkaline electrolytes such as LiOH, NaOH and KOH stand out as suitable candidates due to their compatibility with zinc electrodes and catalyst materials. KOH in particular is remarkable due to its superior ionic conductivity properties and reduced viscosity - two advantages which contribute significantly towards its success here.

Zn-air batteries utilize complex electrochemical reactions for operation. At discharge time, external oxygen interacts through an oxygen reduction reaction (ORR) at the gas-liquid-solid interface to facilitate transfer of electrons from zinc electrode to air electrode via external load. Simultaneously the produced OH^- generate $Zn(OH)_4^{2-}$ that breaks down further to ZnO. Meanwhile during charging it acts in reverse producing energy storage and zinc deposition through the oxygen evolution reaction (OER) [164].

$$O_2 + 2H_2O + 4e^- \rightleftharpoons 4OH^- \qquad E = 0.4V\ vs.SHE \tag{3.1}$$

$$Zn + 4OH^- \rightleftharpoons Zn(OH)_4^{2-} + 2e^- \qquad E = 1.26V\ vs.SHE \tag{3.2}$$

$$Zn(OH)_4^{2-} \rightleftharpoons ZnO + H_2O + 2OH^- \tag{3.3}$$

$$Zn + 2OH^- \rightleftharpoons ZnO + H_2O + 2e^- \qquad E = 1.26V\ vs.SHE \tag{3.4}$$

Zn-air batteries' economic viability enhances their appeal. Constructed using cost-effective materials like zinc, potassium hydroxide, carbon and manganese – zinc correspond to aa low production cost, even lower than that of the cheap lead acid batteries. Additionally, their abundant supply could mitigate concerns regarding resource limitations due to widespread adoption, considering that Zn is about 300 times more abundant than Li. Zn-air batteries also provide environmental friendliness. Their water content, absence of toxic or flammable substances and recyclable zinc components all align with sustainability goals, bolstering their eco-friendliness further.

Precious Pt, Pu and Ir are well known and widely explored catalysts to exceed the sluggish reaction kinetics. However, due to their restricted natural derivation, huge attention turned into the exploration of transition metal sulfides and phosphates, that enhance OER process. Furthermore, suitable for ORR activity are transition metal iron nitrogen-carbon (Fe-Ni-C) catalysts, but the generation of hydrogen and oxygen radicals byproducts and the Fenton reaction Fe may degrade the cell, affecting it's chemical composition and the total durability. Understanding these principles, in a recent experiment, a novel catalyst via Co_9S_8 encapsulation in N, S co-doped carbon matrix (Co_9S_8@N, S-C) developed as a result of the combination of metal sulfides and graphitized carbon, doped with heterogenous atom materials. This composition provides exceptional ORR and OER action, increased stability,259mWcm^{-2} power density and 862mAhg$_{Zn}^{-1}$ specific capacity. Ying Li and his co-researchers investigated the doping of Cu, N and P inside bimetallic transition oxides $C_{0.4}Mn_{0.6}O_2$ two-dimensional nanosheets achieving great ORR performance [26, 165-167].

However, the journey toward perfection is never without challenges and obstacles. Zn-air batteries face obstacles in terms of charging stability as well as dendrite formation on zinc electrodes; though formidable these obstacles highlight ongoing efforts to refine and optimize this technology. Researchers working to develop emerging battery technologies strive to overcome challenges and unlock their full potential. Li-Ion researchers explore advanced solid electrolytes, electrode architectures, interfacial engineering techniques, sulfur host materials, electrode structures and novel electrolyte formulations; Li-S batteries require investigation of sulfur host materials as well as novel electrolyte formulations while Li-Air researchers focus on catalysts, stable electrolytes and electrode materials using advanced characterization techniques in order to gain insights into degradation mechanisms while developing targeted solutions tailored specifically for each battery type.

Li-Ion battery technologies present great promise for the future, with impressive advancements in energy density, fast charging capability, flexibility and safety. These revolutionary technologies hold great promise of revolutionizing multiple industries, from electronics and transportation to renewable energy and beyond. Research and development will further expand Li-Ion battery use as part of daily life and the foundation for an electric future. Research in these emerging battery technologies holds the key to overcoming challenges and unlocking their full potential while addressing limitations, creating safer energy storage solutions with higher energy density and longer shelf lives, essential for many applications.

CHAPTER 4

4.1 Introduction to Battery Recycling

Lithium-ion batteries (LIBs), widely used in electric vehicles (EVs) and electronic industries, has led to an urgent global need for sustainable and efficient battery recycling technologies. As is seen from the chart in **figure 19a** the global market demand for energy is predicted to exceed 1.500 Gwatt/hour by 2030. At the same time a consequent explosion on the Li-ion battery production is anticipated given the global lithium demand forecast from the **figure 19b**, which is expected to outreach 400.000 tons of lithium carbonate equivalent by 2025 [168, 169]. Therefore, this huge battery volume necessitates mature handling when these devices reach the end of their life. As our planet attempts to address waste management issues, LIB recycling has emerged as an integral solution in meeting environmental concerns while mitigating resource scarcity issues. However, so far only a negligible number of spent batteries end up to recycling companies. Just in Europe by the years 2013 - 2014 from the 65.500 tons of produced LIBs only 1.900 tons were recycled which corresponds to 2.9% rate. In this chapter, we explore both its importance and benefits while discussing urgent global requirements for novel recycling technologies.

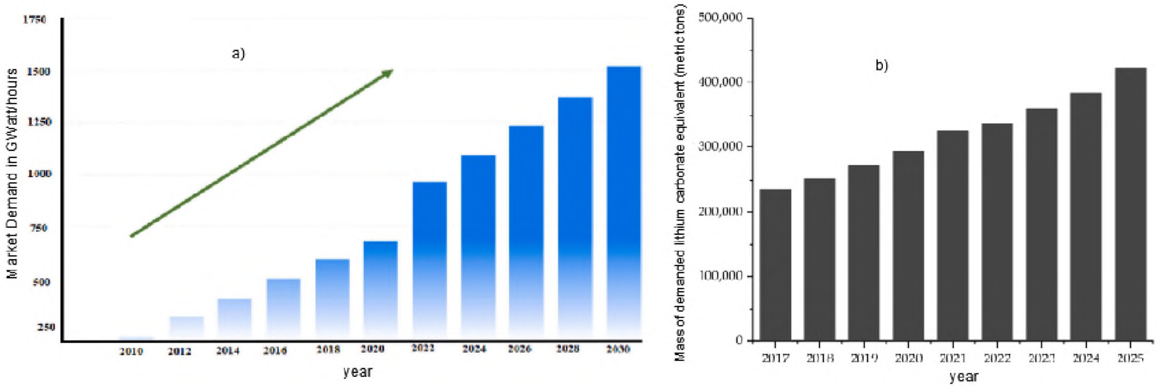


***Figure 19**. **a)** Libs market demand growth estimation [168] and **b)** lithium total demand projection from 2017 to 2025 [169]*

One of the primary goals of an LIB recycling process should be the recovery of high-grade products. Recyclers should strive to recover battery critical raw materials (CRMs) with battery grade quality in order to create a "closed loop" recycling approach and avoid downcycling which refers to recovering low-quality materials meant for construction, metallurgy or pigment production. By recovering battery-grade materials through recycling processes, recycling can contribute towards circular economy by prolonging and protecting these valuable resources for use elsewhere. The circular economy principle is aiming to extend the material's life-cycle in contrast with the moderate linear economic model in which the products end up as waste after their use leading to material downcycling. As is depicted in **figure 20** the natural trajectory of the materials used in LIB industry is to introduce the loop from the point 1 at their virgin form and to end up as waste in point 7 at the end of their life. In order to re-introduce these materials in the chain and to create a ''closed-loop'' model, four recovery processes, reuse, refurbish and later recycle are employed providing different recovery capabilities each time. As further from the point 7 (waste disposal and management) the materials are re-introduced, the more resource-recovery efficient the applied method will be. Recycle in elements and compounds represent the most preferable and efficient method according to this model. However, the market trends define economic and technological criteria and thus the selection of a suitable recovery path [170, 171].

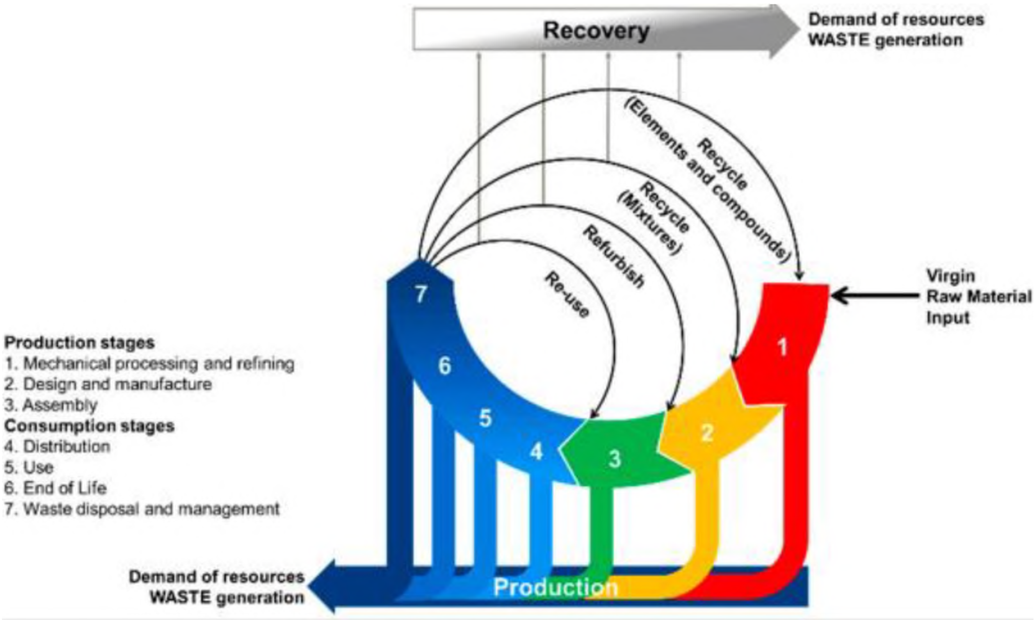


***Figure 20**. Circular economy model for battery material management [171]*

An important consideration in battery recycling is the competitiveness of collection and recycling costs. Market prices for recycled products must cover expenses associated with collecting, transporting, storing, processing and disposing spent LIBs in an economical manner. Additionally, recyclers should aim to achieve an acceptable return on investment that makes recycled product prices comparable with raw material costs. This economic viability will encourage adoption of battery recycling as a practice and promote self-sustaining recycling industries.

Battery recycling plays an integral role in mitigating the environmental footprint associated with LIBs disposal. Traditional practices such as landfilling can have detrimental environmental impacts due to resource depletion and the release of hazardous substances into our ecosystems. LIB recycling provides an effective solution by minimizing mining and refining needs as well as preventing battery waste accumulation in landfills. However, it should be remembered that LIB recycling processes produce water contaminants and require energy compared to primary production. Nevertheless, their environmental impacts tend to be lower. Therefore, comprehensive environmental impact analyses must be carried out in order to assess their sustainability and optimize efficiency [134].

Current LIB recycling ratios remain dismally low due to numerous limitations associated with existing recycling technologies. These shortcomings include lack of mature LIB recycling technologies, environmentally unfriendly processes, production of extensive liquid and toxic waste by-products, medium to low grade recovered products from existing processes, complex processing and purification steps required, low lithium and cobalt recovery rates as well as considerable resource consumption by recycling processes. As such, there is an urgent global need for novel LIB recycling technologies which address these limitations and enhance recycling efficiency.

Circular LIB recycling has multiple environmental and resource conservation advantages. Furthermore, its global necessity makes sustainable LIB recycling even more imperative. Due to their hazardous properties and associated fire and explosion risks, stockpiling, landfilling or exporting LIBs are no longer viable solutions. LIB constituent materials are of economic value and there is a shortage of them worldwide, many from conflict zones, so secondary resource recycling through LIB recycling becomes essential to meeting domestic supply chains in most countries. Hydrometallurgical LIB recycling not only supports electrification efforts but also contributes to reduced greenhouse gas emissions and material recovery rates that are reasonable. Recycling has become mandatory in many countries to follow circular economic principles and ensure a more sustainable future [142].

Once the importance of battery recycling has been highlighted, it is also imperative that we consider its environmental ramifications and any negative environmental impacts arising from improper disposal practices and recycling efforts. Improper battery disposal poses significant environmental and health risks. When lithium-ion batteries (LIBs) are dumped into landfills, they may release toxic substances into the environment that are hazardous to both people and wildlife. LIBs contain heavy metals, conductive salts with fluoride, organic solvents, which leach into soil, water, plants, food chains and human health, potentially having adverse impacts both locally and on human health [172]. Stacked LIBs in landfills may lead to mechanical abuse, leading to short circuiting and exothermal reactions which, if left with remaining energy, could result in fire or explosion. Furthermore, fluoride compounds decomposed in moisture-laden environments may release harmful gasses like hydrogen fluoride into the atmosphere resulting in fire or explosion of LIBs stacked together - further increasing risks [173-175].

Proper battery recycling and disposal can reduce these risks significantly. Recycling allows for the recovery of valuable materials while simultaneously limiting environmental contamination. By employing effective recycling processes, industries can minimize toxic substance releases, fire/explosion hazards and ensure responsible disposal of battery waste.

Battery production involves extracting raw materials like lithium from ore or brine deposits, leading to significant environmental impacts. Brine extraction necessitates drilling and pumping mineral-rich solutions into water tables for processing; in regions like Chile's where lithium production is highly concentrated, mining activities consume a significant portion of local water supplies, harming farmers locally as well as necessitating importation from elsewhere [145].

Primary production of lithium from raw materials requires vast quantities of water; an estimated 1,900 tons are necessary to extract one ton via evaporation, while secondary production using battery recycling would only require 28 tons of used LIBs. So increasing recovery of usable materials from end-of-life LIBs will significantly lessen their environmental impact compared to primary production.

Recycling batteries is key not only to minimizing environmental impacts but also to address ethical concerns associated with the materials supply chain. The natural deposits of raw materials are uneven distributed around the world. Australia produces the highest percentage of Li from spodumene, while Chile the highest percentage from Brine, controlling together more than 70% of global Li production as is shown in **figure 21a** and **b** [142].

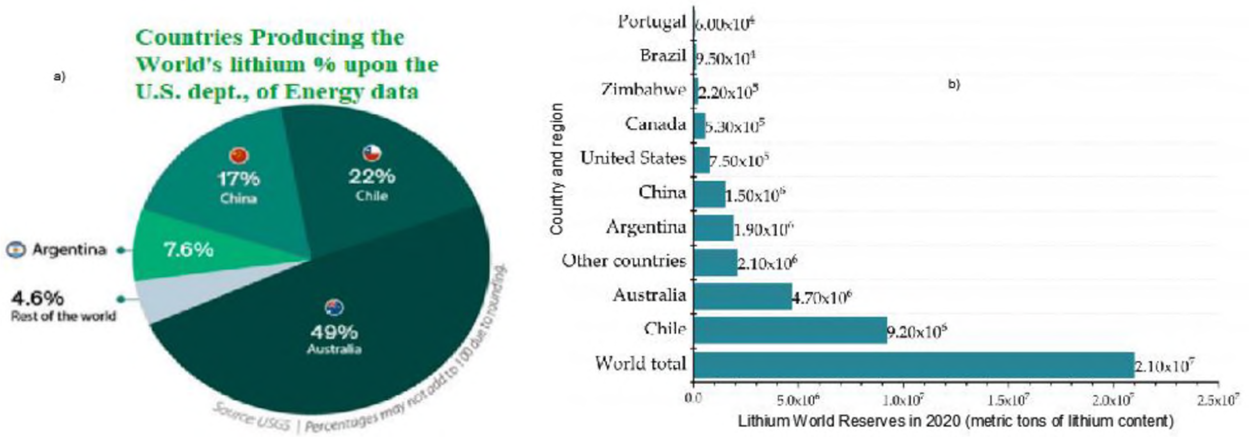


***Figure 21**. **a)** Lithium production distribution around the world [166] and **b)** lithium world reserves in 2020 [169]*

While initial concerns were initially directed toward lithium reserves, recent events in political instability-prone regions like the Democratic Republic of the Congo has brought cobalt reserves into greater focus, accounting for more than 50% of global production [89]. In 2019 the demand for Co was about 19 kilotons, for Mn 22 kilotons and for Li 17 kilotons according to data analysis and ten times increase is expected by 2030 [176]. China on the other hand is responsible for the 70% of the graphite production. Their mining has raised social, ethical, and environmental issues, including child labor in artisanal mines. By encouraging recycling LIBs the industry can address ethical concerns as well as decrease burdens faced by vulnerable communities [135].

Improper disposal of LIBs to landfills creates various environmental concerns. LIB batteries contain toxic heavy metals, conductive salts and organic solvents which release toxic substances when exposed to the environment, including leaching of copper, cobalt and nickel into local ecosystems and human health. Furthermore, stacking LIBs may lead to mechanical abuse that causes short circuiting that leads to fire or explosion hazards in addition to decomposing components at high temperatures releasing harmful gasses like hydrogen fluoride that present further health hazards [139].

Recycling battery processes has environmental ramifications. Pyrometallurgical and hydrometallurgical methods consume both energy and chemicals, leading to detrimental environmental impacts. Methane emissions from reagent production contribute to net environmental burdens from ozone depletion during certain recycling methods; hydrometallurgical recycling may still create environmental burdens through usage of citric acid and manganese sources, however [177].

Battery recycling offers significant potential environmental benefits. By recovering valuable metals and materials from spent LIBs, recycling reduces mining activity, conserves resources, and lessens dependence on other countries for battery supplies. Unfortunately, battery recycling remains challenging to achieve efficiently and sustainably due to issues related to disassembling batteries, treating wastewater generated during recycling processes, as well as conducting research into more environmentally friendly techniques.

For this reason, the European Council proposed the Directive 2006/66/EC for batteries and accumulators, aiming at climatic neutral economy, liable management of both waste and new batteries and smooth functional internal market. According to this directive, Member States obligated to reduce the percentage of hazardous materials into the batteries, limiting Hg 0.0005% by weight and 0.002% Cd by weight. Furthermore, determine as producer responsibility the waste battery selection, with no taxes for the consumers, while specific selection target required, in addition with recycling efficiency targets, to ensure high material recovery. Lastly, comprehensive battery labelling in accordance with standard specification, is a new prohibition for the producers [178].

Another very important factor for the production and recycling of batteries is the costs that these processes require. Recent research revealed a LIB price decrease between 668 $/KWh in 2013 to 137 $/KWh in 2020, and three possible scenarios exist according to experts. The first one foresees, due to deficient raw material supply an overcoming price stabilization. The second one, also envisions a disruption to price decrease but without a raw material supply risk. The third one, expects farther price decrease due to new battery chemistry innovations. Furthermore, experts predicted a Li – ion battery price threshold below 100 $/KWh before 2030 [179].

Transportation cost is another regulator factor that affects the total price assessment of the recycling process. This cost fluctuates from 1,66 $/Kg in European Union to 5,51 $/kg in the United States [180].

From this analysis, it becomes evident that improper battery disposal and lack of recycling processes contributes to environmental degradation, water depletion, toxic substance release, and depletion of valuable resources. Promoting recycling efforts is vital to minimize environmental and ethical impacts associated with battery production as well as ensure sustainable development in the battery industry.

Several research projects aiming the sustainable waste battery management are under investigation with 3R concept being the most attractive model. This concept stands for Remanufacture or redesign, reuse and recycle in the specific hierarchical sequence in order to achieve the minimum valuable material loss and their maximum exploitation before disposal. The scheme in **figure 22** reveals that this principle also conforms with the 4H strategy which means high efficiency, high economic return, high environmental benefit and high safety providing a sustainable future for the material management. More extensive analysis is achieved on the following sections.

***Figure 22**. 4H strategy for LIBs [168]*

4.2 Remanufacture

There is much discussion over what constitutes an "acceptable level" of environmental impacts. Matsumoto and Ijomah (2013) define remanufacturing as the process of returning an already used product to at least its Original Equipment Manufacturers (OEM) performance specifications from customers' standpoint, while providing comparable warranties as newly manufactured counterparts. This approach is considered the most cost- and eco-efficient method for recovering end of life (EoL) products (Ng and Song 2015). Remanufacturing fits seamlessly within the principles of circular economy (CE), with environmental protection as its central goal and economic benefits for businesses as its result. Utilizing recycled components, remanufacturing reduces raw material needs, manufacturing costs and energy consumption thus decreasing overall environmental impacts [174].

Disassembly is an integral step in recovering EoL products for reuse or recycling, yet can often be expensive. Thus, making this research area vital to successful remanufacturing. There have been various methodologies proposed to facilitate the disassembly process for Waste Electrical and Electronic Equipment (WEEE). Traditional disassembly literature focused on complete disassembly, however, with recent economic benefits associated with partial disassembly approaches becoming apparent and unnecessary complete disassembly often being bypassed. Partial disassembly approaches becoming more and more attractive [175].

Remanufacturing electric vehicle (EV) batteries entails refurbishing them for their original automotive applications while adhering to OEM-specified requirements for power, energy, cycle life and other parameters. According to USABC estimates, batteries generally become unsuitable for EV use if their delivered capacity or power falls below 80% of original rating value; in such instances remanufacturing involves replacing inferior cells or modules within battery packs before returning the remanufactured units for use in EVs.

Foster's cost-benefit analysis indicates that battery remanufacturing has already shown itself to be successful within the industry, saving up to 40% compared to buying brand new batteries (Foster 2020). Spiers New Technologies (SNT) and Global Battery Solutions (formerly Sybesma's Electronics) both provide comprehensive repair, remanufacturing, repurposing, and recycling services for vehicle OEMs. SNT conducts comprehensive evaluations to diagnose and sort EoL vehicle battery packs before either remanufacturing them back to OEM specifications or repurposing them for alternative uses. Meanwhile, Global Battery Solutions, with decades of experience repairing electronics, now also specializes in LIB repair for xEVs with LIB remanufacturing services that significantly lower replacement costs.

Remanufacturing batteries has gained momentum as an environmentally friendly solution to an increase in EoL vehicle LIBs. Through refurbishing these batteries, valuable resources are conserved while costs are cut down, and environmental impacts decreased. Remanufacturing represents an opportunity to extend lifespan of existing batteries while contributing towards more eco-friendly future [181].

Remanufacturing batteries involves more than simply disassembling and refurbishing; it also involves the replacement of damaged components and repair of defects to extend their useful lives. This approach allows for optimization of resources while simultaneously decreasing waste during battery lifespans.

Remanufacturing involves replacing any cells or modules within a battery pack which are failing to perform, with either new or refurbished ones. By replacing only those cells or modules identified as defective, overall functionality and performance of the pack may be restored without having to dispose of all its contents at once - saving both costs and minimizing environmental impacts associated with manufacturing new batteries.

Battery remanufacturing also involves the repair of defects. Defects like damaged circuitry, poor connections or degraded thermal management systems can reduce performance or safety concerns and require repair to meet OEM specifications. Remanufacturers perform extensive diagnostic evaluations to identify and address these defects effectively so as to extend battery lifespan while increasing reliability - perfect for continued use in electric vehicles (EVs) or other applications.

Remanufacturing revitalizes batteries that would have otherwise been considered unusable or prematurely disposed. By replacing components and rectifying defects, remanufacturing maximizes value extracted from each battery while simultaneously decreasing new production demand and environmental impacts incurred from extraction of raw materials and energy-intensive manufacturing processes.

Remanufacturing extends the useful life of batteries through cost savings compared to new battery purchases, making EV adoption more accessible to consumers. Furthermore, remanufactured batteries may also be repurposed for other non-car applications resulting in new revenue streams and market opportunities and creating an eco-friendly circular economy.

Remanufacturing processes that include replacing components and correcting defects represent a shift towards more resource-efficient and sustainable battery management practices. Leveraging the expertise of remanufacturers and investing in advanced diagnostic technologies can extend battery lifespan, decreasing environmental impacts and creating a more sustainable energy storage ecosystem.

Remanufacturing batteries entails replacing damaged components and correcting defects to extend their useful life, and maximize value extracted from each battery. Remanufacturers optimize resources, reduce waste, and maximize value extracted from each one - not only does this approach lower costs and lessen environmental impacts but it also contributes to creating a more circular economy by prolonging battery lifespan and supporting their reuse for other applications.

4.3 Repurpose

As electric vehicle (EV) adoption increases so do lithium-ion battery (LIB) end-of-life (EOL) production costs and their end-of-use lifespans (EOULs) to meet rising sustainable energy demands and meet rising costs of production of new LIBs. It is estimated that more than 38.500 LIBs, including 53% Plug-in EV and 47% BEV batteries, could be addressed in second use applications in Europe [182]. Repurposing LIBs offers potential secondary uses such as stationary storage systems or renewable energy integration - in this section we discuss this concept of repurposing LIBs along with potential secondary uses and how these reused batteries may fit into energy storage or renewable energy systems. We explore this idea by exploring its concept, potential secondary applications as well as their integration into energy storage and renewable energy systems [139].

Repurposing LIBs after their initial use in vehicles offers another means of extracting value and prolonging their lifespan. Repurposing LIBs appears most applicable for stationary storage applications, which will be the focus of our cost-benefit analysis. Repurposing involves dismantling individual cells of LIBs before reassembling them in configurations different than their original vehicle use, creating customized control systems tailored specifically for that application as well as specific designs, development, and manufacturing activities that must meet different demands from applications requiring special requirements from projects due to differences between each project that must meet specific design, development, manufacturing requirements.

Battery manufacturers and vehicle production companies should explore ways of using LIBs as energy storage for sustainable electricity generation. LIBs play an essential part in providing sustainable electricity generation. Reliance on commercial LIBs to extend their lifespan is key to energy and material savings, while upgrading and monitoring ensure long-term use. LIBs that have reached their end can also be utilized in smart grid systems to improve energy balance in electric vehicles. Manufacturers have implemented software controls within battery management systems to extend battery life efficiently while optimized electrode designs which reduce heat generation are essential in prolonging both lifespan and capacity.

Repurposing is an ideal option for EOL LIBs, providing them a second life in less demanding applications and increasing the value of the batteries by prolonging their lifespan beyond initial automotive usage. This strategy maximizes their worth, while increasing value through extended lifespan. When battery packs no longer meet capacity needs, repurposing may be more economically viable than remanufacturing, thus making repurposing an effective option. Repurposing involves replacing damaged cells or modules and reconfiguring the battery pack, creating a custom battery management system (BMS) designed specifically for non-vehicular applications. Repurposing presents challenges such as grading EOL packs, accommodating different designs and performance metrics, liability concerns and cost of reconfiguration. To facilitate widespread adoption of repurposing, liability standards must be set forth as well as an acceptable business case being created [183].

Repurposed EOL batteries have found multiple second-use applications, from peak shaving and backup power supply, frequency regulation, renewable integration, EV charging, and frequency regulation systems - depending on their technical requirements for each particular scenario. A representative example is the joint venture between Daimler, GETEC and the Mobility House in 2016. This innovative project utilizes spent batteries from smart EVs and Mercedes electric B-Class to supply battery balancing in a wind farm with total storage capacity 13MWh in Westphalia, Germany. In Osaka, Japan 2014, another collaboration of Nissan and Sumitomo Corporation deployed 16 re-used batteries from Nissan Leaf to establish a 600KW/400KWh storage, besides a 10MW solar farm [184].

Integrating remanufactured batteries into electric vehicle production can significantly lower costs, environmental impacts and labor disputes associated with battery production. By reusing most cells that remain fully operational and only needing minor remanufacturing to reach capacity requirements, this approach significantly lowers battery costs - as evidenced by an estimate for remanufactured Chevrolet Volt batteries as opposed to new ones. Mineta National Transit Research Consortium conducted a cost-benefit analysis that underscores the economic viability of LIB remanufacturing, showing a considerable reduction in LIB costs when compared with manufacturing from raw materials. LIBs should also be considered for secondary uses besides electric vehicles, including energy storage for residential homes and power generation plant applications. Studies indicate the possibility for a flourishing LIB repurposing industry that contributes to emissions reduction and the expansion of renewable energy systems [185].

Repurposing LIBs presents several challenges, including reliable grading of EOL packs, managing various designs and performance metrics, liability concerns and reconfiguration costs.

Overcoming these hurdles requires developing standards, advanced technologies and viable business models - BMSs can assist testing and grading operations by transmitting state-of-health information directly, while service-based business models can ease consumer fears about degraded batteries. Developing liability standards will also ensure widespread adoption and reduce risks to manufacturers.

Repurposing LIBs offers an appealing means of extending their useful lives, cutting costs, and supporting sustainable energy systems. Stationary storage applications, renewable energy integration and remanufacturing are among the key areas where repurposed batteries can have an effect. Although challenges exist such as grading EOL packs and liability concerns, this industry has grown increasingly professional and economically viable over time - playing its part in building towards a circular economy through standards development, advanced technologies, and suitable business models.

4.4 Recycling Processes

Recycling is the last option in the lithium battery management chain when the batteries reach the end of their life and due to their general worn condition is not feasible to address in second use applications or redesigning techniques. Current recycling technology focus on lithium, cobalt, nickel, manganese, cooper aluminum and steel reclamation [186]. Of course, recycling does not represent a singular process rather than a combination of steps and alternatives that are further described below.

4.4.1 Pretreatment

The pretreatment process is essential for the enhancement of the total recycling rate efficiency with main target the satisfactory isolation of the metal components, materials and scraps. Then each category of the corresponding ingredients is following distinct treatment and thus the energy consumption is alleviated as possible. Several individual pretreatment operations have been proposed and implemented in the recycling industry such as discharging, sorting, dismantling, thermal treatment, comminution and separation that are further analyzed below. However, not all the companies follow a specific model, instead some of the aforementioned steps may be absent or show alternative sequence [187].

4.4.1.1 Dismantling

Dismantling or disassembling batteries is another integral component of battery recycling, particularly with end-of-life electric vehicle (EV) batteries. The aim is to recover valuable materials while optimizing material use and life-cycle impacts, including recycling credits or second use market demand.

The main purpose is to divide the pack into individual fragments. Each pack is composed of 10 – 50 modules and each module consist of several hundreds of cells [188]. As with any activity involving high voltage and current, dismantling battery packs from automotive applications involves inherent hazards. High voltage training and insulated tools are necessary to avoid electrocution or short circuiting of the pack which could lead to rapid discharge, heating, thermal runaway, harmful gases being produced, even cell explosion. Furthermore, toxic additives and potentially toxic electrode materials present additional safety threats [136].

Before disassembling batteries, it is vitally important to assess their state of health and state of charge. State of health refers to the extent to which a battery meets initial design specifications while state of charge measures how fully or partially charged/discharged the cell is at present. These assessments allow us to categorize batteries for reuse, remanufacture or recycling while assuring safety during this process.

Disassembling battery packs and modules poses many difficulties due to a lack of standardization in the automotive sector. Each vehicle manufacturer utilizes different physical configurations, cell types and chemistries, making automated disassembly difficult; manual dismantling is performed by qualified technicians due to skill shortages as well as safety risks [189].

Researchers are exploring automated battery disassembly as a solution to these challenges and increase efficiency, to reduce human workers' risks while improving mechanical separation of materials and components, thus increasing recycling rates. Unfortunately, creating robots capable of handling all aspects of battery disassembly remains an enormously complex and variable process in artificial intelligence research. Standardizing battery designs to include machine-readable features like labels, QR codes or RFID tags could facilitate recycling efforts and blockchain technologies are being considered for tracking battery materials and providing transparency throughout their lifespan. Automated disassembly has already been employed in some sectors, such as phone disassembly. Apple has an automated line capable of disassembling over one million iPhones each year; adapting these systems for use with electric vehicle battery designs and chemistries requires advanced control algorithms, robotic perception using computer vision technology, tactile force-sensing capabilities as well as tactile force sensors [145].

4.4.1.2 Sorting

Sorting and segregation of batteries are critical parts of pretreatment recycling processes. Sorting allows the separation of non-battery waste from battery waste while categorizing batteries according to their chemistry, physical appearance and electrical parameters according to specifications of an end recycling plant. Many different sorting techniques ranging from manual sorting processes up to automated processes have been explored to achieve maximum sorting efficiency and accurate battery classification. Physical appearance-based sorting begins by initially sorting batteries based on size, shape, and other visual criteria. This method involves manual presorting, where workers positioned on a conveyor belt remove larger battery packs and devices before employing magnetic sorting and mechanical sorting techniques to complete the sorting process. Although manual sorting remains widely employed, recent research suggests integrating machine learning and X-ray technologies for enhanced sorting efficiency. Electrical parameters, including voltage, internal resistance, discharge capacity and self-discharge rate can provide useful insights into the state and performance of batteries. By employing machine learning models to extract relevant parameters from battery cells, classification of them accurately exceeds direct measurement constraints [190, 191].

Battery Sorting Based on Physical Appearance

Sorting Batteries Based on Physical Appearance Sorting plays an essential part in pretreatment recycling processes, helping separate and categorize batteries according to various factors. This section addresses segregating them based on physical appearance and characteristics. A battery trash crane deposits barrels into large containers before transporting waste via conveyor belt for manual sorting by workers stationed along the belt - large items like batteries from computers, drilling machines, laptops and phones must also be manually removed from these items before entering for manual presorting by workers stationed along this section [189].

To further separate batteries, a magnetic sorting station is employed to capture any batteries still present on the belt. Once collected, mechanical sorting techniques such as shaker screens are utilized to chase down and sort batteries based on size and shape. While most recycling companies currently rely on manual sorting methods alone for sorting purposes, recent research suggests using machine learning or X-ray techniques instead - each approach having their own advantages and disadvantages.

Battery Sorting Based on Electrical Parameters

One method for sorting batteries involves measuring electrical parameters. This approach is considered straightforward and simple as it directly evaluates both static and dynamic parameters of batteries; static parameters reflect their state in an open or idle configuration, while dynamic ones measure when energy flows through them - such as voltage, internal resistance, discharge capacity or self-discharge rate [189].

Battery Sorting Based on a Machine Learning Model

Machine learning models offer a precise and efficient method for battery sorting. By extracting parameters like voltage, current, and internal resistance from battery data sources such as sensors and equivalent circuit models, these models can implement appropriate equivalent circuit models and machine learning algorithms to classify batteries accurately - surpassing direct measurement in terms of both precision and efficiency. Machine learning algorithms - neural network methods included - may also be employed as battery classification methods while pairing this approach with big data and cloud storage can increase sorting speeds even further [189].

Battery Sorting Based on Chemistry Material

Recycling firms frequently categorize batteries based on their chemical or cathode material type in order to optimize hydrometallurgical processes. The technique involves understanding a battery's operating principle such as voltage levels before identifying electrochemical parameters involved with its chemical reaction and quantifying these features as best as possible. Unfortunately, full knowledge of any given battery's internal processes without damage remains challenging, while quantifying many electrochemical characteristics is nearly impossible [189].

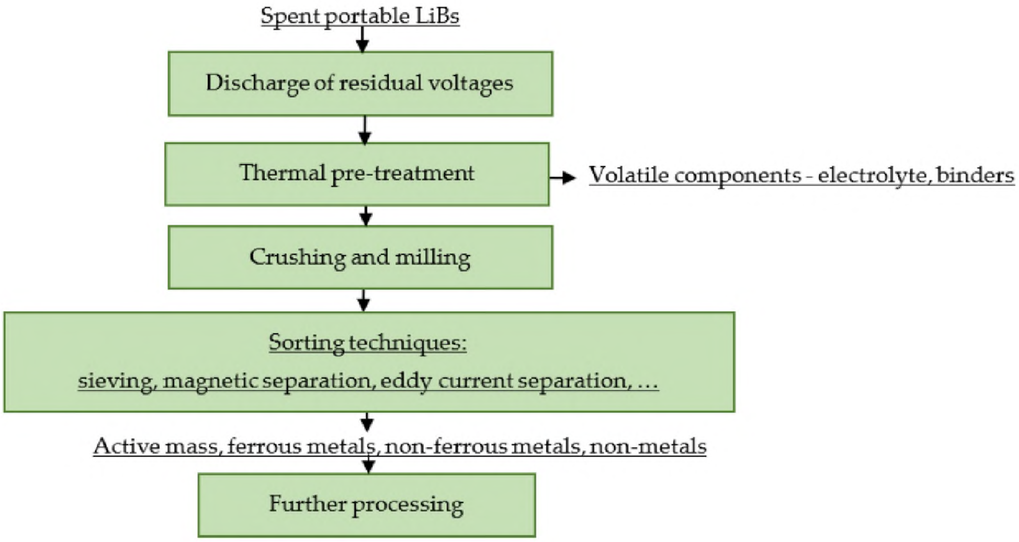


***Figure 23**. Basic pre-treatment diagram for spent LIBs [192]*

4.4.1.3 Discharging

As is shown from the above diagram in **figure 23**, after the major sorting discharging lithium-ion batteries (LIBs) is a key step in recycling processes, with various methods employed to ensure safe and efficient discharge. The spent LIB cells still contain residual energy accumulated at the electrodes that need to release before the following recycling process. If the anode and the cathode get in contact during dismantling short circuit is occurred and thus the produced heat may inevitably ignite the flammable electrolyte. During the pyrometallurgical process, the high-temperature incineration leads to automatic discharge of LIBs into landfill sites and producing nevertheless harmful gasses such as hydrogen fluoride (HF). In hydrometallurgical process LIBs submerge in salt-aqueous solutions such as sodium chloride (NaCl) is used to decrease their voltage and prevent short circuiting and self-ignition. Large-scale discharge models have shown promising results in rapidly lowering LIBs' residual voltage over just hours. Discharging LIBs through aqueous solutions such as saltwater, acid and alkali solutions offer a safe method for discharging them relatively fast with low cost. Typical investigated conductive solutions are NaCl, $NaSO_4$, $FeSO_4$ and $ZnSO_4$. These solutions corrode the battery terminals causing a controlled short-circuiting while protecting internal chemistry of cells and rendering them safe for storage. Ideally in this step the main purpose is the complete residue voltage removal (0V) and thus the formation of thermodynamically stable electrodes, despite that the accumulated voltage of the cell immediately after the discharge does not always correspond to the impartial stored energy. The discharge-efficiency and time depends on various parameters such as the solution, the concentration and the cell voltage. The NaCl brine provide the most preferable alternative while sulfate precipitates stuck on the silver threads blocking the short circuit formation and thus the overall discharge. It is estimated that the immersion in 5% NaCl solution for 24h can completely passivate the spent LIBs. Furthermore, increasing the temperature the discharge time is decreasing but never exceeding 90^{o}C for safety issues. However, discharging via salt solutions may produce harmful gases such as chlorine, losses of Al, Co, Li, Cu, Mn and other volatile compounds such as dimethyl carbonate making their recovery challenging due to associated dangers and challenges [132, 193]. Care must be taken not to compromise cell contents during this process. Any possible contamination that enters cell contents must also be considered when considering downstream chemical processes [135, 189, 194]. Though battery discharge can be an effective and safe solution, several chemical reactions occur during discharge that could contaminate the solution if the batteries become damaged during discharging. Therefore, careful management and choice of solution concentration is required in order to protect both the batteries as well as limit discharge rates [189, 191].

There are also methods involving direct Ohmic discharge through load-bearing circuits and regenerative electronic load banks that allow energy recovery as AC current. In traditional moderate methods, used to discharge mainly small cells, both terminals connected to a resistance wire and thus residual energy is released as heat. New technologies imply the connection of the cells with regenerative converters in order to obtain alternating current. Despite that this method can reach 80-94.5% energy recovery, this happens only when the state of charge is plenty while drained batteries (0-2,5V) show weakness.

Inductive discharge technology used by smartphones and tablets has also gained increased research attention. This method employs magnetic fields to induce current into a secondary coil for discharge without metal connections. However, further development and adaptation for LIBs must take place.

Overall, discharging LIBs during the recycling process is an integral step that demands close consideration of safety, efficiency, and environmental impacts. Numerous methods are being investigated and developed in order to achieve effective discharge while optimizing material recovery from spent batteries.

4.4.1.4 Thermal deactivation

Thermal deactivation is an integral component of battery recycling, especially for removing electrolyte, carbon impurities and biners from batteries. A variety of methods have been devised and employed for thermal deactivation - each offering advantages and considerations of its own.

Cryogenic deactivation or freezing and crystallizing the electrolyte to extremely low temperatures ranging from -175°C to -200°C using liquid nitrogen, is one approach, rendering them nonconductive while temporarily deactivating them to reduce fire risks associated with elemental lithium oxidation. Cryogenic cooling can help solidify the electrolyte, increasing safety during disassembly. While cryogenic deactivation is suitable for high-capacity batteries processing needs, its adoption has been limited due to high capital and equipment costs associated with this method [189].

Heat deactivation involves heating discharged batteries initially temperatures between 100°C and 150°C for a specified duration, in order to safely extract high-energy and organic materials without the risk of overheating during subsequent processing steps. Heating helps release any high-energy or organic material safely before subsequent shredding/disassembling steps are undertaken, helping prevent unexpected overheating incidents from happening during subsequent steps and minimize fluorine compounds emissions into the environment. A particle filtration system may be employed during heat deactivation to ensure the entrapment of hazardous gases or metals during this step.

Heat technologies use high temperature calcination to burn binder and carbon materials from battery components before later extracting active substances - although this requires expensive furnaces, significant energy usage, and may emit dangerous fumes into the environment [193]. A two-step thermal deactivation process was investigated by Lee and Rhee for LCO batteries. In particular the electrodes remained inside a furnace at 300 – 500°C for 1 hour and as a result the contained Li and Co were liberated from the Al current collector through vibrating screening. After the temperature reached 900°C the residual carbon and binders were burned off [133].

Summarizing, thermal treatment allows binders that connect active materials and conductive carbon together to be eliminated through high-temperature binder decomposition, while it also facilitates separation by extracting conductive carbon, acetylene black and organic material from

LIBs for separation purposes. However, thermal treatment can release potentially toxic gases. Thus, adequate treatment of any waste gases generated during this process is required [142].

Sieving, magnetic separation, eddy current separation, electrostatic separation and froth flotation are employed for the separation and recovery of battery components after thermal deactivation. These methods rely on properties like particle size, density, magnetic susceptibility, electrical conductivity and surface chemistry - helping ensure they deliver maximum value to both metals and materials recovered from battery components.

4.4.1.5 Comminution

Comminution is the practice of mechanically disassembling battery packs into smaller fragments using techniques such as ripping, shredding, crushing and milling to produce black materials enriched in metals. Comminution may take place both before and after manual disassembly has taken place and involves three primary processes: shredding, hammer milling and granulating. Each produces materials of differing sizes and shapes that have an effect on downstream separation approaches. To ensure homogenous size distribution and content of final material produced from multiple stages of comminution. Specifically fine crushing should be avoided to protect current collector particles from becoming trapped in black mass material.

Dry crushing of lithium-ion batteries (LIBs) without using water is an alternative comminution technique for recycling old LIBs, starting with sorting batteries before breaking them in batches to maintain particle consistency and improve separation efficiency. Dry crushing does not require chemical reagents and achieves high separation and recovery efficiencies. However, it may be costly in terms of labor and equipment costs, additionally, a dust prevention and control system must be in place [189, 194].

Recently, LIB crushing has increasingly taken place in cryogenic or inert environments to ensure its safety. Cryogenic crushing involves crushing batteries in low temperature environments using liquid nitrogen or other inert gases; this reduces fire risks caused by lithium's highly reactive nature when exposed to air or water and also eliminates hazardous gas releases and makes plastic cases brittle for easy breaking. Thus, crushing using customizable inert environments such as using gases like argon, nitrogen or carbon dioxide is an approach used to ensure inertness of lithium and its byproducts [194].

Wet crushing involves crushing LIB components in water or another solution, using it as a washing agent, to absorb any heat generated during crushing and avoid explosions that often accompany dry crushing methods. Furthermore, high pressured water jets with high velocity can be used to cut spent LIBs to reduce noise pollution and energy costs [189].

After being ground to fragments using mechanical crushing, battery fragments are then separated using various separation techniques in order to extract precious elements that remain. Mechanical crushing provides greater processing efficiency and capacity compared to manual disassembly. However, its use combines all elements contained within the battery pack, making the subsequent separation process more complex and resulting in less purified output.

The recycling process for batteries includes dismantling, which poses numerous hazards and challenges. Automation through robotics could offer potential improvements in safety, efficiency and materials recovery. However, complete automation remains a significant research challenge due to the complex and diverse nature of battery designs. Comminution plays an essential role in battery recycling as it breaks apart battery packs into smaller fragments for easier separation and recovery of valuable materials. While offering greater processing efficiency, comminution requires careful consideration for safety concerns and environmental considerations.

4.4.1.6 Separation Techniques

With an increased demand for lithium-ion batteries (LIBs) across various applications and an emphasis on environmental sustainability, recycling strategies have become more vital than ever. LIBs contain valuable materials like lithium, cobalt, nickel and graphite which makes their recycling essential to resource recovery and minimizing environmental impact. Separation plays an essential part of the recycling process, enabling extraction of high-purity materials for further reclamation and reuse. This section offers a comprehensive overview of LIB recycling's various separation techniques used for reclamation such as sieving, magnetic separation, electrostatic separation, eddy current separation, gravity density separation and froth flotation.

Sieving: Separation based on size

Sieving is an increasingly popular separation technique used in LIB recycling that takes advantage of particle size differences among components. Following comminution, recovered materials undergo sieve processes to sort them by their sizes; this approach has proven particularly successful when dealing with mixtures containing electrode coatings, graphite or metal oxides [189].

Magnetic Separation: Recovery of magnetic materials

Magnetic separation is widely utilized in LIB recycling to remove ferrous metals such as steel casings. By subjecting various mixtures to different intensities of wet magnetic separation, different material streams can be created based on their magnetic vulnerabilities. While direct recycling of cathode materials through magnetic separation poses unique difficulties due to difficultly in separating different ratios of nickel, manganese, and cobalt, magnetic separation still finds uses when combined cell feed recycling operations use it to extract cathodes for cathode extraction operations with mixed cell feed recycling operations with mixed cell feed operations using mixed cell feed to extract cathodes from cathode extraction operations using mixed cell feed mixed cell feed operations for cathode extraction operations using mixed cell feed combined cell feed recycling operations using mixed cell feed for cathode extraction operations using magnetic separation techniques for cathode extraction operations that include nickel manganese, and cobalt ratio separation difficulties when separated separately but recycling operations employ mixed cell feed processes find useful when extracting cathodes using mixed cell feed for cathode extraction [145, 181, 189].

Electrostatic Separation: Separation based on electrical properties

Electrostatic separation is an efficient way of recycling LIBs that relies on electrical properties rather than magnetic attraction to separate metallic fractions from nonmetallic fractions such as polymers. Conductivity differences among components facilitate this method and by employing charges to promote separation, electrostatic separation can effectively separate particles based on electrical rather than magnetic attraction; it has already proven its worth when recycling old printed circuit boards, making this approach applicable for LIB recycling as well [189].

Eddy Current Separation: Separation of non-ferrous metals

Eddy current separation is a technique employed to pre-separate different materials based on variations in physical properties, and is particularly useful for sorting copper, aluminum and polymers in used LIBs. Eddy currents produced by various magnetic fields interact with non-ferrous metals causing them to be isolated from other metals; by taking advantage of this phenomenon eddy current separation is capable of efficient recovery of copper, aluminum and other non-ferrous metals from used LIBs [181, 189].

Gravity Density Separation: Separation based on density differences

Gravity density separation is a method that separates components based on their densities. Fluidized bed processing plays an integral part in recycling LIBs due to their disparate materials' densities, effectively segregating low-density plastics and papers from mixed cell waste. Methods such as rotating belt tables, vibrating screening, intermediate density fluid separation and air separation can all be utilized to achieve effective separation. Gravity density separation provides an effective means to remove plastics from electrode materials as well as facilitates separation of copper and aluminum current collectors [189].

Froth Flotation: Selective separation through flotation

Froth flotation is an efficient technique for selectively separating fine particles according to their surface hydrophilicity, making it the go-to technique for LIB recycling when it comes to distinguishing hydrophobic anodic graphite from hydrophilic cathodic materials. Flotation relies on adding tiny bubbles into a container containing the substance to be separated. Hydrophobic materials attach themselves to these bubbles, rising to the surface in an orderly froth formation process. Froth flotation allows us to recover and process desired hydrophobic material more efficiently, maintaining electrode material functional integrity while increasing energy efficiency of downstream processes and producing high-value metal-rich products [142, 189].

Recycling lithium-ion batteries is crucial for both resource utilization and reducing environmental impacts, with effective separation techniques playing a critical role in recovering valuable materials from these batteries. LIB recycling uses sieving, magnetic separation, electrostatic separation, eddy current separation, gravity density separation and froth flotation as key methods for extracting high-purity components. Selection and optimization of battery recycling techniques depend upon their unique composition and characteristics, and by employing separation technologies the recycling industry can increase resource efficiency, advance circular economy principles, and create a more sustainable future.

Recent years have witnessed exponentially increasing battery demand due to rapid advances in electronics devices and electric vehicles. Yet their widespread use has raised significant environmental and resource utilization challenges. Recycling methods have become an integral component of battery production cycles. This section highlights the state of art recycling methods; specifically: pyrometallurgy, hydrometallurgy, purification technologies and direct recycling that are employed within the battery industry.

4.4.2 Pyrometallurgy

Pyrometallurgy: Metal Extraction through High-Temperature Processes

Pyrometallurgy is the prevalent and most industrial applicable recycling method for consumer LIBs. The main difference against hydrometallurgy is the use of thermal processes in spite of chemical. This method of recycling is compatible with a large variety of electrode chemical composition, without requiring significant adjustments to apply, except from the temperature that varies depending on the desirable outcome. Thus, versatility of feedstock to contain both LIBs and other chemistries like NiMh simultaneously, is a solution when cell sorting is absent [188]. The philosophy behind pyrometallurgy operation is relatively simple compared with hydrometallurgy. The Li ion battery packs are burned inside special industrial furnaces and three new fractions obtained, the metallic fraction, slag and released gasses. Each of these phases requires special handling in consequent steps in order to be the method sufficient. In particular, the metal fraction represents a Ni, Co, Cu riched alloy that usually is treated by further hydrometallurgy process in order to obtain these metals with higher purity. The slag fraction is a stone shape mixture that contain Li, Al, and Mn, that needs additional process for the constituent reclamation. Unfortunately, slag is addressed to cement industries and Li, Al, and Mn downcycled due to lack of mature technology, affecting the circular economy. The high Li price however leads the laboratory research potential for new technology investigation. The released gasses are volatile compounds and PMs produced during the smelting and require capturing and inactivation. PM, also called particle pollution is a mixture of solid particles and liquid droplets found in the air and some of these particles such as dust, dirt and smoke are large enough to be seen with naked eye. VOCs are volatile organic compounds that may be dangerous for human health and for the environment. Most of them are nontoxic however may cause long-term health effects.

At the lower temperatures the electrolyte and binder evaporated and at higher temperatures organic plastics and anode oxidized. The combustion of the electrolyte and plastics provide residual energy for the process, [188] in addition with Al that also serves as reductant [181].

Several pyrometallurgy methods exist, smelting and combustion are less popular techniques, while pyrolysis and calcination are more applicable in industrial use. From a better scope calcination smelts the LIBs using temperatures less than 1500°C in addition with inorganic reactants. Usually, the slag byproduct is not intended for further processing but is adopted by cement industries as concrete material. Pyrolysis is a fast and easy to apply method that decomposes thermal the product in high temperatures 450-1100°C in an oxygen free atmosphere. Main purpose is via irreversible reactions the simultaneously phase and chemical composition change of the product. This procedure entails the acquisition of decarbonized product, that consists of valuable battery metals and other byproducts that can be used as fuel [139]. So, summarizing, we detect that this method is not very rigorous, represents the most technological developed recycling method, is compatible with various LIB chemistries, there is no need for pretreatment or presorting, and in comparison, with hydrometallurgy, water consumption is 50% less for this processing. These are some of the main advantages of pyrometallurgy. However, there are a lot of short comes and concerns that both laboratory researchers and companies need to exceed. In particular, except from the hazardous volatile gases produced, the high temperature furnaces require big amount of energy in order to smelt the battery. This could be disregarded if the efficiency of the method was high, however pyrometallurgy cannot recycle the whole battery content. In contrast, a significant part of the LIB (electrolyte, plastics, graphite etc.) is treated as waste, so the efficiency is assessed about 40%, which is not satisfactory. Moreover, pyrometallurgy depends on consequent processes most of the times, increasing the total cost and the equipment requirement [134-136, 171, 189, 195, 196].

4.4.3 Hydrometallurgy

Hydrometallurgy is another method employed in battery recycling that utilizes leaching agents like acids or alkaline solutions to dissolve metals from lithium-ion battery materials, with selective dissolution occurring allowing separation and subsequent purification [177, 189].

4.4.3.1 Acid leaching

Acid leaching is a prevalent leaching method for metal reclamation of the positive electrode. It is further divided in organic or inorganic acid leaching depending on the leaching agent used. Typical inorganic agents are hydrochloric acid HCl, phosphoric acid H_3PO_4, sulfuric acid H_2SO_4 and nitric acid HNO_3, while the organic acid list contains citric, ascorbic, oxalic, formic, acetic, tartaric and malic acid. Reducing agents such as hydrogen peroxide H_2O_2 or sulfurous acid H_2SO_3 or hydroxylamine NH_2OH can accelerate the leaching kinetics, without also being mandatory. Other factors that influence the process are stirring intensity, temperature and solvent concentration. Peng et al. obtained a sufficient rate of 95,7% Li and 93,8% Co, combining 2 mol/L H_2SO_4 inorganic leaching agent and 0,11 mol/L ascorbic acid in operational conditions of 80oC for 90min. In similar conditions of temperature and operational time Sun et al. added 1 mol/L inorganic oxalic acid with 50 g/L solid to liquid ratio to achieve 98% efficiency for Co and Li [136]. Studies revealed that inorganic acid leaching represents an advantageous process, however unwanted byproducts during the operation such as Cl_2, SO_2 and NOx constitute environmental and human health hazard, that requires specialized treatment and equipment. On the other hand, organic acid leaching is considered an eco-friendlier method with good recyclability, however the low treatment capacity in addition with the high cost and relative low efficiency restrict the widespread industrial development [181, 194-196].

4.4.3.2 Alkali leaching

Alkali leaching exploits the advantage of ammonia-based reagents to form stable compounds with metals like Co, Cu, Ni to achieve selective leaching. Typical reagents are ammonium carbonate, ammonium sulfate and ammonium chloride. Optionally, reducing agents and thermal treatment entails in improved efficiency and reaction kinetics. Other parameters that affect the process are the concentration, pH, temperature etc. Ku et al. proposed the combination of ammonia as leaching agent with ammonium carbonate as pH buffer and ammonium sulfite as reducing agent to extract sufficiently Co, Ni, Li (>98,6%). Zheng et al. in another study, achieved more than 98,6% leaching efficiency of Co, Ni, Li combining both ammonia-ammonium sulfate as leaching agent and sodium sulfite as reductant. Generally, alkali leaching is a sufficient leaching operation, however the excess water consumption, the consequent secondary pollution and the equipment corrosion need to exceed for further industrial-scale implementation [136, 181, 195].

4.4.3.3 Bioleaching

Bioleaching process exploits the acids emerged by the metabolization of microorganisms to turn insoluble metal oxides from cathode electrode into water soluble metal sulfates. More specific, bacteria and fungi are cultured to produce inorganic and organic acid respectively. The effectiveness of this method depends on regulatory parameters such as pH, pulp density, temperature, time etc. or the addition of reducing agents for further enhancement [181]. Niu et al. achieved 72% Co and 89% Li recycling, using Alicyclobacillus sp. And sulfobacillus sp. while Bahalloo – Horeh et al. investigation employed the culture of fungus Aspergillus niger, which generates citric, oxalic, gluconic and malic acids. Thus, bioleaching represents an eco-friendly, economic and relative sufficient method with the extra benefit of low consumption of energy. However, main drawbacks remain the slow kinetic of the process, depending on the culturing time of the microorganism – few days may need to reach efficiency rates compared to acid leaching, and the low leaching efficiency. These reasons prevent the industrial adoption of this promising method. Lastly, not a lot of studies accomplished on bioleaching so far, so further scientific research is imperative [135, 136, 145, 181, 195, 196].

4.4.3.4 Purification Technologies: Refining Extracted Metals to Remove Impurities

Once metals have been extracted via pyrometallurgical or hydrometallurgical processes, they may undergo purification technologies in order to remove impurities such as other metals, residual organic compounds or any undesirable substances that could compromise performance or reliability of recycled materials.

Purification technologies use various processes, including precipitation, solvent extraction and electrorefining. Precipitation involves adding specific reagents to the solution which precipitate any impurities present, separating them from desired metals. Solvent extraction uses certain solvents specifically tailored to remove these impurities from metal solutions while electrorefining employs an electrolytic cell with electric current applied which separates impurities that may deposit on electrodes by applying an electrical current and depositing them on an electrode plate. Purification technologies help ensure that recovered metals meet quality standards necessary for use in battery production, ensuring performance and safety in recycled materials.

4.4.4 Direct recycling

Direct recycling is an innovative approach to battery recycling that involves directly using recovered materials in the production of new batteries, thus minimizing energy and resource consumption associated with traditional metal extraction processes. Instead of extracting metals from spent batteries for refining purposes, direct recycling aims at reincorporating them back into manufacturing, closing the material loop while decreasing our dependence on primary raw materials [189].

Direct recycling typically entails sorting and processing spent batteries to extract intact or partially intact battery components, such as electrode materials, separators, and current collectors that are undamaged from prior battery use. After evaluation and if suitable reintegration into production process if approved. This approach offers several advantages such as decreasing energy consumption, cost, environmental impact associated with primary material extraction as well as conserving valuable resources by decreasing mining activities.

Direct recycling presents some challenges; its quality and condition depend on the state of spent batteries, making its performance crucial to ensure integrity in new battery manufacturing processes. Furthermore, direct recycling requires certain modifications or adaptations for existing manufacturing processes that use recycled material; compatibility may require modifications and adaptations as well.

Recycling methods play a vital role in the sustainable production of batteries. Pyrometallurgy and hydrometallurgy enable extraction of valuable metals from spent batteries at high resource recovery rates; purification technologies further refine them for reuse, while direct recycling focuses on using recovered materials directly in new battery production, mitigating environmental impacts associated with traditional extraction processes. Pyrometallurgy percentage of global recycling methods accounts 16,79%, while hydrometallurgy accounts 57% [171].

The choice of recycling method depends on various factors, including battery chemistry, desired metals for recovery, and specific requirements of a recycling facility. A combination of methods may be employed within one facility to maximize resource recovery while simultaneously minimizing waste generation. As battery demand continues to soar, optimizing recycling methods becomes ever more essential. Ongoing research and technological innovations will further increase battery recycling's effectiveness and contribute to creating a more circular economy.

In conclusion, adopting recycling methods into battery production serves as an integral component in mitigating environmental impact, conserving resources, and encouraging sustainable development within the battery industry.

4.5 Battery recycling companies worldwide

Upon examining the procedures employed for battery recycling, along with the separation techniques and various recycling methods, this section highlights several companies from around the world that actively operate in this sector. These distributed companies all around the world, as is demonstrated in **figure 24**, serve as significant players in the battery recycling industry, showcasing diverse and innovative recycling approaches that minimize environmental impact.

Figure 24. *Lithium-Ion Battery Recycling Facilities Worldwide [181]*

BATREC

BATREC specializes in recycling lithium-based batteries (LIBs) using various methods. One of their key processes is the Batrec process, which involves crushing batteries in a CO_2 atmosphere to prevent reactions and form a protective layer on lithium metal. Shredded batteries are neutralized with moist air and collected for further treatment. The active electrode materials are detached, refined through hydrometallurgical processes, and separated from cases and foils [181, 183]. BATREC also employs a hydrometallurgical process where used batteries are sorted, crushed in a CO_2 atmosphere, and neutralized. Scrap materials undergo acidified aqueous treatment, resulting in separated leaching liquor and solid fractions for purification.

Since the late 1980s, BATREC has focused on recovering metals from alkaline and Zn-C batteries. They emphasize sorting, cleaning, and manual dismantling of LIBs from consumer goods and electric vehicles. Vacuum thermal treatment removes electrolytes and volatile substances. Mechanical separation steps, including vibrating screens and magnetic separators, extract base metals. The remaining fraction undergoes agglomeration and a two-step pyrometallurgical process to recover cobalt and manganese. Lithium recovery is pursued through hydrometallurgical means, yielding lithium carbonate suitable for cathode production or glass manufacturing [171]. Overall, BATREC's recycling methods prioritize efficient LIB recycling while minimizing environmental impact.

ACCUREC

Accurec, a German battery recycling specialist, has devised efficient and innovative techniques for recycling lithium-ion batteries (LIBs). Their process utilizes mechanical, pyrometallurgical, and hydrometallurgical techniques in order to reach high recycling rates while recovering valuable materials from spent batteries. The recycling process begins by disassembling LIBs and sorting their components: steel components, electronic parts, copper cables and plastic components are separated before being separated out into separate piles for recycling. Any remaining battery cells then undergo autothermal pyrolysis at around 250^{o}C to evaporate their electrolyte and collect it through condensers downstream before deactivating and destroying any harmful organic materials and thus minimizing emissions [183].

After thermal treatment, mechanical processes are employed to further separate materials. Ferromagnetic steel, aluminum cases and aluminum/copper foils are separated from active electrode materials by sieving, magnetic separation or air separation techniques; those materials then go through vacuum pyrolysis where lithium can either be recovered in its pure metallic form via evaporation and distillation or as lithium oxide through selective gas evaporation [177]. Accurec utilizes both pyrometallurgical and hydrometallurgical methods of metal recovery for maximum metal extraction. Electrode materials including cobalt (Co), nickel (Ni), and magnesium (Mg), are combined and smelted in various furnaces such as the rotary hearth furnace or electric arc furnace to create Co-based alloys, while copper can be selectively isolated using sodium sulfide (Na_2S) solutions or cementation with iron shots [189, 197].

Lithium recovery utilizes precipitation techniques that produce lithium carbonate (Li_2CO_3) from sodium carbonate solutions, such as Na_2CO_3. Once created, this recycled lithium carbonate can be used as cathode material or for glass manufacturing - with Accurec aiming for a recovery rate of 90% during its recycling process [134]. Accurec's recycling methods prioritize safe and controlled treatment of LIBs to minimize their environmental impact, with their technology constantly being refined in order to increase recycling capacities and recover additional materials such as graphite. Overall, their innovative recycling techniques contribute towards supporting circular economy of battery materials in an eco-friendly manner.

RECUPYL

Recupyl, a recycling company based in France, specializes in the recycling of alkaline batteries and lithium-ion batteries (LIBs) using a combination of mechanical and hydrometallurgical processes. With an annual capacity of 110 tons, Recupyl operates in Europe, Asia, and North America [135]. Their recycling process begins with mechanical treatment under an inert atmosphere, utilizing gases like CO_2 and argon to prevent fire risks. Crushing occurs in two stages using rotary and impact mills at controlled speeds. The crushed material is then screened to separate active electrode materials from larger fractions like steel, paper, plastics, and foils. Steel components are isolated using a magnetic separator, while densimetric tables separate non-magnetic materials based on density differences [134].

In the subsequent hydrometallurgical steps, the separated active electrode materials undergo leaching in water with low oxygen levels. Soluble lithium is dissolved, and the remaining solid is filtered. The lithium is precipitated as lithium carbonate (Li_2CO_3) or lithium phosphate (Li_3PO_4) by adding CO_2 or phosphoric acid. The filtered solid undergoes a leaching process with sulfuric acid to recover cobalt. Copper is removed through purification steps, and cobalt is recovered via electrolysis [181, 183].

Recupyl's recycling methods also involve physical separation of steel, copper, and plastics from fine powders. Leaching these powders results in an alkali solution containing lithium and mixed metal oxides. Lithium is precipitated as Li_2CO_3 or Li_3PO_4, and cobalt is recovered by adding sodium hypochlorite [171]. In summary, Recupyl employs a comprehensive recycling process, combining mechanical treatments and hydrometallurgical techniques to safely and efficiently recover valuable materials from alkaline batteries and LIBs.

RETRIEV

Retriev Technologies Incorporated, formerly known as Toxco, is a leading North American recycling company specializing in the hydrometallurgical recycling of lithium-ion batteries (LIBs). With an annual capacity of around 4,500 tons, Retriev has established itself as a prominent player in the battery recycling industry. The company employs a multi-step process to extract valuable materials while ensuring safety and environmental considerations [183, 189]. The recycling procedure begins with manual dismantling of LIBs to the module or cell level, followed by cryogenic cooling using liquid nitrogen to reduce lithium reactivity. The cooled batteries are then shredded and separated to isolate active electrode materials from plastic, steel, and foil fractions. The active electrode materials undergo dissolution in a lithium hydroxide solution, and undissolved components are filtered and recovered. Precipitation of lithium salts occurs in the filtrate, which is further processed to separate lithium ions from anions using a hybrid electrolytic cell. The recovered lithium is either directly dewatered or converted to lithium carbonate [135]. Throughout the process, various metals are recovered and sold to downstream smelters, while plastics are either recycled or appropriately disposed of. Retriev Technologies' commitment to research and innovation has resulted in patented recycling methods, further advancing the circular economy and promoting sustainable practices.

INMETCO

INMETCO (International Metals Reclamation Company) is an established pyrometallurgical facility renowned for its expertise in recycling metal wastes and End-of-Life (EOL) batteries. While its primary focus lies in recovering cobalt, nickel, and iron for the production of iron-based alloys, INMETCO has expanded its capabilities to include the recycling of spent batteries as a secondary feed [171, 181].

The INMETCO process follows a well-defined schematic diagram. Initially designed to handle stainless steel manufacturing waste like flue dust, mill scale, and swarf, the facility now incorporates the treatment of spent batteries. The recycling procedure begins with milling, screening, and blending stainless steel wastes, which are subsequently pelletized with reductant carbon and liquid waste containing nickel and cadmium. As for the spent batteries, they undergo a series of meticulous steps. After opening the batteries and removing plastic materials and electrolyte, the remaining components are calcined to evaporate and distill cadmium. The batteries are then shredded and combined with the main feed and organic materials, entering the reduction stage in a rotatory hearth furnace operated at a temperature of 1260 °C [183].

Throughout the reduction stage, the organic components and carbon act as crucial energy sources and reducing agents during the carbothermic reduction process of the active cathode material. The off gas produced in the rotary hearth furnace undergoes scrubbing, with the resulting scrub solution directed to a wastewater treatment facility to recover cadmium, zinc, and lead. In an electric arc furnace, the reduced metals are further melted, yielding an iron-cobalt-nickel alloy and a slag containing lithium and aluminum.

It's important to note that the INMETCO process isn't specifically designed for lithium recovery, resulting in the non-recovery of this valuable metal and other non-recovered components in the slag phase.

Operating at a capacity of 6,000 tons per year, INMETCO's recycling methodology, based on a direct-reduced iron (DRI) process, ensures the retrieval of cobalt, nickel, and iron in the form of an iron-based alloy. While the primary focus lies on iron-based alloys, the inclusion of spent batteries in the recycling process contributes to the secondary recovery of precious metals, aligning with the industry's sustainability goals and resource conservation efforts [189].

UMICORE

Umicore is an international material processing group specializing in recycling and refining energy materials, performance materials, catalysts, batteries, as well as Val'eas battery recycling specifically tailored for rechargeable NiMH and Li-ion batteries.

Umicore Recycling's recycling process involves both pyrometallurgical and hydrometallurgical techniques. At its pyrometallurgical stage, batteries are disassembled into individual cells and modules and shipped directly to a recycling facility for recycling. Once there, these are mixed with limestone sand coke and reducing agents before being introduced into a vertical shaft furnace with three zones including preheating zone, plastics pyrolysis zone, smelting reduction zone as well as two further fractions consisting of Cu, Co, Ni & Fe [134, 177, 197]. After going through the pyrometallurgical stage, an alloy then undergoes additional refining using hydrometallurgical processes. Crushing and leaching with H_2SO_4 solution produces metal sulfate salts dissolved in an aqueous solution; copper and iron are removed by precipitation; then using a mixer-settler with organic extractant as extraction process separate cobalt from nickel; these solutions containing Co and Ni ions undergo further precipitation steps for purified Co and Ni salts [134]. Umicore's process aims to achieve high material recovery rates of valuable metals such as Co, Ni, Cu and Fe while simultaneously recycling these resources in new cathode material production. Slag made up of aluminum, lithium, silica, calcium and some iron can either be sold as additives for construction materials or undergo further processing for Li recovery [183].

Consideration should be given to the fact that Umicore's process is energy intensive and its economic viability depends on cobalt and nickel prices, though unfortunately this process doesn't yet recover other valuable metals such as lithium from its slag.

More distinguished efforts are listed below in the **figure 25** which provides briefly informations about the company brand, the location, the volume that are able to manage per year, the method of the process and the status of implementation.

label	company	location	volume (tons/year)	method	status
1	ABT	Fernley, NV, US	20,000	Unknown	Planned
2	Retriev (Toxco)	Trail, BC, CA	4,500	Hydro	Established
3	Li-Cycle	Gilbert, AZ, US	10,000	Hydro	Planned
4	Ganfeng Li	Sonora, MX	Unknown	Unknown	Planned
5	Li-Cycle	Tuscaloosa, AL, US	10,000	Hydro	Planned
6	Inmetco	Elwood, PA, US	6,000	Pyro	Established
7	Li-Cycle	Rochester, NY, US	5,000	Hydro	Established
8	Li-Cycle	Kingston, ON, CA	5,000	Hydro	Established
9	Fenix	Whitehall, UK	10,000	Hydro	Planned
10	Valdi	Commentry, FR	20,000	Pyro	Established
11	Umicore Valeas	Hoboken, BE	7,000	Pyro/hydro combo	Established
12	Recupyl	Grenoble, FR	110	Hydro	Established
13	Accurec	Krefeld, DE	4,000	Pyro/hydro combo	Established
14	Glencore	Baar, CH	3,000	Pyro/hydro combo	Established
15	Redux	Offenbach, DE	50,000	Pyro	Established
16	Northvolt	Frederikstad, NO	8,000	Unknown	Planned
17	Fortum	Harjavalta, FI	Unknown	Unknown	Planned
18	Akkuser	Nivala, FI	4,000	Pyro/hydro combo	Established
19	Green Li-ion	Singapore	Unknown	Unknown	Planned
20	Brunp Recycling Technologies	Hunan, CN	100,000	Pyro/hydro combo	Established
21	Taisen	Hunan, CN	6,000	Hydro	Established
22	GEM	Jingmen, CN	30,000	Hydro	Established
23	Guanghua Sci-Tech	Guangdong, CN	12,000	Preprocessing	Established
24	Gotion High-Tech	Hefei, CN	Unknown	Unknown	Planned
25	Quzhou Huayou	Quzhou, CN	40,000	Pyro	Established
26	Tesla	Shanghai, CN	Unknown	Unknown	Planned
27	SungEel HiTech	Gunsan, KR	8,000	Hydro	Established
28	Posco Hy Clean Metal	Gwangyan, KR	12,000	Unknown	Planned
29	JX Nippon Mining	Tsuruga, JP	5,000	Pyro/hydro combo	Established
30	Dowa Eco-System	JP	6,500	Pyro	Established
31	Sumitomo/Sony	Namie, JP	150	Pyro	Established
32	Envirostream	Melbourne, AU	3,000	Preprocessing	Established

Figure 25. *Companies Involved in LIB Recycling and Volumes Processed by Technique [198]*

CHAPTER 5

5.1 Conclusion and Future Prospects

The exponential expansion of the electric vehicle (EV) market and demand for lithium-ion batteries (LIBs) has raised major environmental and sustainability issues related to battery waste disposal and usage of precious metals like lithium (Li) and cobalt (Co). Production is increasing annually with production projected to surpass 1000GWh by 2025 [199]. Battery recycling technologies have emerged as key solutions to address these challenges and promote material sustainability within the battery industry. Current recycling processes focus mainly on extracting valuable components of LIBs, including cathodes, anodes, cases, and current collectors. Therefore, it is critical that recycling processes continue to develop and optimize in order to maximize recovery of all valuable elements found within LIBs [194].

In recent years serious technology steps have been gained at the battery recycling section both in terms or research and implementation. New techniques were born, a lot of foregone obstacles were surpassed while persistent concerns still exist. Pyrometallurgy is the most widely preferred recycling process for batteries nowadays. Spent battery packs are first dismantled in order to obtain the individual cells and are crushed and converted in tiny fragments. Subsequently, the crushed components are addressed in high temperature furnaces where remain for a while in order to fully burn and safely remove the explosive electrolyte. Then, the temperature is elevated causing the smelting of the batteries producing alloy metals and slag. The main advantage of pyrometallurgy is the feedstock flexibility and the simple know-how operation. However, this method is dependent in further recovery steps in order to obtain pure metals, requires extensive energy supply and produces various toxic gases and dust during the smelting that need optimization.

Hydrometallurgy serves as an alternative eco-friendly recycling process in comparison with the aforementioned pyrometallurgy. Various alkaline and acidic reagents such as hydrochloric acid (HCl), nitric acid (HNO_3), sulfuric acid (H_2SO_4), phosphoric acid (H_3PO_4) and hydrogen peroxide (H_2O_2) are implemented in order to extract precious metals such as Cobalt, Nickel and Lithium. Recent advancements in this method imply the exploration of biohydrometallurgy where bacteria and fungi are cultured to produce inorganic and organic acid respectively in order to turn insoluble cathode metal oxides into soluble compounds and to selectively recover valuable metals.

Direct recycling represents an economical option for material reclamation in chemistries such as NMC and NCA with main enforcement the environmental preservation. This method is aiming at the active material purification of the cathode and the bulk refinement without modifying the original compound via re-lithiation or hydrothermal steps avoiding the extensive metallurgical and chemical methods that convert the active materials into raw constituents. Evidently, the secondary pollution is alleviated as possible, the active materials are ready to use directly after the process, that surprisingly appears not so complicated. However, direct recycling requires challenging pre-sorting treatment according to the chemistry composition because reveals sensitivity to feedstock variations. Yet a dynamic production line still not exist and mature feasibility is not proven. Instead, represents lab scale venture with enticing prospects.

In order to render the recycling viable and fundamental to the battery industry it is vital to address existing economic issues. In this regard the demonstration of large recycling facilities in terms of construction, permitting and manning necessitates high capital costs up to 500 million dollars that further require national financing programs and dynamic partnerships. The high operational costs caused by the specialized staff, expensive emission recovery processes, the continuous maintenance, system malfunctions and of course of the chemicals in case of hydrometallurgy and of the high amount of energy consumed in the furnaces during pyrometallurgy can not be disregarded. As a result, these economical burdens in addition with the low-purity products and the consequent emissions may render recycling less profitable option against mining of raw materials. Moreover, by the time these costs cannot be held by small existing companies, economy of scale is hindered and evidently many pilot processes may stay stagnant.

Despite the fact that recycling represents an environmental-friendly method in comparison with mining, researchers have to get rid of or alleviate serious environmental obstacles. Pyrometallurgy produces dust, VOC emissions and particulate pollutants that require special management. Similarly, hydrometallurgy generates considerable acid and alkaline wastewater and simultaneously involves the consumption of various organic and inorganic acid reagents that need careful disposal. The pretreatment stage including shredding, smelting, crushing etc. is considered an energy intensive procedure. The integration of renewable energy supply may serve as an alternative minimizing this secondary pollution issue.

Battery sorting and collection represent another pivotal concern. The lack of properly distributed collection facilities around the world and each nation results in diffused waste streams that hinder the overall process. A few facilities are able to manage big proportion of spent LIBs while a lot of the existing companies are focused on the research rather than the implementation. Furthermore, the absence of well-established infrastructure combined with the deficient logistic network motivate the rejection of the spent LIBs in landfills or in illegal areas promoting resource loss and further soil contamination. Therefore, the establishment of initiatives and regulations that would promote the public participation are essential. Additional is imperative the foundation of a generally accepted around the world standardization in terms of labelling, marking and modulation that will probably enable robot-based dismantling.

Indeed, recent directives reveal that the governors strive to tackle the lack of overall framework that unfortunately lead to improper battery disposal. More specific, the 2006/66/EC battery and accumulator Directive covers the subject of battery production and disposal and refers mainly to batteries that contain Hg, Pb and Cd which constitute environmental and human health hazards if are incinerated or landfilled. For this reason, thus framework includes maximum thresholds on on the percentage of specific meals and chemicals included in each battery composition, sets goals for waste battery collection and distributes responsibility for proper management. Furthermore, a new and enriched version of this Directive, in order to integrate and Li-ion battery too, is under conversation between the European Commission, the Parliament and the EU which sets new environmental limitations, stricter recycling rate targets, chemistry labeling and producer-consumer responsibilities. Summarizing, governments should establish a dynamic regulation framework with strict penalties in order to enhance the low recycling adoption. The new battery cell's design should provide recycling-friendly modulation according to standardization and as low possible hazard metals composition. The requirement for minimum recycled material content limitation in the new produced batteries is also an imperative policy. Moreover, the new regulations may require multinational agreements especially in the transportation and logistics section while mandatory is the cementation of accurate protocols for the exposed emissions, waste production and safety standards. Lastly, high priority should be given to the attribution of responsibility both from consumers and producers against the recycling of the final products.

The scientific public opinion undeniably promotes the establishment of circular economy models based on the 3R concept -redesign reuse and recycle in hierarchically implementation sequence. Several research and development projects have been held, a lot of them have been commercialized managing satisfactory volume of waste streams while meticulous research must keep pace in order to conform with the emerging innovations and trends.

References

1. Pataro G., G. Donsì, and G. Ferrari, *Modeling of Electrochemical Reactions During Pulsed Electric Field Treatment*, in *Handbook of Electroporation*, D. Miklavcic, Editor. 2016, Springer International Publishing: Cham. p. 1-30.
2. Petrovic S., *Electrochemistry Crash Course for Engineers*. 2021: Springer.
3. Seeber R., C. Zanardi, and G. Inzelt, *Links between electrochemical thermodynamics and kinetics.* ChemTexts, 2015. **1**(4): p. 18.
4. O'Mullane A.P., *Electrochemistry*, in *Reference Module in Chemistry, Molecular Sciences and Chemical Engineering*. 2013, Elsevier.
5. Lefrou C., P. Fabry, and J.-C. Poignet, *Electrochemistry: the basics, with examples*. 2012: Springer Science & Business Media.
6. Breitkopf C. and K. Swider-Lyons, *Springer Handbook of Electrochemical Energy*. 2017.
7. Paleček E., M. Heyrovský, and V. Dorčák, *J. Heyrovský's Oscillographic Polarography. Roots of Present Chronopotentiometric Analysis of Biomacromolecules.* Electroanalysis, 2018. **30**(7): p. 1259-1270.
8. Dreyer W., C. Guhlke, and R. Müller, *A new perspective on the electron transfer: recovering the Butler–Volmer equation in non-equilibrium thermodynamics.* Physical Chemistry Chemical Physics, 2016. **18**(36): p. 24966-24983.
9. Medvedev D., V. Maragou, E. Pikalova, A. Demin, and P. Tsiakaras, *Novel composite solid state electrolytes on the base of BaCeO3 and CeO2 for intermediate temperature electrochemical devices.* Journal of Power Sources, 2013. **221**: p. 217-227.
10. Wu R., P. Tsiakaras, and P.K. Shen, *Facile synthesis of bimetallic Pt-Pd symmetry-broken concave nanocubes and their enhanced activity toward oxygen reduction reaction.* Applied Catalysis B: Environmental, 2019. **251**: p. 49-56.
11. Zhu X., L. Huang, M. Wei, P. Tsiakaras, and P.K. Shen, *Highly stable Pt-Co nanodendrite in nanoframe with Pt skin structured catalyst for oxygen reduction electrocatalysis.* Applied Catalysis B: Environmental, 2021. **281**: p. 119460.
12. Gorbova E., V. Maragou, D. Medvedev, A. Demin, and P. Tsiakaras, *Influence of Cu on the properties of gadolinium-doped barium cerate.* Journal of Power Sources, 2008. **181**(2): p. 292-296.
13. Luo Y., W. Lou, H. Feng, Z. Liu, Q. Chen, G. Liao, X. Huang, P. Tsiakaras, and P. Shen, *Ultra-Small Nanoparticles of Pd-Pt-Ni Alloy Octahedra with High Lattice Strain for Efficient Oxygen Reduction Reaction.* Catalysts, 2023. **13**(1): p. 97.
14. Feng H., Y. Luo, B. Yan, H. Guo, L. He, Z. Qun Tian, P. Tsiakaras, and P. Kang Shen, *Highly stable cathodes for proton exchange membrane fuel cells: Novel carbon supported Au@PtNiAu concave octahedral core-shell nanocatalyst.* Journal of Colloid and Interface Science, 2022. **626**: p. 1040-1050.
15. Li X., Y. Liu, J. Zhu, P. Tsiakaras, and P.K. Shen, *Enhanced oxygen reduction and methanol oxidation reaction over self-assembled Pt-M (M = Co, Ni) nanoflowers.* Journal of Colloid and Interface Science, 2022. **607**: p. 1411-1423.
16. Li X., Y. Huang, Z. Chen, S. Hu, J. Zhu, P. Tsiakaras, and P. Kang Shen, *Novel PtNi nanoflowers regulated by a third element (Rh, Ru, Pd) as efficient multifunctional electrocatalysts for ORR, MOR and HER.* Chemical Engineering Journal, 2023. **454**: p. 140131.
17. Shah S.S.A., T. Najam, M.S. Javed, M.M. Rahman, and P. Tsiakaras, *Novel Mn-/Co-Nx Moieties Captured in N-Doped Carbon Nanotubes for Enhanced Oxygen Reduction Activity and Stability in Acidic and Alkaline Media.* ACS Applied Materials & Interfaces, 2021. **13**(19): p. 23191-23200.
18. Barbir F., *Chapter Two - Fuel Cell Basic Chemistry and Thermodynamics*, in *PEM Fuel Cells (Second Edition)*, F. Barbir, Editor. 2013, Academic Press: Boston. p. 17-32.
19. O'hayre R., S.-W. Cha, W. Colella, and F.B. Prinz, *Fuel cell fundamentals*. 2016: John Wiley & Sons.

20. Brouzgou A., A. Seretis, S. Song, P.K. Shen, and P. Tsiakaras, *CO tolerance and durability study of PtMe(Me = Ir or Pd) electrocatalysts for H2-PEMFC application.* International Journal of Hydrogen Energy, 2021. **46**(26): p. 13865-13877.
21. Barbir F., *Chapter Three - Fuel Cell Electrochemistry*, in *PEM Fuel Cells (Second Edition)*, F. Barbir, Editor. 2013, Academic Press: Boston. p. 33-72.
22. Andreadis G.M., A.K.M. Podias, and P.E. Tsiakaras, *The effect of the parasitic current on the Direct Ethanol PEM Fuel Cell Operation.* Journal of Power Sources, 2008. **181**(2): p. 214-227.
23. Tan A.-d., Y.-f. Wang, Z.-y. Fu, P. Tsiakaras, and Z.-x. Liang, *Highly effective oxygen reduction reaction electrocatalysis: Nitrogen-doped hierarchically mesoporous carbon derived from interpenetrated nonporous metal-organic frameworks.* Applied Catalysis B: Environmental, 2017. **218**: p. 260-266.
24. Wang Y., C. He, A. Brouzgou, Y. Liang, R. Fu, D. Wu, P. Tsiakaras, and S. Song, *A facile soft-template synthesis of ordered mesoporous carbon/tungsten carbide composites with high surface area for methanol electrooxidation.* Journal of Power Sources, 2012. **200**: p. 8-13.
25. Lagaeva J., D. Medvedev, A. Demin, and P. Tsiakaras, *Insights on thermal and transport features of BaCe0.8–xZrxY0.2O3–δ proton-conducting materials.* Journal of Power Sources, 2015. **278**: p. 436-444.
26. Najam T., S.S.A. Shah, S. Ibraheem, X. Cai, E. Hussain, S. Suleman, M.S. Javed, and P. Tsiakaras, *Single-atom catalysis for zinc-air/O2 batteries, water electrolyzers and fuel cells applications.* Energy Storage Materials, 2022. **45**: p. 504-540.
27. Molochas C. and P. Tsiakaras *Carbon Monoxide Tolerant Pt-Based Electrocatalysts for H2-PEMFC Applications: Current Progress and Challenges*. Catalysts, 2021. **11**, DOI: 10.3390/catal11091127.
28. Wang K., H. Chen, X. Zhang, Y. Tong, S. Song, P. Tsiakaras, and Y. Wang, *Iron oxide@graphitic carbon core-shell nanoparticles embedded in ordered mesoporous N-doped carbon matrix as an efficient cathode catalyst for PEMFC.* Applied Catalysis B: Environmental, 2020. **264**: p. 118468.
29. Coutelieris F.A., S. Douvartzides, and P. Tsiakaras, *The importance of the fuel choice on the efficiency of a solid oxide fuel cell system.* Journal of Power Sources, 2003. **123**(2): p. 200-205.
30. Liu J., J. Wang, Y. Fo, B. Zhang, C. Molochas, J. Gao, W. Li, X. Cui, X. Zhou, L. Jiang, and P. Tsiakaras, *Engineering of unique Ni-Ru nano-twins for highly active and robust bifunctional hydrogen oxidation and hydrogen evolution electrocatalysis.* Chemical Engineering Journal, 2023. **454**: p. 139959.
31. Li S., Z.Q. Tian, Y. Liu, Z. Jang, S.W. Hasan, X. Chen, P. Tsiakaras, and P.K. Shen, *Hierarchically skeletal multi-layered Pt-Ni nanocrystals for highly efficient oxygen reduction and methanol oxidation reactions.* Chinese Journal of Catalysis, 2021. **42**(4): p. 648-657.
32. Barbir F., *Chapter Five - Fuel Cell Operating Conditions*, in *PEM Fuel Cells (Second Edition)*, F. Barbir, Editor. 2013, Academic Press: Boston. p. 119-157.
33. Vayenas C., S. Bebelis, I. Yentekakis, P. Tsiakaras, and H. Karasali, *Non-faradaic electrochemical modification of catalytic activity reversible promotion of platinum metals catalysts.* Platinum Met. Rev, 1990. **34**: p. 122-130.
34. Wang K., Y. Wang, Z. Liang, Y. Liang, D. Wu, S. Song, and P. Tsiakaras, *Ordered mesoporous tungsten carbide/carbon composites promoted Pt catalyst with high activity and stability for methanol electrooxidation.* Applied Catalysis B: Environmental, 2014. **147**: p. 518-525.
35. Chen Z., C. Hao, B. Yan, Q. Chen, H. Feng, X. Mao, J. Cen, Z.Q. Tian, P. Tsiakaras, and P.K. Shen, *ZIF-Mg(OH)2 Dual Template Assisted Self-Confinement of Small PtCo NPs as Promising Oxygen Reduction Reaction in PEM Fuel Cell.* Advanced Energy Materials, 2022. **12**(32): p. 2201600.
36. Barbir F., *Chapter Ten - Fuel Cell Applications*, in *PEM Fuel Cells (Second Edition)*, F. Barbir, Editor. 2013, Academic Press: Boston. p. 373-434.
37. Giorgi L. and F. Leccese, *Fuel cells: Technologies and applications.* The Open Fuel Cells Journal, 2013. **6**(1).
38. Brouzgou A., A. Demin, and P.E. Tsiakaras, *Interconnects for Solid Oxide Fuel Cells*, in *Advances in Medium and High Temperature Solid Oxide Fuel Cell Technology*. 2017. p. 119-153.

39. Mekhilef S., R. Saidur, and A. Safari, *Comparative study of different fuel cell technologies.* Renewable and Sustainable Energy Reviews, 2012. **16**(1): p. 981-989.
40. Sharaf O.Z. and M.F. Orhan, *An overview of fuel cell technology: Fundamentals and applications.* Renewable and Sustainable Energy Reviews, 2014. **32**: p. 810-853.
41. Chen Z., J. Liu, B. Yang, M. Lin, C. Molochas, P. Tsiakaras, and P. Shen, *Two-stage confinement derived small-sized highly ordered L10-PtCoZn for effective oxygen reduction catalysis in PEM fuel cells.* Journal of Colloid and Interface Science, 2023. **652**: p. 388-404.
42. Singhal S.C., *Advances in solid oxide fuel cell technology.* Solid State Ionics, 2000. **135**(1): p. 305-313.
43. Minh N.Q., *Solid oxide fuel cell technology—features and applications.* Solid State Ionics, 2004. **174**(1): p. 271-277.
44. Guaitolini S.V.M., I. Yahyaoui, J.F. Fardin, L.F. Encarnação, and F. Tadeo. *A review of fuel cell and energy cogeneration technologies*. in *2018 9th International Renewable Energy Congress (IREC)*. 2018.
45. Bischoff M., *Molten carbonate fuel cells: A high temperature fuel cell on the edge to commercialization.* Journal of Power Sources, 2006. **160**(2): p. 842-845.
46. Sammes N., R. Bove, and K. Stahl, *Phosphoric acid fuel cells: Fundamentals and applications.* Current Opinion in Solid State and Materials Science, 2004. **8**(5): p. 372-378.
47. Ferriday T.B. and P.H. Middleton, *Alkaline fuel cell technology - A review.* International Journal of Hydrogen Energy, 2021. **46**(35): p. 18489-18510.
48. McLean G.F., T. Niet, S. Prince-Richard, and N. Djilali, *An assessment of alkaline fuel cell technology.* International Journal of Hydrogen Energy, 2002. **27**(5): p. 507-526.
49. Chen Q., Z. Chen, A. Ali, Y. Luo, H. Feng, Y. Luo, P. Tsiakaras, and P. Kang Shen, *Shell-thickness-dependent Pd@PtNi core–shell nanosheets for efficient oxygen reduction reaction.* Chemical Engineering Journal, 2022. **427**: p. 131565.
50. Tsiakaras P., C. Athanasiou, G. Marnellos, M. Stoukides, J.E. ten Elshof, and H.J.M. Bouwmeester, *Methane activation on a La0.6Sr0.4Co0.8Fe0.2O3 perovskite: Catalytic and electrocatalytic results.* Applied Catalysis A: General, 1998. **169**(2): p. 249-261.
51. Tsiakaras P. and C.G. Vayenas, *Oxidative Coupling of CH4 on Ag Catalyst-Electrodes Deposited on ZrO2 (8 mol% Y2O3).* Journal of Catalysis, 1993. **144**(1): p. 333-347.
52. Gorbova E., V. Maragou, D. Medvedev, A. Demin, and P. Tsiakaras, *Influence of sintering additives of transition metals on the properties of gadolinium-doped barium cerate.* Solid State Ionics, 2008. **179**(21): p. 887-890.
53. Shah S.S.A., T. Najam, C. Molochas, M.A. Nazir, A. Brouzgou, M.S. Javed, A.u. Rehman, and P. Tsiakaras, *Nanostructure Engineering of Metal–Organic Derived Frameworks: Cobalt Phosphide Embedded in Carbon Nanotubes as an Efficient ORR Catalyst.* Molecules, 2021. **26**(21): p. 6672.
54. Sharma S. and S.K. Ghoshal, *Hydrogen the future transportation fuel: From production to applications.* Renewable and Sustainable Energy Reviews, 2015. **43**: p. 1151-1158.
55. Abdalla A.M., S. Hossain, O.B. Nisfindy, A.T. Azad, M. Dawood, and A.K. Azad, *Hydrogen production, storage, transportation and key challenges with applications: A review.* Energy Conversion and Management, 2018. **165**: p. 602-627.
56. Yu C., J. Lu, L. Luo, F. Xu, P.K. Shen, P. Tsiakaras, and S. Yin, *Bifunctional catalysts for overall water splitting: CoNi oxyhydroxide nanosheets electrodeposited on titanium sheets.* Electrochimica Acta, 2019. **301**: p. 449-457.
57. Yan L., B. Zhang, J. Zhu, Y. Li, P. Tsiakaras, and P. Kang Shen, *Electronic modulation of cobalt phosphide nanosheet arrays via copper doping for highly efficient neutral-pH overall water splitting.* Applied Catalysis B: Environmental, 2020. **265**: p. 118555.
58. Saad A., Y. Gao, K.A. Owusu, W. Liu, Y. Wu, A. Ramiere, H. Guo, P. Tsiakaras, and X. Cai, *Ternary Mo2NiB2 as a Superior Bifunctional Electrocatalyst for Overall Water Splitting.* Small, 2022. **18**(6): p. 2104303.

59. Cen J., E. Jiang, Y. Zhu, Z. Chen, and P. Shen, *Enhanced electrocatalytic overall water splitting over novel one-pot synthesized Ru–MoO3- and Fe3O4–NiFe layered double hydroxide on Ni foam.* Renewable Energy, 2021. **177**.
60. Liu D., Z. Song, S. Cheng, Y. Wang, A. Saad, S. Deng, J. Shen, X. Huang, X. Cai, and P. Tsiakaras, *Mesoporous IrNiTa metal glass ribbon as a superior self-standing bifunctional catalyst for water electrolysis.* Chemical Engineering Journal, 2022. **431**: p. 134210.
61. Zhang B., J. Shan, W. Wang, P. Tsiakaras, and Y. Li, *Oxygen Vacancy and Core–Shell Heterojunction Engineering of Anemone-Like CoP@CoOOH Bifunctional Electrocatalyst for Efficient Overall Water Splitting.* Small, 2022. **18**(12): p. 2106012.
62. Long G.-f., K. Wan, M.-y. Liu, Z.-x. Liang, J.-h. Piao, and P. Tsiakaras, *Active sites and mechanism on nitrogen-doped carbon catalyst for hydrogen evolution reaction*. Journal of Catalysis, 2017. **348**: p. 151-159.
63. Zhang L., J. Lu, S. Yin, L. Luo, S. Jing, A. Brouzgou, J. Chen, P.K. Shen, and P. Tsiakaras, *One-pot synthesized boron-doped RhFe alloy with enhanced catalytic performance for hydrogen evolution reaction.* Applied Catalysis B: Environmental, 2018. **230**: p. 58-64.
64. Goula M.A., S.K. Kontou, and P.E. Tsiakaras, *Hydrogen production by ethanol steam reforming over a commercial Pd/γ-Al2O3 catalyst.* Applied Catalysis B: Environmental, 2004. **49**(2): p. 135-144.
65. Yu C., F. Xu, L. Luo, H.S. Abbo, S.J.J. Titinchi, P.K. Shen, P. Tsiakaras, and S. Yin, *Bimetallic Ni–Co phosphide nanosheets self-supported on nickel foam as high-performance electrocatalyst for hydrogen evolution reaction.* Electrochimica Acta, 2019. **317**: p. 191-198.
66. Long B., H. Yang, M. Li, M.-S. Balogun, W. Mai, G. Ouyang, Y. Tong, P. Tsiakaras, and S. Song, *Interface charges redistribution enhanced monolithic etched copper foam-based Cu2O layer/TiO2 nanodots heterojunction with high hydrogen evolution electrocatalytic activity.* Applied Catalysis B: Environmental, 2019. **243**: p. 365-372.
67. Lu J., Z. Tang, L. Luo, S. Yin, P. Kang Shen, and P. Tsiakaras, *Worm-like S-doped RhNi alloys as highly efficient electrocatalysts for hydrogen evolution reaction.* Applied Catalysis B: Environmental, 2019. **255**: p. 117737.
68. Jing S., D. Wang, S. Yin, J. Lu, P.K. Shen, and P. Tsiakaras, *P-doped CNTs encapsulated nickel hybrids with flower-like structure as efficient catalysts for hydrogen evolution reaction.* Electrochimica Acta, 2019. **298**: p. 142-149.
69. Xu P., L. Qiu, L. Wei, Y. Liu, D. Yuan, Y. Wang, and P. Tsiakaras, *Efficient overall water splitting over Mn doped Ni2P microflowers grown on nickel foam.* Catalysis Today, 2020. **355**: p. 815-821.
70. Xie Z., Z. Song, J. Zhao, Y. Li, X. Cai, D. Liu, J. Shen, and P. Tsiakaras, *CuZr Metal Glass Powder as Electrocatalysts for Hydrogen and Oxygen Evolution Reactions.* Catalysts, 2022. **12**(11): p. 1378.
71. Xie W., J. Huang, L. Huang, S. Geng, S. Song, P. Tsiakaras, and Y. Wang, *Novel fluorine-doped cobalt molybdate nanosheets with enriched oxygen-vacancies for improved oxygen evolution reaction activity.* Applied Catalysis B: Environmental, 2022. **303**: p. 120871.
72. Saad A., D. Liu, Y. Wu, Z. Song, Y. Li, T. Najam, K. Zong, P. Tsiakaras, and X. Cai, *Ag nanoparticles modified crumpled borophene supported Co3O4 catalyst showing superior oxygen evolution reaction (OER) performance.* Applied Catalysis B: Environmental, 2021. **298**: p. 120529.
73. Shah S.S.A., N.A. Khan, M. Imran, M. Rashid, M.K. Tufail, A.U. Rehman, G. Balkourani, M. Sohail, T. Najam, and P. Tsiakaras, *Recent Advances in Transition Metal Tellurides (TMTs) and Phosphides (TMPs) for Hydrogen Evolution Electrocatalysis.* Membranes (Basel), 2023. **13**(1).
74. Santos D., C. Sequeira, and J. Figueiredo, *Hydrogen production by alkaline water electrolysis.* Química Nova, 2012. **36**: p. 1176-1193.
75. Rashid M., M. Al Mesfer, H. Naseem, and M. Danish, *Hydrogen Production by Water Electrolysis: A Review of Alkaline Water Electrolysis, PEM Water Electrolysis and High Temperature Water Electrolysis.* International Journal of Engineering and Advanced Technology, 2015. **ISSN**: p. 2249-8958.

76. Falcão D.S. and A.M.F.R. Pinto, *A review on PEM electrolyzer modelling: Guidelines for beginners.* Journal of Cleaner Production, 2020. **261**: p. 121184.
77. Görgün H., *Dynamic modelling of a proton exchange membrane (PEM) electrolyzer.* International Journal of Hydrogen Energy, 2006. **31**(1): p. 29-38.
78. Ni M., M.K.H. Leung, and D.Y.C. Leung, *Technological development of hydrogen production by solid oxide electrolyzer cell (SOEC).* International Journal of Hydrogen Energy, 2008. **33**(9): p. 2337-2354.
79. Nechache A. and S. Hody, *Alternative and innovative solid oxide electrolysis cell materials: A short review.* Renewable and Sustainable Energy Reviews, 2021. **149**: p. 111322.
80. Şahin M.E., F. Blaabjerg, and A. Sangwongwanich, *A Comprehensive Review on Supercapacitor Applications and Developments.* Energies, 2022. **15**(3): p. 674.
81. Iro Z.S., C. Subramani, and S.S. Dash, *A Brief Review on Electrode Materials for Supercapacitor.* International Journal of Electrochemical Science, 2016. **11**(12): p. 10628-10643.
82. Gautham Prasad G., N. Shetty, S. Thakur, Rakshitha, and K.B. Bommegowda, *Supercapacitor technology and its applications: a review.* IOP Conference Series: Materials Science and Engineering, 2019. **561**(1): p. 012105.
83. Pan H., J. Li, and Y. Feng, *Carbon Nanotubes for Supercapacitor.* Nanoscale Research Letters, 2010. **5**(3): p. 654.
84. Rafik F., H. Gualous, R. Gallay, A. Crausaz, and A. Berthon, *Frequency, thermal and voltage supercapacitor characterization and modeling.* Journal of Power Sources, 2007. **165**(2): p. 928-934.
85. Chen R., M. Yu, R.P. Sahu, I.K. Puri, and I. Zhitomirsky, *The Development of Pseudocapacitor Electrodes and Devices with High Active Mass Loading.* Advanced Energy Materials, 2020. **10**(20): p. 1903848.
86. Karthikeyan S., B. Narenthiran, A. Sivanantham, L.D. Bhatlu, and T. Maridurai, *Supercapacitor: Evolution and review.* Materials Today: Proceedings, 2021. **46**: p. 3984-3988.
87. Yang W., M. Ni, X. Ren, Y. Tian, N. Li, Y. Su, and X. Zhang, *Graphene in Supercapacitor Applications.* Current Opinion in Colloid & Interface Science, 2015. **20**(5): p. 416-428.
88. Pal B., S. Yang, S. Ramesh, V. Thangadurai, and R. Jose, *Electrolyte selection for supercapacitive devices: a critical review.* Nanoscale Advances, 2019. **1**(10): p. 3807-3835.
89. Eftekhari A., L. Li, and Y. Yang, *Polyaniline supercapacitors.* Journal of Power Sources, 2017. **347**: p. 86-107.
90. Afzal A., F.A. Abuilaiwi, A. Habib, M. Awais, S.B. Waje, and M.A. Atieh, *Polypyrrole/carbon nanotube supercapacitors: Technological advances and challenges.* Journal of Power Sources, 2017. **352**: p. 174-186.
91. Zhong C., Y. Deng, W. Hu, J. Qiao, L. Zhang, and J. Zhang, *A review of electrolyte materials and compositions for electrochemical supercapacitors.* Chemical Society Reviews, 2015. **44**(21): p. 7484-7539.
92. Chodankar N.R., H.D. Pham, A.K. Nanjundan, J.F.S. Fernando, K. Jayaramulu, D. Golberg, Y.-K. Han, and D.P. Dubal, *True Meaning of Pseudocapacitors and Their Performance Metrics: Asymmetric versus Hybrid Supercapacitors.* Small, 2020. **16**(37): p. 2002806.
93. Raza W., F. Ali, N. Raza, Y. Luo, K.-H. Kim, J. Yang, S. Kumar, A. Mehmood, and E.E. Kwon, *Recent advancements in supercapacitor technology.* Nano Energy, 2018. **52**: p. 441-473.
94. Muzaffar A., M.B. Ahamed, K. Deshmukh, and J. Thirumalai, *A review on recent advances in hybrid supercapacitors: Design, fabrication and applications.* Renewable and Sustainable Energy Reviews, 2019. **101**: p. 123-145.
95. Chatterjee D.P. and A.K. Nandi, *A review on the recent advances in hybrid supercapacitors.* Journal of Materials Chemistry A, 2021. **9**(29): p. 15880-15918.
96. Volkov A., E. Gorbova, A. Vylkov, D. Medvedev, A. Demin, and P. Tsiakaras, *Design and applications of potentiometric sensors based on proton-conducting ceramic materials. A brief review.* Sensors and Actuators B: Chemical, 2017. **244**: p. 1004-1015.

97. Balkourani G., A. Brouzgou, C.L. Vecchio, A.S. Aricò, V. Baglio, and P. Tsiakaras, *Selective electro-oxidation of dopamine on Co or Fe supported onto N-doped ketjenblack.* Electrochimica Acta, 2022. **409**: p. 139943.
98. Brouzgou A., E. Gorbova, Y. Wang, S. Jing, A. Seretis, Z. Liang, and P. Tsiakaras, *Nitrogen-doped 3D hierarchical ordered mesoporous carbon supported palladium electrocatalyst for the simultaneous detection of ascorbic acid, dopamine, and glucose.* Ionics, 2019. **25**(12): p. 6061-6070.
99. Yuan X., D. Yuan, F. Zeng, W. Zou, F. Tzorbatzoglou, P. Tsiakaras, and Y. Wang, *Preparation of graphitic mesoporous carbon for the simultaneous detection of hydroquinone and catechol.* Applied Catalysis B: Environmental, 2013. **129**: p. 367-374.
100. Kalyakin A., A.K. Demin, E. Gorbova, A. Volkov, and P.E. Tsiakaras, *Sensor Based on a Solid Oxide Electrolyte for Measuring the Water-Vapor and Hydrogen Content in Air.* Catalysts, 2022. **12**(12): p. 1558.
101. Dunyushkina L.A., A.A. Pankratov, V.P. Gorelov, A. Brouzgou, and P. Tsiakaras, *Deposition and Characterization of Y-doped CaZrO3 Electrolyte Film on a Porous SrTi0.8Fe0.2O3-δ Substrate.* Electrochimica Acta, 2016. **202**: p. 39-46.
102. Ma L., L. Wang, R. Chen, K. Chang, S. Wang, X. Hu, X. Sun, Z. Lu, H. Sun, Q. Guo, M. Jiang, and J. Hu, *A Low Cost Compact Measurement System Constructed Using a Smart Electrochemical Sensor for the Real-Time Discrimination of Fruit Ripening.* Sensors, 2016. **16**(4): p. 501.
103. Kalyakin A., A. Demin, E. Gorbova, A. Volkov, and P. Tsiakaras, *Combined amperometric-potentiometric oxygen sensor.* Sensors and Actuators B: Chemical, 2020. **313**: p. 127999.
104. Kalyakin A., A. Volkov, A. Demin, E. Gorbova, and P. Tsiakaras, *Determination of nitrous oxide concentration using a solid-electrolyte amperometric sensor.* Sensors and Actuators B: Chemical, 2019. **297**: p. 126750.
105. Kalyakin A., A. Volkov, J. Lyagaeva, D. Medvedev, A. Demin, and P. Tsiakaras, *Combined amperometric and potentiometric hydrogen sensors based on BaCe0.7Zr0.1Y0.2O3−δ proton-conducting ceramic.* Sensors and Actuators B: Chemical, 2016. **231**: p. 175-182.
106. Gorbova E., G. Balkourani, C. Molochas, D. Sidiropoulos, A. Brouzgou, A. Demin, and P. Tsiakaras, *Brief Review on High-Temperature Electrochemical Hydrogen Sensors.* Catalysts, 2022. **12**(12): p. 1647.
107. Gorbova E., F. Tzorbatzoglou, C. Molochas, D. Chloros, A. Demin, and P. Tsiakaras, *Fundamentals and Principles of Solid-State Electrochemical Sensors for High Temperature Gas Detection.* Catalysts, 2022. **12**(1): p. 1.
108. Balkourani G., A. Brouzgou, and P. Tsiakaras, *A review on recent advancements in electrochemical detection of dopamine using carbonaceous nanomaterials.* Carbon, 2023. **213**: p. 118281.
109. Kalyakin A., G. Fadeyev, A. Demin, E. Gorbova, A. Brouzgou, A. Volkov, and P. Tsiakaras, *Application of Solid oxide proton-conducting electrolytes for amperometric analysis of hydrogen in H2+N2+H2O gas mixtures.* Electrochimica Acta, 2014. **141**: p. 120-125.
110. Kalyakin A., J. Lyagaeva, D. Medvedev, A. Volkov, A. Demin, and P. Tsiakaras, *Characterization of proton-conducting electrolyte based on La0.9Sr0.1YO3– and its application in a hydrogen amperometric sensor.* Sensors and Actuators B: Chemical, 2016. **225**: p. 446-452.
111. Fadeyev G., A. Kalyakin, E. Gorbova, A. Brouzgou, A. Demin, A. Volkov, and P. Tsiakaras, *A simple and low-cost amperometric sensor for measuring H2, CO, and CH4.* Sensors and Actuators B: Chemical, 2015. **221**: p. 879-883.
112. Balkourani G., A. Brouzgou, M. Archonti, N. Papandrianos, S. Song, and P. Tsiakaras, *Emerging materials for the electrochemical detection of COVID-19.* Journal of Electroanalytical Chemistry, 2021. **893**: p. 115289.
113. Brouzgou A., S. Song, and P. Tsiakaras, *Carbon-supported PdSn and Pd3Sn2 anodes for glucose electrooxidation in alkaline media.* Applied Catalysis B: Environmental, 2014. **158-159**: p. 209-216.

114. Zhao F., J. Xiao, S. Geng, Y. Wang, P. Tsiakaras, and S. Song, *Novel Fe7S8/C nanocomposites with accelerating iron cycle for enhanced heterogeneous electro-Fenton degradation of dyes.* Electrochimica Acta, 2022. **436**: p. 141381.
115. Wang A., H. Liang, F. Chen, X. Tian, S. Jing, and P. Tsiakaras, *Preparation and characterization of novel NiIn2S4/UiO-66 photocatalysts for the efficient degradation of antibiotics in water.* Chemosphere, 2022. **307**: p. 135699.
116. Chen Z., S. Geng, J. Xiao, F. Zhao, K. Wang, Y. Wang, P. Tsiakaras, and S. Song, *Understanding the selectivity trend of water and sulfate (SO42−) oxidation on metal oxides: On-site synthesis of persulfate, H2O2 for wastewater treatment.* Chemical Engineering Journal, 2022. **431**: p. 134332.
117. Liu D., A. Barbar, T. Najam, M.S. Javed, J. Shen, P. Tsiakaras, and X. Cai, *Single noble metal atoms doped 2D materials for catalysis.* Applied Catalysis B: Environmental, 2021. **297**: p. 120389.
118. Fadeyev G., A. Kalakin, A. Demin, A. Volkov, A. Brouzgou, and P. Tsiakaras, *Electrodes for solid electrolyte sensors for the measurement of CO and H2 content in air.* International Journal of Hydrogen Energy, 2013. **38**(30): p. 13484-13490.
119. Liu Y., X. Zhang, Z. Chen, X. Zhang, P. Tsiakaras, and P.K. Shen, *Electrocatalytic reduction of nitrogen on FeAg/Si for ammonia synthesis: A simple strategy for continuous regulation of faradaic efficiency by controlling H+ ions transfer rate.* Applied Catalysis B: Environmental, 2021. **283**: p. 119606.
120. Balkourani G., T. Damartzis, A. Brouzgou, and P. Tsiakaras, *Cost Effective Synthesis of Graphene Nanomaterials for Non-Enzymatic Electrochemical Sensors for Glucose: A Comprehensive Review.* Sensors, 2022. **22**(1): p. 355.
121. Dell R.M., *Batteries: fifty years of materials development.* Solid State Ionics, 2000. **134**(1): p. 139-158.
122. ENGINEERING A. *ANGSTROM ENGINEERING*: https://angstromengineering.com/applications/thin-film-batteries/.
123. Köhler U., C. Antonius, and P. Bäuerlein, *Advances in alkaline batteries.* Journal of Power Sources, 2004. **127**(1): p. 45-52.
124. Islam J., R. Anwar, M. Shareef, H.M. Zabed, J.N. Sahu, X. Qi, M.U. Khandaker, A. Ragauskas, I. Boukhris, M.R. Rahman, and F. Islam Chowdhury, *Rechargeable metal-metal alkaline batteries: Recent advances, current issues and future research strategies.* Journal of Power Sources, 2023. **563**: p. 232777.
125. Bullock K.R., *Lead/acid batteries.* Journal of Power Sources, 1994. **51**(1): p. 1-17.
126. Tian X., Y. Wu, Y. Gong, and T. Zuo, *The lead-acid battery industry in China: outlook for production and recycling.* Waste Management & Research, 2015. **33**(11): p. 986-994.
127. Bukhari S.M.A.S., J. Maqsood, M.Q. Baig, S. Ashraf, and T.A. Khan. *Comparison of Characteristics -- Lead Acid, Nickel Based, Lead Crystal and Lithium Based Batteries*. in *2015 17th UKSim-AMSS International Conference on Modelling and Simulation (UKSim)*. 2015.
128. Wang Y., B. Liu, Q. Li, S. Cartmell, S. Ferrara, Z.D. Deng, and J. Xiao, *Lithium and lithium ion batteries for applications in microelectronic devices: A review.* Journal of Power Sources, 2015. **286**: p. 330-345.
129. Lisbona D. and T. Snee, *A review of hazards associated with primary lithium and lithium-ion batteries.* Process Safety and Environmental Protection, 2011. **89**(6): p. 434-442.
130. Tarabay J. and N. Karami. *Nickel Metal Hydride battery: Structure, chemical reaction, and circuit model*. in *2015 Third International Conference on Technological Advances in Electrical, Electronics and Computer Engineering (TAEECE)*. 2015.
131. Dehghani-Sanij A.R., E. Tharumalingam, M.B. Dusseault, and R. Fraser, *Study of energy storage systems and environmental challenges of batteries.* Renewable and Sustainable Energy Reviews, 2019. **104**: p. 192-208.
132. Lai X., Y. Huang, H. Gu, C. Deng, X. Han, X. Feng, and Y. Zheng, *Turning waste into wealth: A systematic review on echelon utilization and material recycling of retired lithium-ion batteries.* Energy Storage Materials, 2021. **40**: p. 96-123.

133. Kim S., J. Bang, J. Yoo, Y. Shin, J. Bae, J. Jeong, K. Kim, P. Dong, and K. Kwon, *A comprehensive review on the pretreatment process in lithium-ion battery recycling.* Journal of Cleaner Production, 2021. **294**: p. 126329.
134. Latini D., M. Vaccari, M. Lagnoni, M. Orefice, F. Mathieux, J. Huisman, L. Tognotti, and A. Bertei, *A comprehensive review and classification of unit operations with assessment of outputs quality in lithium-ion battery recycling.* Journal of Power Sources, 2022. **546**: p. 231979.
135. Martins L.S., L.F. Guimarães, A.B. Botelho Junior, J.A.S. Tenório, and D.C.R. Espinosa, *Electric car battery: An overview on global demand, recycling and future approaches towards sustainability.* Journal of Environmental Management, 2021. **295**: p. 113091.
136. Gao S.-j., W.-f. Liu, D.-j. Fu, and X.-g. Liu, *Research progress on recovering the components of spent Li-ion batteries.* New Carbon Materials, 2022. **37**(3): p. 435-460.
137. Nitta N., F. Wu, J.T. Lee, and G. Yushin, *Li-ion battery materials: present and future.* Materials Today, 2015. **18**(5): p. 252-264.
138. Backhaus R., *Battery Raw Materials - Where from and Where to?* ATZ worldwide, 2021. **123**(9): p. 8-13.
139. Arambarri J., J. Hayden, M. Elkurdy, B. Meyers, Z.S. Abu Hamatteh, B. Abbassi, and W. Omar, *Lithium ion car batteries: Present analysis and future predictions.* Environmental Engineering Research, 2019. **24**(4): p. 699-710.
140. Zhang G., Y. Shi, H. Wang, L. Jiang, X. Yu, S. Jing, S. Xing, and P. Tsiakaras, *A facile route to achieve ultrafine Fe2O3 nanorods anchored on graphene oxide for application in lithium-ion battery.* Journal of Power Sources, 2019. **416**: p. 118-124.
141. Miao Y., P. Hynan, A. von Jouanne, and A. Yokochi, *Current Li-Ion Battery Technologies in Electric Vehicles and Opportunities for Advancements.* Energies, 2019. **12**(6): p. 1074.
142. Kaya M., *State-of-the-art lithium-ion battery recycling technologies.* Circular Economy, 2022. **1**(2): p. 100015.
143. Manthiram A., *A reflection on lithium-ion battery cathode chemistry.* Nature Communications, 2020. **11**(1): p. 1550.
144. Schipper F., E.M. Erickson, C. Erk, J.-Y. Shin, F.F. Chesneau, and D. Aurbach, *Review—Recent Advances and Remaining Challenges for Lithium Ion Battery Cathodes.* Journal of The Electrochemical Society, 2017. **164**(1): p. A6220.
145. Harper G., R. Sommerville, E. Kendrick, L. Driscoll, P. Slater, R. Stolkin, A. Walton, P. Christensen, O. Heidrich, S. Lambert, A. Abbott, K. Ryder, L. Gaines, and P. Anderson, *Recycling lithium-ion batteries from electric vehicles.* Nature, 2019. **575**(7781): p. 75-86.
146. Najam T., S.S.A. Shah, L. Peng, M.S. Javed, M. Imran, M.-Q. Zhao, and P. Tsiakaras, *Synthesis and nano-engineering of MXenes for energy conversion and storage applications: Recent advances and perspectives.* Coordination Chemistry Reviews, 2022. **454**: p. 214339.
147. Rahardian S., B.A. Budiman, P.L. Sambegoro, and I.P. Nurprasetio. *Review of Solid-State Battery Technology Progress*. in *2019 6th International Conference on Electric Vehicular Technology (ICEVT)*. 2019.
148. Manthiram A., Y. Fu, and Y.-S. Su, *Challenges and Prospects of Lithium–Sulfur Batteries.* Accounts of Chemical Research, 2013. **46**(5): p. 1125-1134.
149. Jing S., P. Ding, Y. Zhang, H. Liang, S. Yin, and P. Tsiakaras, *Lithium-sulfur battery cathodes made of porous biochar support CoFe@NC metal nanoparticles derived from Prussian blue analogues.* Ionics, 2019. **25**(11): p. 5297-5304.
150. Nazar L.F., M. Cuisinier, and Q. Pang, *Lithium-sulfur batteries.* MRS Bulletin, 2014. **39**(5): p. 436-442.
151. Kolosnitsyn V. and E. Karaseva, *Lithium-sulfur batteries: Problems and solutions.* Russian Journal of Electrochemistry, 2008. **44**: p. 506-509.
152. Capsoni D., M. Bini, S. Ferrari, and E. Quartarone, *Recent advances in the development of Li–air batteries.* Journal of Power Sources, 2012. **220**: p. 253–263.

153. Kraytsberg A. and Y. Ein-Eli, *Review on Li–air batteries—Opportunities, limitations and perspective.* Journal of Power Sources, 2011. **196**(3): p. 886-893.

154. Christensen J., P. Albertus, R.S. Sanchez-Carrera, T. Lohmann, B. Kozinsky, R. Liedtke, J. Ahmed, and A. Kojic, *A Critical Review of Li/Air Batteries.* Journal of The Electrochemical Society, 2011. **159**(2): p. R1.

155. Liang H., X. Gong, L. Jia, F. Chen, Z. Rao, S. Jing, and P. Tsiakaras, *Highly efficient Li-O2 batteries based on self-standing NiFeP@NC/BC cathode derived from biochar supported Prussian blue analogues.* Journal of Electroanalytical Chemistry, 2020. **867**: p. 114124.

156. Jing S., Y. Zhang, F. Chen, H. Liang, S. Yin, and P. Tsiakaras, *Novel and highly efficient cathodes for Li-O2 batteries: 3D self-standing NiFe@NC-functionalized N-doped carbon nanonet derived from Prussian blue analogues/biomass composites.* Applied Catalysis B: Environmental, 2019. **245**: p. 721-732.

157. Liang H., Y. Zhang, F. Chen, S. Jing, and S. Yin, *A novel NiFe@NC-functionalized N-doped carbon microtubule network derived from biomass as a highly efficient 3D free-standing cathode for Li-CO2 batteries.* Applied Catalysis B: Environmental, 2018. **244**.

158. Liang H., F. Chen, M. Zhang, S. Jing, B. Shen, S. Yin, and P. Tsiakaras, *Highly performing free standing cathodic electrocatalysts for Li-O2 batteries: CoNiO2 nanoneedle arrays supported on N-doped carbon nanonet.* Applied Catalysis A: General, 2019. **574**: p. 114-121.

159. Liang H., Z. Gai, F. Chen, S. Jing, W. Kan, B. Zhao, S. Yin, and P. Tsiakaras, *Fe3C decorated wood-derived integral N-doped C cathode for rechargeable Li-O2 batteries.* Applied Catalysis B: Environmental, 2023. **324**: p. 122203.

160. Jing S., Z. Gai, M. Li, S. Tang, S. Ji, H. Liang, F. Chen, S. Yin, and P. Tsiakaras, *Enhanced electrochemical performance of a Li-O2 battery using Co and N co-doped biochar cathode prepared in molten salt medium.* Electrochimica Acta, 2022. **410**: p. 140002.

161. Liang H., L. Jia, F. Chen, S. Jing, and P. Tsiakaras, *A novel efficient electrocatalyst for oxygen reduction and oxygen evolution reaction in Li-O2 batteries: Co/CoSe embedded N, Se co-doped carbon.* Applied Catalysis B: Environmental, 2022. **317**: p. 121698.

162. Jing S., J. Chen, M. Li, H. Liang, P. Kannan, and P. Tsiakaras, *Rechargeable non-aqueous lithium-O2 batteries: Novel bimetallic (Ni-Cu) conductive coordination polymer cathodes.* Journal of Energy Storage, 2023. **66**: p. 107331.

163. Toussaint G., P. Stevens, L. Akrour, R. Rouget, and F. Fourgeot, *Development of a Rechargeable Zinc-Air Battery.* ECS Transactions, 2010. **28**(32): p. 25.

164. Chen P., K. Zhang, D. Tang, W. Liu, F. Meng, Q. Huang, and J. Liu, *Recent Progress in Electrolytes for Zn–Air Batteries.* Frontiers in Chemistry, 2020. **8**.

165. Lyu D., S. Yao, A. Ali, Z.Q. Tian, P. Tsiakaras, and P.K. Shen, *N, S Codoped Carbon Matrix-Encapsulated Co9S8 Nanoparticles as a Highly Efficient and Durable Bifunctional Oxygen Redox Electrocatalyst for Rechargeable Zn–Air Batteries.* Advanced Energy Materials, 2021. **11**(28): p. 2101249.

166. Li Y., S.H. Talib, D. Liu, K. Zong, A. Saad, Z. Song, J. Zhao, W. Liu, F. Liu, Q. Ji, P. Tsiakaras, and X. Cai, *Improved oxygen evolution reaction performance in Co0.4Mn0.6O2 nanosheets through Triple-doping (Cu, P, N) strategy and its application to Zn-air battery.* Applied Catalysis B: Environmental, 2023. **320**: p. 122023.

167. Saad A., Y. Gao, A. Ramiere, T. Chu, G. Yasin, Y. Wu, S. Ibraheem, M. Wang, H. Guo, P. Tsiakaras, and X. Cai, *Understanding the Surface Reconstruction on Ternary WxCoBx for Water Oxidation and Zinc–Air Battery Applications.* Small, 2022. **18**(17): p. 2201067.

168. Abdalla A.M., M.F. Abdullah, M.K. Dawood, B. Wei, Y. Subramanian, A.T. Azad, S. Nourin, S. Afroze, J. Taweekun, and A.K. Azad, *Innovative lithium-ion battery recycling: Sustainable process for recovery of critical materials from lithium-ion batteries.* Journal of Energy Storage, 2023. **67**: p. 107551.

169. Duan X., W. Zhu, Z. Ruan, M. Xie, J. Chen, and X. Ren, *Recycling of Lithium Batteries—A Review.* Energies, 2022. **15**(5): p. 1611.

170. Pagliaro M. and F. Meneguzzo, *Lithium battery reusing and recycling: A circular economy insight.* Heliyon, 2019. **5**(6): p. e01866.
171. Velázquez-Martínez O., J. Valio, A. Santasalo-Aarnio, M. Reuter, and R. Serna-Guerrero, *A Critical Review of Lithium-Ion Battery Recycling Processes from a Circular Economy Perspective.* Batteries, 2019. **5**(4): p. 68.
172. Ma X., L. Azhari, and Y. Wang, *Li-ion battery recycling challenges.* Chem, 2021. **7**(11): p. 2843-2847.
173. Tao Y., C.D. Rahn, L.A. Archer, and F. You, *Second life and recycling: Energy and environmental sustainability perspectives for high-performance lithium-ion batteries.* Science Advances, 2021. **7**(45): p. eabi7633.
174. Alfaro-Algaba M. and F.J. Ramirez, *Techno-economic and environmental disassembly planning of lithium-ion electric vehicle battery packs for remanufacturing.* Resources, Conservation and Recycling, 2020. **154**: p. 104461.
175. Foster M., P. Isely, C.R. Standridge, and M.M. Hasan, *Feasibility assessment of remanufacturing, repurposing, and recycling of end of vehicle application lithium-ion batteries.* Journal of Industrial Engineering and Management; Vol 7, No 3 (2014)DO - 10.3926/jiem.939, 2014.
176. Fan M., X. Chang, Q. Meng, L.-J. Wan, and Y.-G. Guo, *Progress in the sustainable recycling of spent lithium-ion batteries.* SusMat, 2021. **1**(2): p. 241-254.
177. Reiner Sojka Q.P., Laura Billmann, *Comparative study of Li-ion battery recycling processes*. September 2020: Krefeld, Germany.
178. Halleux V., *New EU regulatory framework for batteries Setting sustainability requirements*, E.E.P.R. Service), Editor. 2022.
179. Bajolle H., M. Lagadic, and N. Louvet, *The future of lithium-ion batteries: Exploring expert conceptions, market trends, and price scenarios.* Energy Research & Social Science, 2022. **93**: p. 102850.
180. Slattery M., J. Dunn, and A. Kendall, *Transportation of electric vehicle lithium-ion batteries at end-of-life: A literature review.* Resources, Conservation and Recycling, 2021. **174**: p. 105755.
181. Chen M., X. Ma, B. Chen, R. Arsenault, P. Karlson, N. Simon, and Y. Wang, *Recycling End-of-Life Electric Vehicle Lithium-Ion Batteries.* Joule, 2019. **3**(11): p. 2622-2646.
182. Bobba S., F. Mathieux, and G.A. Blengini, *How will second-use of batteries affect stocks and flows in the EU? A model for traction Li-ion batteries.* Resources, Conservation and Recycling, 2019. **145**: p. 279-291.
183. Pinegar H. and Y. Smith, *Recycling of End-of-Life Lithium Ion Batteries, Part I: Commercial Processes.* Journal of Sustainable Metallurgy, 2019. **5**.
184. Podias A., A. Pfrang, F. Di Persio, A. Kriston, S. Bobba, F. Mathieux, M. Messagie, and L. Boon-Brett, *Sustainability Assessment of Second Use Applications of Automotive Batteries: Ageing of Li-Ion Battery Cells in Automotive and Grid-Scale Applications.* World Electric Vehicle Journal, 2018. **9**(2): p. 24.
185. Alexandra Wu R.L., *Current and Future State of the European Li-ion Battery Recycling Market.* 2022, IVL Swedish Environmental Research Institute.
186. Toro L., E. Moscardini, L. Baldassari, F. Forte, I. Falcone, J. Coletta, and L. Toro, *A Systematic Review of Battery Recycling Technologies: Advances, Challenges, and Future Prospects.* Energies, 2023. **16**(18): p. 6571.
187. Sun Y., *Lithium-Ion Battery Recycling: Challenges and Opportunities.* Highlights in Science, Engineering and Technology, 2023. **58**: p. 365-370.
188. Fujita T., H. Chen, K.-t. Wang, C.-l. He, Y.-b. Wang, G. Dodbiba, and Y.-z. Wei, *Reduction, reuse and recycle of spent Li-ion batteries for automobiles: A review.* International Journal of Minerals, Metallurgy and Materials, 2021. **28**(2): p. 179-192.
189. Ali H., H.A. Khan, and M. Pecht, *Preprocessing of spent lithium-ion batteries for recycling: Need, methods, and trends.* Renewable and Sustainable Energy Reviews, 2022. **168**: p. 112809.

190. Larouche F., F. Tedjar, K. Amouzegar, G. Houlachi, P. Bouchard, G.P. Demopoulos, and K. Zaghib, *Progress and Status of Hydrometallurgical and Direct Recycling of Li-Ion Batteries and Beyond.* Materials, 2020. **13**(3): p. 801.
191. Windisch-Kern S., E. Gerold, T. Nigl, A. Jandric, M. Altendorfer, B. Rutrecht, S. Scherhaufer, H. Raupenstrauch, R. Pomberger, H. Antrekowitsch, and F. Part, *Recycling chains for lithium-ion batteries: A critical examination of current challenges, opportunities and process dependencies.* Waste Management, 2022. **138**: p. 125-139.
192. Takacova Z., D. Orac, J. Klimko, and A. Miskufova, *Current Trends in Spent Portable Lithium Battery Recycling.* Materials (Basel), 2023. **16**(12).
193. Neumann J., M. Petranikova, M. Meeus, J.D. Gamarra, R. Younesi, M. Winter, and S. Nowak, *Recycling of Lithium-Ion Batteries—Current State of the Art, Circular Economy, and Next Generation Recycling.* Advanced Energy Materials, 2022. **12**(17): p. 2102917.
194. Tian G., G. Yuan, A. Aleksandrov, T. Zhang, Z. Li, A.M. Fathollahi-Fard, and M. Ivanov, *Recycling of spent Lithium-ion Batteries: A comprehensive review for identification of main challenges and future research trends.* Sustainable Energy Technologies and Assessments, 2022. **53**: p. 102447.
195. Wei Q., Y. Wu, S. Li, R. Chen, J. Ding, and C. Zhang, *Spent lithium ion battery (LIB) recycle from electric vehicles: A mini-review.* Science of The Total Environment, 2023. **866**: p. 161380.
196. Bai Y., N. Muralidharan, Y.-K. Sun, S. Passerini, M. Stanley Whittingham, and I. Belharouak, *Energy and environmental aspects in recycling lithium-ion batteries: Concept of Battery Identity Global Passport.* Materials Today, 2020. **41**: p. 304-315.
197. Makuza B., Q. Tian, X. Guo, K. Chattopadhyay, and D. Yu, *Pyrometallurgical options for recycling spent lithium-ion batteries: A comprehensive review.* Journal of Power Sources, 2021. **491**: p. 229622.
198. Baum Z.J., R.E. Bird, X. Yu, and J. Ma, *Lithium-Ion Battery Recycling–Overview of Techniques and Trends.* ACS Energy Letters, 2022. **7**(2): p. 712-719.
199. Abdelbaky M., J.R. Peeters, and W. Dewulf, *On the influence of second use, future battery technologies, and battery lifetime on the maximum recycled content of future electric vehicle batteries in Europe.* Waste Management, 2021. **125**: p. 1-9.