Batteries Energy Storage Systems: Review of materials, technologies, performances and challenges.

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***Abstract*— Due to the increase of renewable energy generation, different energy storage systems have been developed, leading to the study of different materials for the elaboration of batteries energy systems. This paper presents a brief review of the main technologies developed around secondary batteries such as lead-acid batteries, lithium ion batteries, sodium and nickel ion batteries, emphasizing the interest of the storage system, its main characteristics for operation at the positive and negative electrode level, its performance, efficiency ranges and its main disadvantages.**

Keywords—batteries energy system, anode, cathode, lithium, sodium, lead-acid, nickel-based, specific capacity.

I. INTRODUCTION

Nowadays, renewable energies represent an alternative for the reduction of the fossil and nuclear energy exploitation. Renewable energy is understood as energy from natural, unlimited and restorable sources [1]. Among these energies are from the wind, solar, geothermal, hydroelectric and biomass sources. In spite of the free access to these energies, they are intermittent due to the fluctuation of the source which originates from weather conditions, time of day or the season of the year. This intermittency can lead to problems of security and flexibility in the electric smart grids. Energy Storage Systems (ESS) are used as a solution to this problem by storing energy [2]. In addition, by choosing the appropriate ESS, the overall performance of smart grids can be beneficial for distribution and reliability of electricity [3].

Depending on the mechanism and the form in which the energy is stored, these systems can be classified into 5 major groups: mechanical, electrical, chemical, electrochemical and thermal [4], as shown in Figure 1. In Mechanical ESS the energy is stored in the form of kinetic energy as in flywheels or in potential energy as in compressed air systems and hydraulic pumps [5]. On the other hand, Electrical ESS are characterized by using the electrostatic and magnetic energy of capacitors and superconductors [6]. Meanwhile, Thermal ESS store energy in the form of heat as is the case with phase change materials and molten salt storage [7]. In addition to these systems, there are chemical ESS where energy is released or recovered following a chemical reaction as in the case of hydrogen and gas energy production systems [4]. Finally, Electrochemical ESS are characterized by storing the energy in the form of chemical bonds of the electrodes that compose this system [8]. Figure 2 shows a comparison between the different types of ESS previously mentioned, considering the storage capacity and their respective discharge time.

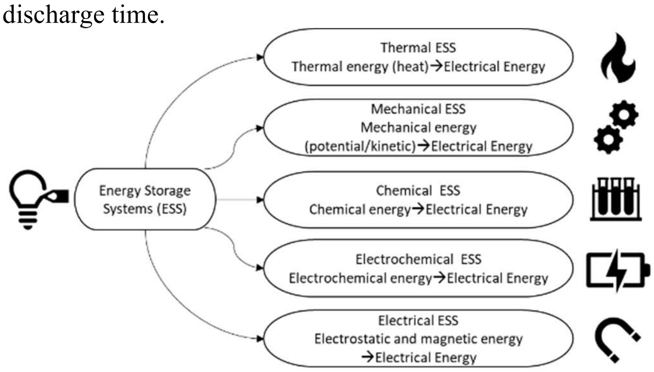

Fig. 1. Energy Storage System classification.

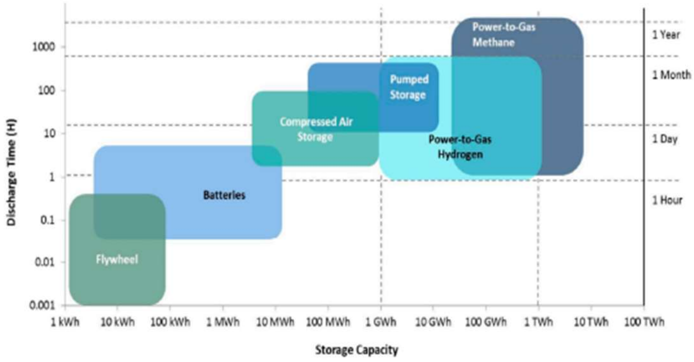

Fig. 2. Discharge time vs Storage capacity of Energy Storage Systems [9].

The Electrochemical Energy Storage System is one of the most used worldwide for energy storage due to its capacity to store energy with respect to its weight (specific energy) and dimensions (energy density), which makes it a versatile and useful system for mobile and automotive purposes as well as for stationary storage of renewable energies [10]. In this type of system, there are two categories: the batteries energy system and the flow batteries [11]. This review highlights the main technologies of the Battery Energy Storage System.

II. BATTERIES ENERGY STORAGE SYSTEM (BESS)

The batteries are part of the electrochemical ESS group where energy is stored in cells composed of 3 essential components: two electrodes, a negative one called anode and a positive one called cathode, and an ionic exchange medium known as electrolyte [2]. According to the reusability of the storage, ECSS are classified into: primary batteries, which are for single use only, and secondary batteries are those that can be recharged. In the case of secondary batteries, during the charging process, electrons are released from the cathode due to the electrochemical reaction, which will travel through the electrolyte to the anode. In the case of the discharge process, the electrons travel the opposite path, i.e. from the anode to the cathode [12]. Figure 3 shows the operation of this energy storage system in charge and discharge operation.

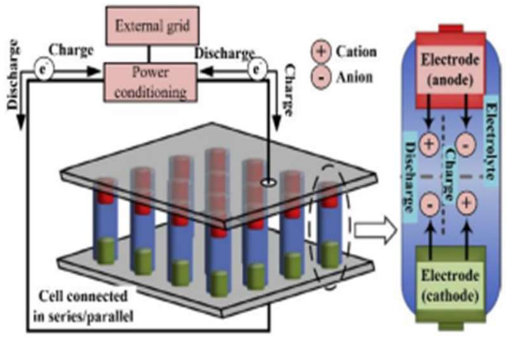

Fig. 3. Battery Energy Storage System [13].

Currently, worldwide, emphasis is being placed on the development of secondary life batteries due to the interest in storing energy from renewable resources [14]. These secondary batteries can be subclassified according to the chemical components found in the electrodes such as lead-acid, lithium-ion, nickel-based, sodium-ion and metal air batteries [15]. In the continuation the main characteristics of these technologies will be discussed in terms of their modes of operation, their performance, their applications and the main disadvantages.

A. *Lead-acid batteries (LAB)*

Lead-acid batteries were the first electrochemical energy storage technologies developed in 1859 by Gaston Planté [16]. These batteries are composed of a lead dioxide (PbO_2) cathode, a lead sponge anode (Pb) and an electrolytic medium composed of 37.7% sulfuric acid (H_2SO_4) and the remainder of water [11]. During the charging process, the electrical source brings electrons to the system causing a chemical reaction in which sulfuric acid is converted into water and lead sulfate on the negative plates and lead on the positive plates [2]. As for the discharge of the battery, the chemical reaction is the reverse of the charging process, i.e., the lead sulfate and water on the plates are converted back to sulfuric acid releasing the electrons that will serve as electric current for charging [17]. These reactions are described in the overall equation 1 shown below [18].

$$Pb\ (s) + PbO_2(s) + 2H_2SO_4(l) \leftrightarrow 2PbSO_4(s) + 2H_2O(l) \qquad (1)$$

These batteries can be classified into two categories according to the way in which they are designed: Flooded Lead Acid Batteries and the Sealed Lead Acid Batteries [19].

- Flooded lead acid batteries represent the basic design of this type of batteries where the electrolyte is inside the structure in free movement [2]. In addition, this system has vents through which the toxic gases that are produced during the chemical reaction are released. For this reason, although they represent a low manufacturing cost, they must be kept upright to avoid leakage of components and a high maintenance rate due to the constant loss of water in the form of gases and corrosion, especially of the positive electrolyte [20].
- Sealed Lead Acid Batteries have a pressure regulating valve, which allows the exchange of the gases produced with the outside, without letting air in. This hermetic storage system allows to have a higher safety factor, but its manufacturing cost is higher [21].

Regarding the disadvantages of this type of batteries, there is a tendency to decrease their durability and energy capacity, mainly due to the performance of the negative electrode [18]. As a solution to these problems, the new technologies of lead-acid batteries implement active carbon additives such as graphite, carbon nanotubes and carbon black in the anode [22]. This insertion of carbon allows for enhanced sulfidation at the negative electrode, which prevents large lead sulfate from being converted to lead [17]. Additionally, the presence of carbon acts as a protective layer against corrosion due to the contact of sulfuric acid with the negative electrode. Finally, the implementation of carbon increases the electrical conductivity of the battery, which counteracts the loss of charge due to chemical reactions [16].

B. *Lithium-ion Batteries (LIB)*

Lithium is a key element in the manufacture of rechargeable batteries because it is a lightweight, highly reactive element with good cycling stability and high reaction reversibility, which makes it an excellent material for storing and releasing energy [23]. The specific capacity of lithium in lithium-ion batteries is around 3860 mAh/g, which means that it can store a large amount of energy in relation to its weight [24]. This is the reason why it is commonly used in portable electronic devices, electric vehicles and energy storage systems [25].

The cathode is a critical element in the performance of the lithium battery since it defines intrinsic characteristics such as power density, energy density, stability over different temperature ranges and reversibility of the electrochemical reaction. According to the structure hosting the lithium ions, the positive electrode can be classified into three types: olivine structure, layered oxide structure and spinel structure[26]. Table 1 summarizes the fundamental characteristics of each of these types of cathodes, and Figures 4 and 5 graphically represent the performance values and the structure of each of the previous mentioned cathodes, respectively.

TABLE I. LITHIUM-ION BATTERY CATHODES.

Cathode	**Olivine structure**	**Layered oxide structure**	**Spinel structure**
General equation	$LiFePO_4$	$Li[M]O_2$: $Li[Ni_xMn_yCo_z]O_2$	$Li[B_2]X_4$
Materials concerned	Iron phosphate	Cobalt, nickel, aluminum, manganese	Aluminum, manganese.
Structure	Orthorhombic structure	Octahedral layers	Spinel structure
Features	Extended lifetime and stability due to covalent bonds present. Fast charge and discharge cycles.	Location of lithium in the interleaf spaces directions. Lower self-discharge rate compared to other cathodes. Effects of nickel concentration: -Increased energy density. -Decrease in thermal stability.	High thermal stability and cycling capability Relatively low cost Lower risk of fire or explosion.
Disadvantages	Low energy density. Limited charging and discharging speed due to low ionic conductivity. High manufacturing cost.	Toxic components such as cobalt. Reduced thermal stability. Risk of fire or explosion due to overloading or overheating. Shortened lifetime.	Low energy density resulting in lower storage capacity. Relatively low loading and unloading speed compared to the other structures.
Voltage (V vs Li+/Li)	3.5 – 5.2	3.7 – 4.2	3.45-4.7
Specific capacity (mAh/g)	120-150	190-200	110-150
Specific density (Wh/kg)	379-400	400-530	330-450
Lifetime (Cycles)	200-2000	100-500	200-1200
Developed technologies	LFP, LFMP, LCP.	LCO, NMC, NCA, LNO.	LMNO, LMNO.
References	[25], [27], [28].	[25], [28]–[30].	[26], [28], [31].

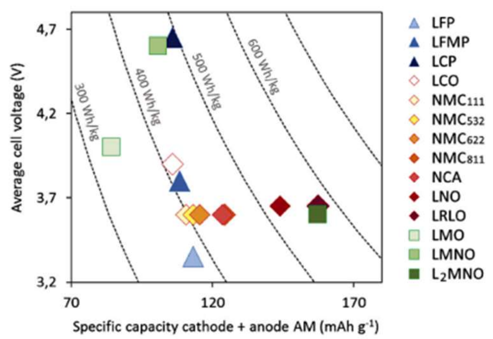

Fig. 4. Comparison of lithium battery cathode performance: average cell voltage, specific capacity and specific energy [25].

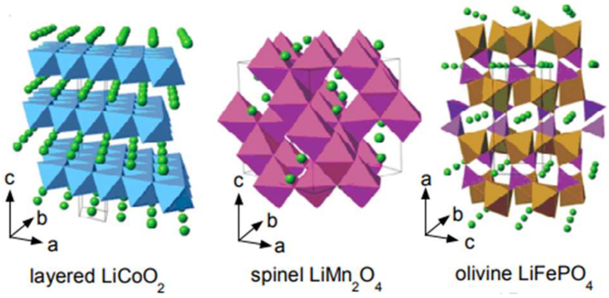

Fig. 5. Crystal structures of lithium ion batteries' cathodes [26].

The anode is another crucial component of lithium-ion batteries, as it is where the chemical reaction takes place that releases the lithium ions and generates the electrical current that powers the device. The factors to be considered for the selection of the anodes are the voltage V vs Li/Li+ and the specific capacity, since the aim is to maximize the voltage difference between the electrodes and the capacity to store the largest amount of lithium [32]. The fundamental characteristics of lithium batteries are summarized in Table 2.

TABLE II. LITHIUM-ION BATTERY ANODES.

Anode	**Conversion**	**Intercalation**	**Alloy formation**
General equation	$2Li^+ + MO + 2e^- \leftrightarrow Li_2O + M$	LiC_6 et $Li_7Ti_5O_{12}$	Li_xM_y
Materials concerned	Iron, cobalt, nickel and chromium.	Titanium and graphite.	Silicium, germanium, aluminum, bismuth, tin.
Features	Electrochemical reaction based on metal center change and reversible oxide formation.	Graphite: presents a 10% change in volume of the mesh which produces instability for the use. Titanium: no volume changes due to its spinel structure, decrease of the specific capacity	Reaction of lithium with metals or metalloids that contribute to the increase of the energy density of the anode.
Disadvantages	Loss of specific capacity due to low columbic efficiency, which reduces anode life cycles.	Prone to dendrite formation when exposed to high speed loading and unloading. Degradation and formation of a layer of solid electrolyte inclusions (SEI) on the anode surface.	Significant changes in the anode structure during the charging and discharging process.
Voltage (V vs Li+/Li)	0.5-1.5	Graphite: 0.6 Titanium: 1.5	0-0.5
Specific capacity (mAh/g)	500-1700	Graphite: 372 Titanium: 175-4200	660-3600
Developed technologies	Fe, Ni, Cu, Cr.	LTO, C6	Sn, Si, Ge, Bi.
References	[31]– [33].	[32], [33], [35].	[31]– [33].

The main problem with lithium batteries is the generation of dendrites which can cause a short circuit [36]. These lithium branched structures grow because during the charging and discharging process, a volume change occurs, which due to imperfections in the crystalline structure can generate cracks that in turn lead to the formation of dendrites [37]. As a solution to this problem, different alternatives are proposed such as the use of solid electrolyte interface (SEI), the use of solid additives in liquid electrolytes and 3D current collectors as an internal strategy for dendrite suppression and the use of magnetic fields as an external strategy [37], [38].

C. Sodium-Ion Batteries (SIB)

Following the emergence of lithium for use in ESS, new technologies focused on developing materials of greater abundance in the earth's crust in order to reduce battery production costs [36]. Among the materials studied is sodium which is present in 2% of the earth's crust and is found in a delocalized manner, so in comparison with lithium it only represents 0,002% and is localized in certain parts of the world such as Australia, Chile and Argentina [36], [39].

The materials that are commonly used to make the anode of these batteries can be classified into two categories: hard carbons and non-carbons [40]. Hard carbons are characterized by being non-graphitizable disordered carbons which provide a good capacity to store alkali metal ions while maintaining a high chemical stability. In spite of these advantages, the use of this negative electrode is under study due to the manufacturing difficulties regarding the insertion of these ions and their actual operation of these batteries. On the other hand, the use of titanium and Nasicon based oxides, and the formation of tin, germanium and potassium alloys, is being considered for non-carbon anodes. These last ones allow the development of a higher theoretical capacity compared to carbonated cathodes, however, high volume changes are produced, which makes their use difficult [40]–[42]. The different performance parameters of the sodium-ion battery anodes are summarized in Table 3.

TABLE III. SODIUM-ION BATTERY ANODODES.

Anode	Hard carbons	Non-carbons
Voltage (V vs Li+/Li)	0.02 – 3	0.01 – 3.8
Specific capacity (mAh/g)	20-40	100-430
Lifetime (Cycles)	100-200	100-1000
Developed technologies	Carbonaceous materials non-graphitizable	$TiS_2, Na_3P, NaGe$.
References	[39]– [41].	

Moreover, the most commonly used positive electrodes in SIBs are mostly classified into two groups: Layered Transition Metal Oxides (LTMO) and Polyanion compounds [43]. Layered transition metal oxides, as the name indicates, present a layered crystal structure of the form Na_xMO_2, where M is a transition metal such as cobalt, nickel, or manganese. Due to its composition, this type of cathodes presents a high theoretical capacity and a good stability along the life cycles [44]. On the other hand, Polyanion compounds which are constituted by a tetrahedron anion $(XO_4)_m^{n-}$ and a MO_x polyhedral of covalent bonds, where "X" represents elements such as sulfur, potassium, silicon, arsenic and molybdenum and "M" is a transition metal such as iron, manganese and cobalt [43]. The presence of strong covalent bonding between the polyanions and the metal ions in the crystal structure allows for high thermal stability. However, the intercalation of the sodium ions reduces the conductivity, the gravimetry capacity and produces significant volume changes, which can cause mechanical stress and ultimately lead to structural degradation through time [45]. Table 4 describes the main performance parameters of the aforementioned cathodes.

TABLE IV. SODIUM-ION BATTERY CATHODES.

Cathode	Layered Transition Metal Oxides (LTMO)	Polyanion compounds
Voltage (V vs Li+/Li)	1.5-4	1.8-4.5
Specific capacity (mAh/g)	150-190	80-150
Lifetime (Cycles)	30-200	80-1000
Developed technologies	$NaCoO_2$, $Na_{2/3}Fe_{1/2}Mn_{1/2}O_2$, $NaNi_{1/3}Mn_{1/3}O_2, NaFeO_2$.	$NaFePO_4, NaTi_2(PO_4)_3$ $Na_3V_2(PO_4)_2F_3$.
References	[43], [44] .	[43], [45].

D. Nickel-Based Batteries

Nickel-based batteries are one of the most developed technologies in Energy Storage System [46]. These batteries use nickel oxide hydroxide as anode and depending on the type of component used in the cathode, these energy storage systems can be classified into: nickel-iron, nickel-metal hydride, nickel-zinc, nickel-hydrogen and nickel-cadmium [47]. This last type of battery is characterized by being one of the most commercialized and developed at industrial level.

Nickel-cadmium batteries implement metallic cadmium as electrodes [14]. Due to the high availability of the materials that compose it, this battery represents an alternative in terms of manufacturing and maintenance costs [48]. Additionally, these batteries are characterized by a high range of temperatures and operating currents [49]. However, the main drawback of this technology is the low specific energy compared to lithium and sodium batteries, and the toxicity of cadmium [48].

III. CONCLUSIONS

The paper presented the main types of Battery Energy Storage Systems and their respective distinguishing characteristics. Especially, the positive and negative electrodes were detailed in terms of their crystalline structures and/or constituent materials, relating these physic-chemical properties to the impact on the individual performance within the battery. Additionally, the issues and drawbacks of each of these battery technologies have been mentioned addressing the possible solutions and the state of development of these technologies. From this description it can be concluded that lithium technology is still one of the most used technologies due to its electrochemical characteristics, which makes it a highly used material in batteries. However, there are challenging materials for the implementation in these storage systems such as sodium, which represents an economic, safety and raw material supply advantage. Finally, the different developers of storage systems continue to search for new materials, structures and technologies to improve battery performance in terms of operating parameters, lifetime, safety and manufacturing costs.

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