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A comparative review of electrical energy storage systems for better sustainability

Pavlos Nikolaidis[a], Andreas Poullikkas[b,*]

[a]Department of Electrical Engineering, Cyprus University of Technology, P.O. Box 50329, 3603 Limassol, Cyprus
[b]Cyprus Energy Regulatory Authority, P.O. Box 24936, 1305 Nicosia, Cyprus

Abstract

The accelerated growth of the energy economy is still highly dependent on finite fossil fuel reserves. Modern power systems could not exist without the many forms of electricity storage that can be integrated at different levels of the power chain. This work contains a review of the most important applications in which storage provides electricity-market opportunities along with other benefits such as arbitrage, balancing and reserve power sources, voltage and frequency control, investment deferral, cost management and load shaping and levelling. Using a 5 function normalization technique a comparative assessment of 19 electrical energy storage (EES) technologies, based on their technical and operational characteristics, is carried out and the technology-application pairs identified across the power chain are presented. In terms of safety and simplicity, Pb-acid and Li-ion systems are viable options for small-scale residential applications, while advanced Pb-acid and molten-salt batteries are suited to medium-to-large scale applications including commercial and industrial consumers. In addition to their expected use in the transportation sector in the coming years, regenerative fuel cells and flow batteries have intriguing potential to offer in stationary applications once they are mature for commercialization. For large-scale/energy-management applications, pumped hydro is the most reliable energy storage option (over compressed-air alternatives) whereas flywheels, supercapacitors and superconducting magnetic energy storage (SMES) are still focused on power-based applications. As different parts in the power system involve different stakeholders and services, each technology with its own benefits and weaknesses requires research and development in order to emerge over others and contribute to more effective energy production in the future.

Keywords: electricity storage; power sources; electricity markets

1. Introduction

Power generation systems are being asked to meet growing demand for electricitywith uninterruptible and high-quality supply. For several years now, this requirement has been fulfilled mostly by using fossil fuels, because their concentrated energy can be transported through various means (rail, road or pipelines) to its point of use where it can be stored as long as needed, and the output of traditional production methods is easy to adjust to match power requirements [1]. However, under the constraints of climate change policies and the need for independence from diminishing fossil fuel reserves, energy sources must meet the new requirements of being emission-free and renewable [2–4].

Certain renewable energy sources (RES) are problematic in terms of power generation due to their intermittent and unpredictable availability. Electricity demand varies seasonally and fluctuates during the day and, as a result, the target of increasing the share of RES and gradually phasing out conventional sources is a major challenge. Even conventional coal or nuclear plants cannot quickly change their power output and for the purpose of co-operating with renewables, significant investment in fast-response gas turbine generation is needed. To deal with such a critical concern, the focus should be turned on alternative sources which increase flexibility in power systems. Since electricity is the most versatile form of energy and can be transmitted over extremely long distances and distributed to consumers with negligible losses, electrical energy storage (EES) systems have attracted much interest [5–9].

EES technologies find ready application in a diverse range of sectors, including portable electronics, automotive vehicles and stationary systems, providing traction and propulsion, the ubiquitous automotive starting, lighting and ignition, standby power, remote area power supply, etc. [10]. Improvements in both renewable and storage technologies are

*Corresponding author
Email address: andreas.poullikkas@cut.ac.cy (Andreas Poullikkas)

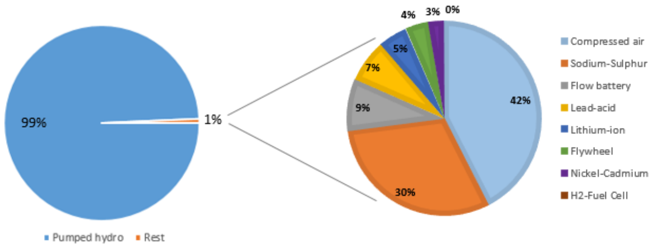

Figure 1: Global EES capacity by technology

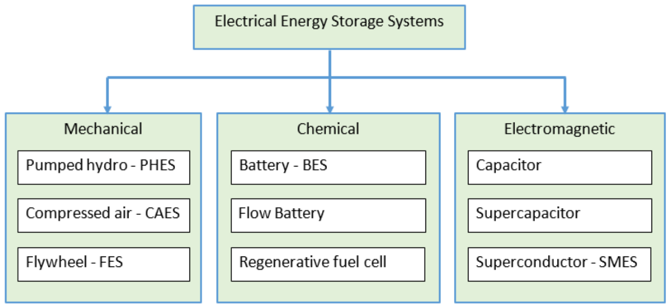

Figure 2: Classification of EES technologies by the form of stored energy

continuously needed, in order for the grid to accommodate the ever increasing variable sources. However, for increased penetration, energy storage for non-renewables too may become essential for the transition to sustainable energy production. For several years now, EES has been attracting increasing interest for power grid applications that provide regulation, contingency and management reserves [11].

The term 'storage' refers to a wide variety of technologies and potential applications across the power chain and hence can be confusing, as it occasionally acts as increased demand or generator [12, 13]. In fact, there is limited storage, accounting for around 5% of total installed capacity and almost 99% of it stems from pumped hydro. As can be observed from Fig. 1, this is followed by compressed air and sodium sulfur with a contribution of 440 MW and 316 MW respectively, while the rest âĂŞ 280 MW âĂŞ is held by flow battery (89 MW), lead-acid (75 MW), lithium-ion (49 MW), flywheel (40 MW), nickel cadmium (27 MW) and hydrogen-fuel cell (1 MW) [14, 15].

In this work a comprehensive and comparative overview of the existing and emerging EES systems is carried out, to provide an updated summary and guide to information which is published extensively in the literature. The operating principles together with the critical technical and operational features concerning each technology are analyzed. The potential applications that provide support and management functions in existing and future power system operations are also reviewed. Developing a deep understanding of the individual requirements and preferences of the various applications in the power chain from central generation to end user, a comparative assessment is conducted in order to determine the best-fit EES option. The assessment uses a normalization technique based on 5 different functions representing the cost, self-discharge rate, rating, specific power and energy, and technical maturity of each EES technology.

In Section 2 the state-of-the-art EES technologies are classified and discussed in detail. Section 3 deals with the importance and requirements of the various potential applications identified across the power chain from generation to end user. In Section 4 the technical and operational features of a total of 19 EES systems are compared and assessed, and their contribution as technology-application pairs in the future power systems is evaluated. Finally, the conclusions are summarized in Section 6.

2. Electrical energy storage technologies

EES technologies can be categorized by various criteria, such as: suitable storage duration (short-term, mid-term or long-term), response time (rapid or not), scale (small-scale, medium-scale or large-scale) or based on the form of stored energy. A classification of the EES technologies according to the latest method is presented in Fig. 2. Depending on the form in which the electrical energy can be stored, EES systems are divided into chemical, electrical, magnetic and mechanical. Batteries and hydrogen storage-fuel cells fall into chemical systems, whereas electromagnetic systems involve supercapacitors and superconductors. Mechanical systems can be subdivided into kinetic energy storage, including flywheels and potential energy storage where pumped hydro and compressed air systems are classified. A detailed description along with the main technical characteristics regarding each storage technology is then carried out.

2.1. Pumped hydro

Pumped hydro energy storage (PHES) is currently the only proven, and by far the most widely adopted, technology for large scale (>100 MW) energy storage [16, 17]. As shown in Fig. 3, a PHES station typically consists of reversible pumps/generators, through which electricity is utilized by pumps to move water from a lower to an upper reservoir during off-peak hours and thus electric energy is stored in the form of hydraulic potential energy. Water is released from the upper reservoir during peak hours to power generators to produce electricity[1]. Hence, the amount of stored energy is proportional to the height difference between the reservoirs and the mass of water stored according to equation (1):

$$E = mgh \tag{1}$$

PHES technology is readily available offering long life in the range of 30-50 years, low operation and maintenance (O&M) cost and cycle efficiencies of average 75% due to elevation plus conversion losses [18]. It provides the highest capacity of all available technologies, since its size is limited only by the size of the upper reservoir. However, this technology requires specific site conditions the most essential of which are the availability of technically suitable locations with access to water [16]. High capital cost and environmental concerns are limiting factors impacting use of PHES as a storage

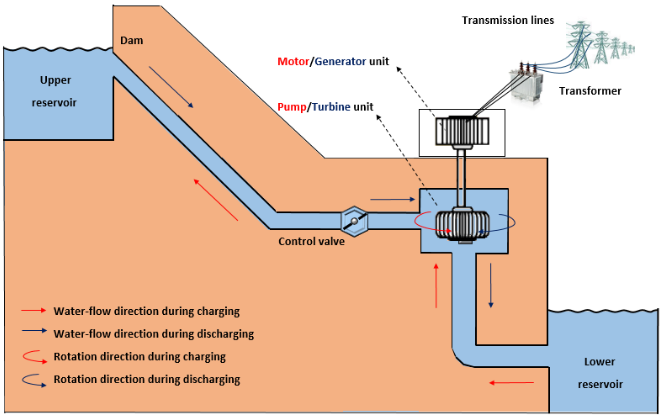

Figure 3: Schematic diagram of pumped hydro storage plant

technology[19]. The world's first large scale plant was constructed in 1929 and now there are over 300 PHES plants with a total installed capacity of over 120 GW, representing almost 99% of worldwide installed electrical storage capacity and about 3% of global generation [20–22]. Due to their not-rapid response, PHES plants were initially built for energy management applications to maximize base-load generation. Assuming that most of the suitable locations with a major height difference have already been exploited, in the short-term, innovative pumped hydro should be upgraded by adding more turbines so as to increase flexibility and offer higher ramp rates over a shorter time [25]. This will bypass the main drawback, which is the extremely long construction time needed. A second innovation developed in recent years and being the focus of research for PHES technology is the variable-speed pump-turbine, enabling increased flexibility, efficiency and reliability at the expense of initial cost [23–25].

Aiming to address the constraints of suitable site availability and environmental impact, alternative reservoir types such as sub-surface, instead of over-ground reservoirs, storing sea-water instead of fresh water and other innovative sea-based solutions have been studied. In addition to increasing the number of suitable locations, by utilizing the open sea as the lower reservoir, concerns over fresh water use are reduced. However, additional costs related to pumping may occur in both proposed technologies due to an event of a fracture or even a collapse in the sub-surface of a PHES, or the corrosive operational environment of sea-water pumped hydro [25, 26]. Finally, minimal environmental impact, larger energy capacities and reduced costs are also expected from other solutions proposed, such as the hydraulic lifting of masses during charging and discharge by releasing them to sink gravitationally, forcing water to pass through a turbine. Although these research proposals seem technically and economically feasible, a demonstration plant is needed for their commercialization and their contribution in a sustainable development [27].

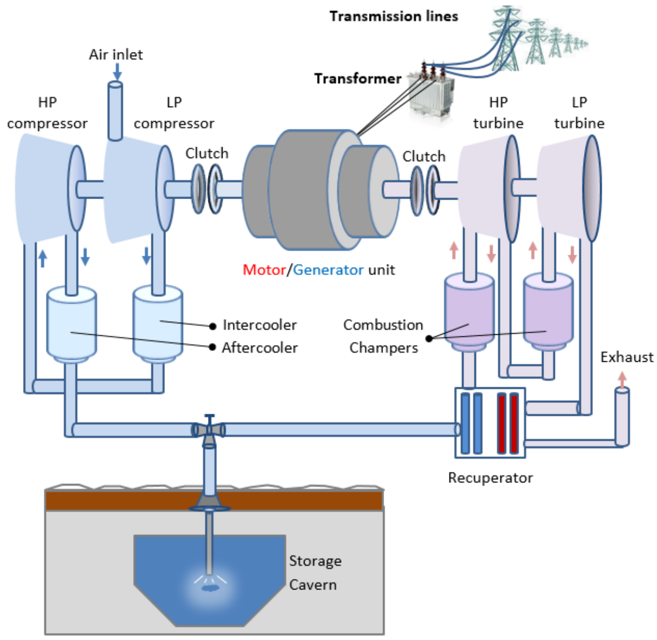

Figure 4: Schematic diagram of compressed air storage plant

2.2. Compressed air

Compressed air energy storage (CAES) systems are mainly equipped with a motor/generator, compressor and expander units, a turbine train and a storing cavity [18]. Typically, during off-peak hours, low-cost or excess electricity is used for storing high-pressure compressed air in a suitable underground cavern so electrical energy is converted into potential energy, which can be converted back into electricity during peak demand by the air being heated and expanded in a gas turbine [28]. In Fig. 4, a schematic diagram of such a facility plant is presented. CAES is achieved at high pressures (typically 40-80 bar) at near ambient temperatures, resulting in less volume and consequently smaller storage reservoirs, the best option of which is given by deep caverns made of high quality rock, ancient salt mines or underground natural gas storage caves [29].

CAES is considered as a highest economic utility-scale storage technology, which may contribute to future sustainable energy systems with a high share of fluctuating energy sources [28, 30]. This technology offers high reliability in combination with low environmental impact and in addition the storage volume is located underground, which means that no further use of land is required [31]. Possessing high commercial maturity, CAES systems can provide huge capacities (>100 MW) but they require both special site preparations and underground storage caverns, which may not exist [1]. However, in areas without water or suitable reservoir locations CAES is the only storage technology option that could be used on a large scale [31]. There are only two operating first-generation systems, the first built in Germany (in 1978) and the second in Alabama (in 1991) [12, 32].

Although CAES occupies a small area of land, it is associated with greenhouse gas emissions. In addition, first-generation, traditional CAES systems exhibit low efficiencies in the range of 42-54% due to increased heat losses to the atmosphere during compression and thermal energy requirements when the decompressed air cools down the turbine [33]. To address the two critical issues constraining overall efficiency, advanced adiabatic and isothermal CAES systems have been designed. Second-generation CAES systems exploit the heat released during the compression process, which is transferred and stored in heat storage sites [34, 35]. Advanced adiabatic CAES (AA-CAES) tends to consume little or no fuel or external energy to heat up the air during expansion, increasing overall efficiency to a theoretical 70% and eliminating associated emissions [36–40]. Isothermal CAES includes the by-produced heat removal during compression to maintain a constant temperature and thus avoid the expense needed to create a thermal storage. This can be achieved by compressing the air slowly, allowing the temperature to equalize with the surroundings [41]. These systems look promising in terms of improved efficiencies, in the range of 70-80%, and relatively low costs [38].

Liquid air energy storage (LAES) is a new concept that is attracting attention. The equipment making up a LAES plant is similar to that of a CAES facility. It differs in that with LAES the heat lost to the atmosphere during air compression is stored in a phase change material (PCM). Typically, employing cryogenic energy storage, atmospheric air is converted into cryogen liquid and thus electrical and thermal storage are simultaneously achieved. When needed, the stored liquid is converted back to the gaseous state by being exposed to ambient temperature and expanded in the turbine. LAES offers long storage duration and promising round-trip efficiency of up to 80% [18].

CAES options without the need of thermal or suitable underground storage caverns can be built on a smaller scale. Small scale CAES (SS-CAES) has attracted interest especially for industrial applications, to provide uninterruptible and back-up power supply [42]. By using efficient and well-designed artificial storage vessels, it can also significantly reduce costs and associated emissions in distributed generation systems [38, 43, 44]. Further advances in the absence of underground cavern have been explored in underwater-ocean storage in chambers to maintain constant stored air pressure. Although they could be integrated with offshore renewable generation technologies, they are in their infancy or exist only on a pilot scale [26].

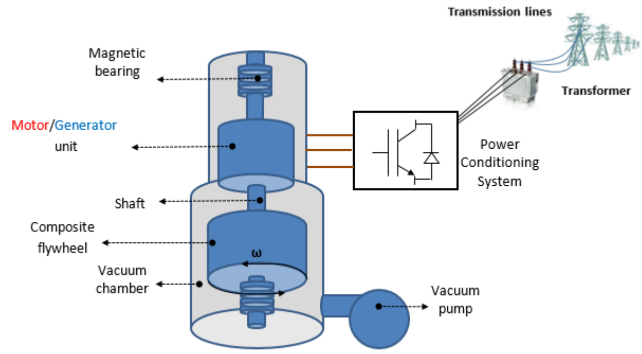

Figure 5: Schematic diagram of flywheel energy storage system

2.3. Flywheels

A flywheel energy storage (FES) device is comprised of a massive cylinder supported by bearings. In a high-speed structure (up to 100,000 rpm) magnetic bearings and a composite disk are used, all contained in a vacuum to eliminate frictional losses and protect them from external disturbances. A low-speed FES (up to 10,000 rpm) includes mechanical bearings, a steel flywheel and no vacuum [45–47]. In Fig. 5, a modern high-tech FES system is depicted in an upright position to prevent the influence of gravity. In an FES system, electricity powers an electric motor which spins and increases the speed of the flywheel, thus converting electricity into kinetic energy âĂŞ the amount of which is proportional to the flywheel's rotor inertia (J) and to the square of its angular velocity (ω) [48]. When short-term back-up power is demanded, electricity is recovered by the same motor, acting then as a generator, which causes the flywheel to slow down thus the rotational energy is converted back into electricity [49]. The energy stored in a flywheel can be calculated by equation (2). Since the moment of inertia depends on the shape and mass of the flywheel ($J = 0.5mr^2 = 0.5\rho\alpha\pi r^4$), the stored energy increases by increasing the disk radius or using high density material [47]:

$$E = \frac{1}{2}J\omega^2 \quad (2)$$

Flywheels have the ability to provide both high energy and power density for short duration discharges. High efficiency in the range of 90-95% can also be achieved through the use of a vacuum pump, permanent and magnetic bearings, which are necessary to overcome the friction forces during operation [1, 18]. Furthermore, they offer extended life cycles and as a buffer store could remove the need for downstream power electronics, to track the fluctuations derived from variable sources, which results in improved overall electrical efficiency [50]. Further advantages compared to other EES systems include their insensitivity to environmental conditions and no hazardous chemicals production [51]. Apart from the fact that flywheel technology is highly expensive, in order to store energy in an electrical power system high capacity flywheels are needed which results in increased friction losses and reduced efficiency [29]. According to the researchers mentioned above, it is apparent that long-term storage of this type of device is not feasible, thus flywheels are employed in high power/short duration applications or as a supplement to batteries in uninterruptible power supply (UPS) systems [18, 49]. In the short term, their contribution in the transport sector is expected to increase as an environmentally benign technology, capable of improving overall efficiency and fuel economy in vehicles [52, 53].

2.4. Batteries

Batteries are classified as either primary ones, which are non-rechargeable, or secondary, which can be recharged. Secondary batteries consist of cells each comprising two electrodes immersed in an electrolyte and they can store and provide energy by electrochemical reversible reactions. Generally, during these reactions, the anode or negative electrode is oxidized, providing electrons, while the cathode or positive electrode is reduced, accepting electrons through an external circuit connected to the cell terminals [1]. In order to adjust power generation to changing demand many technologies have been proposed and depending on the materials used as electrodes and electrolytes, secondary batteries can be divided into lead-acid, alkaline, metal-air, high temperature and lithium-ion [9].

As the oldest type of rechargeable batteries (invented in 1859), lead-acid (Pb-acid) is widely used in vehicles and boats for starting engines and a host of other facilities. It is considered as one of the best suited for stationary applications, as it can supply excellent pulsed power [9, 37, 43]. A schematic diagram of a Pb-acid battery operation is shown in Figure 6. In the charged state, the battery consists of lead (Pb) and lead oxide (PbO_2) both in 37% sulfuric acid (H_2SO_4), whereas in the discharged state, lead sulfate ($PbSO_4$) is produced both at the anode and the cathode, while the electrolyte changes to water [26]. The chemical reactions at the anode and cathode are presented by equations (3) and (4), respectively [54].

The rated voltage of a Pb-acid cell is 2V and capable of operating in the range of -5 and 40°C [1, 55, 56]. Although lead-acid technology has a century long maturity and a low manufacturing cost, the lead and sulfuric acid used to form the anode and the electrolyte respectively are toxic and its cycle life is relatively limited. In addition, flooded type devices require periodic water maintenance and a large footprint due to their low specific energy (25Wh/kg) and discharging depth (70%), thus they become unfavorable for large-scale applications. Owing to the invention of valve regulated lead-acid (VRLA) batteries, banks of up to 36 MW are already being utilized for power generation from RES, as they achieve higher specific energy (30-50Wh/kg) and depths of discharge (80%) with negligible maintenance requirements [55, 57]:

$$Pb + SO_4^{2-} \rightleftharpoons PbSO_4 + 2e^- \tag{3}$$

$$PbO_2 + SO_4^{2-} + 4H^+ + 2e^- \rightleftharpoons PbSO_4 + 2H_2O \tag{4}$$

Nickel-iron (NiFe), nickel-cadmium (NiCd) and nickel-metal-hydride (NiMH) represent alkaline batteries, comprising nickel oxide for cathode and potassium hydroxide for electrolyte. The nickel-iron battery is considered unsuitable for electrical storage as it provides low electrical efficiency, in combination with its self-discharge effect, and because the corrosive iron anode requires high water maintenance [9]. Conversely, nickel-cadmium batteries are widely used in both portable and stationary applications providing strong advantages compared to lead-acid such as higher specific energy (60Wh/kg), longer cycle life (1500-3000 cycles) and lower water maintenance requirements, but for a higher manufacturing cost [10]. In the charging state, they consist of a nickel oxyhydroxide NiOOH cathode, a metallic cadmium Cd anode, a separator and an alkaline electrolyte [18]. During the discharging process, the cathode NiO-OH reacts with water which exists in the aqueous potassium hydroxide ($KOH.H_2O$) to produce $Ni(OH)_2$ and hydroxide ions at the anode.

The reversible reactions are given in equations (5) and (6) for the anode and cathode, respectively, while a better explanation can be obtained in Fig. 7, by means of a flow diagram. However, both its maximum capacity and whole life are subject to the memory effect and thus cannot be repeatedly recharged after being partially discharged [58]. Similar to lead-acid, nickel-cadmium spent batteries create environmental concerns because of cadmium and nickel toxicity, and consequently are largely being displaced [59]. As regards nickel-metal-hydride (NiMH), it differs in that a hydrogen-absorbing alloy is used to form the electrode instead of cadmium. The electrochemical reactions at the anode and cathode of such a device are represented by equations (7) and (8) respectively. Possessing the same with NiCd cell voltage of 1.2V, NiMH can achieve higher specific energy (up to 75 Wh/kg) and reduced memory effect. However, it suffers from severe self-discharge issues (20% per day) and lower efficiency, thus it becomes an undesirable candidate for electrical storage from RES [45, 60–62]. Nevertheless, the distinct advantage of the wide temperature-range of operation (from a minimum of -40 to 50°C) of Ni-based batteries, make their use possible for some utility-scale EES applications [33]:

$$Cd + 2OH^- \rightleftharpoons Cd(OH)_2 + 2e^- \tag{5}$$

$$2NiOOH + 2H_2O + 2e^- \rightleftharpoons 2Ni(OH)_2 + 2OH^- \tag{6}$$

$$MH_x + OH^- \rightleftharpoons M + H_2O + e^- \tag{7}$$

$$NiO(OH) + H_2O + e^- \rightleftharpoons Ni(OH)_2 + OH^- \tag{8}$$

Metal-air batteries can be considered as special types of fuel cell which use metal instead of fuel and air as the oxidant. The anodes in these batteries are commonly available metals with high energy density such as lithium (Li), aluminum (Al) or zinc (Zn), while the cathodes are made

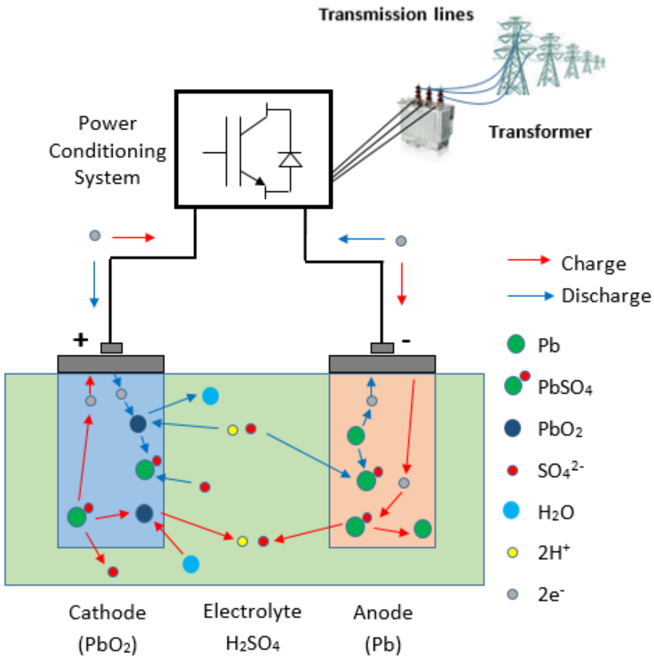

Figure 6: Schematic diagram of Pb-acid battery energy storage system

of either porous carbon or metal mesh capable of absorbing oxygen (O_2) from air. The liquid or solid electrolytes are mainly good hydroxide ion (OH^-) conductors like potassium hydroxide (KOH) [55]. Although Li-air has a theoretical specific energy as high as 11,140 Wh/kg, there are concerns about a probable fire hazard due to the high reactivity of Li with humid air [22, 54, 63]. Moreover, it possesses a much more expensive cell compared to Zn-air, which is environmentally benign and exhibits a long storage life while un-activated [58]. Hence, Zn-air represents the only technically feasible example of metal-air batteries to date, offering a high energy density (650 Wh/kg). It provides a cell voltage of 1.6V, temperature range from -20 to 50°C and negligible self-discharge rate.

However, it is difficult to recharge and offers a limited cycling capability of a few hundred cycles along with a quite low efficiency of 50% [18]. However, Zn-air constitutes a developing technology that looks promising and able to contribute in future energy management applications. The chemical reactions, at the anode and cathode of a Zn-air cell shown in Fig. 8, are provided in equations (9) and (10), respectively. Other metals proposed to form the anode of a metal-air cell can be represented in a similar manner. Equations (11) and (12) are given as an example of an under-research metal-air battery with aluminum (Al) anode:

$$Zn + 2OH^- \rightleftharpoons Zn(OH)_2 + 2e^- \tag{9}$$

$$H_2O + \frac{1}{2}O_2 + 2e^- \rightleftharpoons 2OH^- \tag{10}$$

$$Al + 4OH^- \rightleftharpoons Al(OH)_4 + 3e^- \tag{11}$$

$$\frac{3}{4}O_2 + \frac{3}{2}H_2O + 3e^- \rightleftharpoons 3OH^- \tag{12}$$

High temperature batteries consist of molten sodium anode material, a solid electrolyte of beta-alumina and according to the cathode solid reactant they are subdivided into sodium-sulfur (NaS) and sodium-metal-chloride (NaNiCl or ZEBRA) [64]. NaS batteries are constructed from inexpensive materials and are considered an attractive option for large-scale stationary electrical storage applications, since they offer high energy density (150-345 kWh/m^3) and cycle efficiency (89-92%), long cycle life (1500-5000 cycles) and they are much smaller and lighter than NiCd, NiMH and Pb-acid [45, 57, 65]. The main disadvantages of NaS technology are the corrosive nature of the manufacturing materials and the requirement for constant heat input in order to maintain the electrolyte's molten state, which is ensured at 300-350°C increasing the hazard of probable reaction between electrode materials and the associated fire risk [9].

A demonstration of a charge/discharge cycle concerning a NaS cell is illustrated in Fig. 9 while the reactions at the negative and positive electrodes are shown in equations (11) and (12) respectively. On the other hand, ZEBRA technology has some advantages relative to NaS systems including lower mean temperature of 250 to 350°C and a much safer cell, no corrosion problems, high cell voltage (2.58 V) and the ability to withstand limited overcharge and discharge [10, 66]. The overall chemical reaction occurring in a ZEBRA battery is represented by the equation (13):

$$2Na \rightleftharpoons 2Na^+ + 2e^- \tag{13}$$

$$S + 2e^- \rightleftharpoons S^{2-} \tag{14}$$

$$2NaCl + Ni \rightleftharpoons NiCl_2 + 2Na \tag{15}$$

The last major type of battery storage technology is the lithium-ion (Li-ion) system containing a graphite anode,

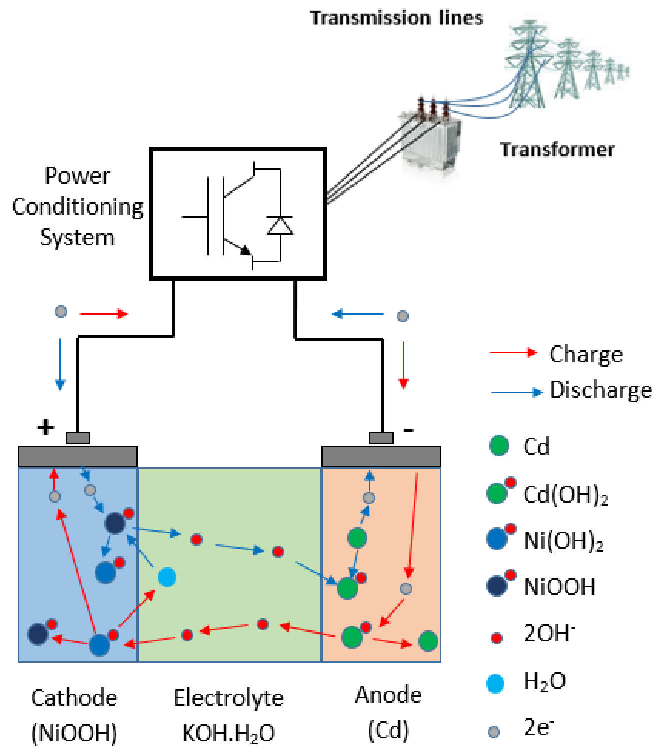

Figure 7: Schematic diagram of Ni-Cd battery energy storage system

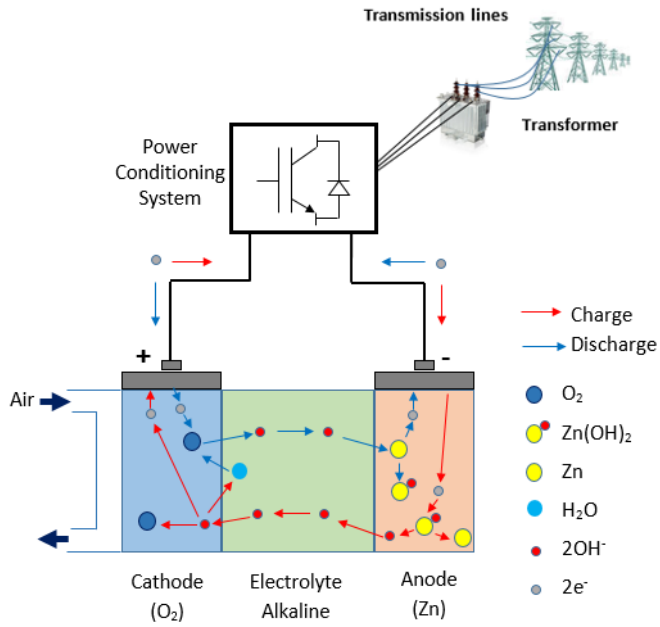

Figure 8: Schematic diagram of Zn-air battery energy storage system

a cathode formed by a lithium metal oxide ($LiCoO_2$, $LiMO_2$, $LiNiO_2$ etc.) and an electrolyte consisting of a lithium salt dissolved in an organic liquid (such as $LiPF_6$), thus electrodes can reversibly accommodate ions and electrons [67]. Finally, a separator is deployed in order to prevent a short-circuit between the electrodes and associated hazard of flame burst. A typical structure of a Li-ion battery with a cathode made of $LiCoO_2$ is demonstrated in Fig. 10. During discharging, lithium atoms (Li) are oxidized to lithium ions (Li^+) releasing electrons. While the electrons are flowing through the external circuit to reach the cathode, Li^+ are moving through the electrolyte to the cathode where they react with the cobalt oxide (CoO_2) and electrons to form lithium cobalt oxide ($LiMO_2$) [68].

Equations (16) and (17) show the chemical reactions at the anode and cathode of the demonstrated example. However, the reactions can be generalized into equations (18) and (19) to explain the similar operation occuring if different lithium metal oxides ($LiMO_2$) are used to form the cathode [20][36]. Lithium-ion batteries offer strong advantages over nickel-cadmium and lead-acid, as they provide the highest specific energy (200 Wh/kg), specific power (500-2000 W/kg) and nominal voltage (3.7 V), energy storage efficiency of close to 100%, lower self-discharge rate (0.03% per), no memory effect and extremely low maintenance requirements [1, 26].

Moreover, their small size and low weight make them suitable for portable applications (such as in smartphones and laptops) where they are almost exclusively used and electric vehicles where they have proved to be the most promising option [57]. Despite the above advantages, the high cost as well as the prohibitive for their lifetime deep discharging, are the main drawbacks of lithium-ion batteries which restrict their use in large-scale applications [45]. Although considerable efforts are being made to lower the cost, concerns still exist relating to increasing consumption in the future, since the depleting worldwide lithium reserves may lead to higher raw material costs [53, 69]. A further disadvantage is their sensitivity to high temperatures and their need to be equipped with a battery management system to at least provide overvoltage, over-temperature and over-current protection [53, 70]. Their suitable temperature range of operation is rated between -30 and 60°C [55]:

$$\mathrm{LiC_6} \rightleftharpoons \mathrm{Li^+} + \mathrm{e^-} + 6\mathrm{C} \tag{16}$$

$$\mathrm{CoO_2} + \mathrm{Li^+} + \mathrm{e^-} \rightleftharpoons \mathrm{LiCoO_2} \tag{17}$$

$$\mathrm{Li}_x\mathrm{C} \rightleftharpoons x\mathrm{Li^+} + x\mathrm{e} + \mathrm{C} \tag{18}$$

$$\mathrm{Li}MO_2 + x\mathrm{Li^+} + x\mathrm{e^-} \rightleftharpoons \mathrm{Li}_{1-x}\mathrm{MO_2} \tag{19}$$

2.5. Flow Batteries

In contrast to conventional batteries, which store energy in solid state electrodes, flow batteries convert electrical energy into chemical potential, which is stored in two liquid electrolyte solutions located in external tanks, the size of which determines the capacity of the battery [10]. The three principal existing types of flow batteries are vanadium-redox (reduction-oxidation), zinc-bromine and polysulfide bromide. Flow batteries may require additional equipment, such as pump sensors and control units. They may also provide variable and generally low energy density, but they present major advantages in comparison with standard batteries as they

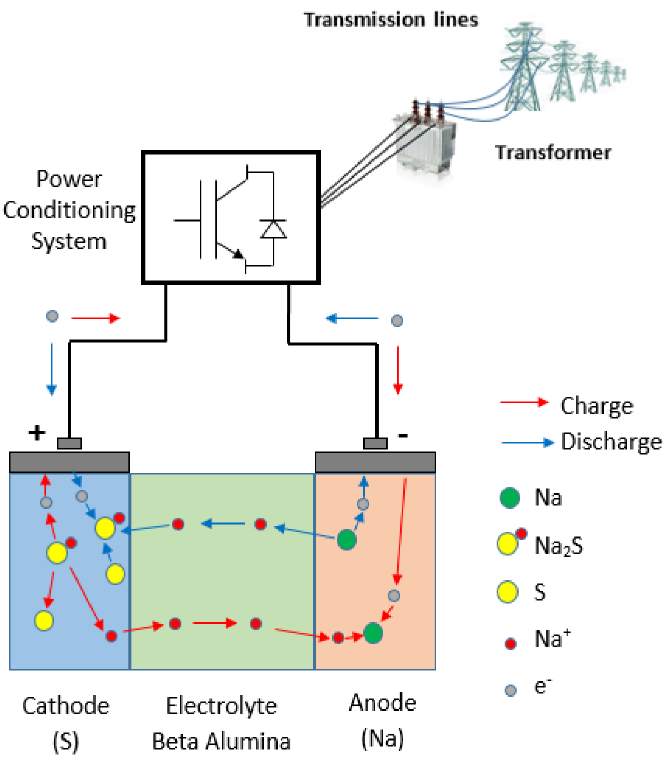

Figure 9: Schematic diagram of Na-S battery energy storage system

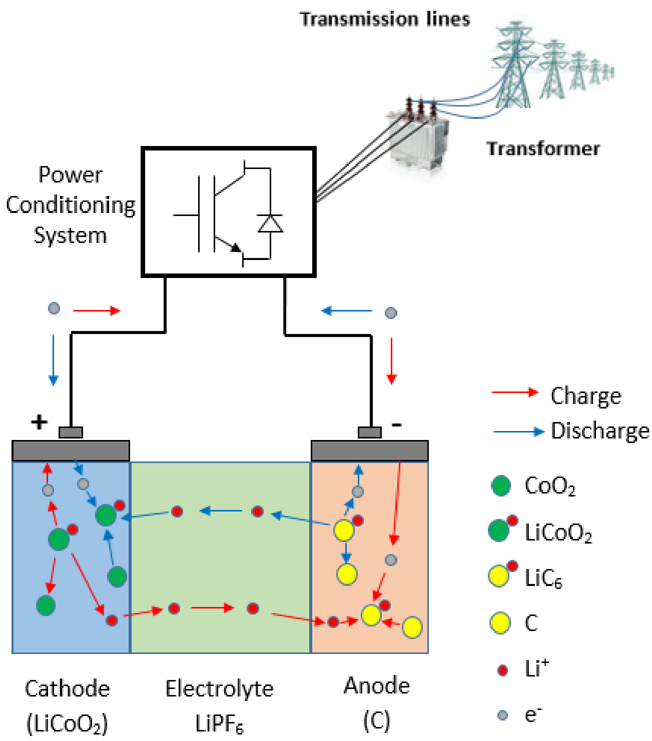

Figure 10: Schematic diagram of Li-ion battery energy storage system

have long cycle life, quick response times, can be fully discharged and can offer unlimited capacity through increasing their storage tank size [57].

The vanadium redox flow battery (VRB) is one of the most mature flow battery system [18, 55]. In such a system, vanadium in sulfuric acid is employed in both the electrolyte loops but in different valence states [9]. Thus, it stores energy by using vanadium redox couples (V^{2+}/V^{3+} and V^{4+}/V^{5+}) in the anolyte and catholyte tanks, respectively, as can be seen in Fig. (11). By using a hydrogen-ion permeable polymer membrane, H^+ are allowed to reversibly exchange through it, balancing the charge in the cell and allowing the chemical reactions of equations (20) and (21) to occur at the negative and positive half-cells. Consequently, in the charging state the anolyte contains V^{3+} and the catholyte V^{4+}, whereas their containments in the absolute discharged state are V^{2+} and V^{5+}, respectively.

The technical and operational features of a VRB system include 30-50 Wh/kg specific energy and 80-150 W/kg specific power, fast responses in the order of milliseconds, high cycling capability (>16000 cycles) and relatively high efficiencies of up to 85%. The cell voltage is 1.2-1.6 V and the operating temperature in the range of 0-40°C [53, 55]. Also, they offer no self-discharge rate, can withstand deep discharging and require low maintenance [66]. Being able to provide an energy capacity of near 2 MWh and considering the aforementioned benefits, VRB is considered an attractive option for large scale EES applications but the high capital cost (1500 $/kW) needs to be reduced [18, 33, 71, 72]:

$$V^{3+} + e^- \rightleftharpoons V^{2+} \quad (20)$$

$$V^{4+} \rightleftharpoons V^{5+} + e^- \quad (21)$$

Zinc bromine (ZnBr) falls into the hybrid flow batteries category. Hybrid flow batteries are distinguished from conventional redox flow batteries by the fact that at least one redox couple species is not fully soluble and may be either a metal or a gas [71]. In ZnBr both of the electrolyte loops employ an electrolyte of zinc-bromine [10]. In the charge state, metallic zinc (Zn) is plated as a thin film on one side of the carbon-plastic composite electrode, while bromine oil (Br_2) sinks to the bottom of the electrolytic tank at the other side (Figure 12). The two compartments are separated by a microporous polyolefin membrane [18]. Equations (22) and (23) represent the chemical reactions at negative and positive compartment of the ZnBr cell during the reversible process of the charge/discharge cycle. Similar to VRB, ZnBr offers no self-discharge rate, no degradation due to deep discharge and as narrow a temperature operation as VRB [55]. Compared to VRB, ZnBr offers higher specific energy (75-85Wh/kg) and cell voltage (1.8V) [53, 66]. The disadvantages of this system are the lower efficiency (75%), cycling capability (2000-3500 cycles) and metal corrosion [33]. Although many ZnBr devices have been built and tested, their use in utility-scale EES applications is in the early stage of demonstration:

$$Zn^{2+} + 2e^- \rightleftharpoons Zn \quad (22)$$

$$2Br^- \rightleftharpoons Br_2 + 2e^- \quad (23)$$

Polysulfide bromide (PSB) or Regenesys is a regenerative fuel cell involving a reversible electrochemical reaction between two salt solution electrolytes, namely sodium bromide

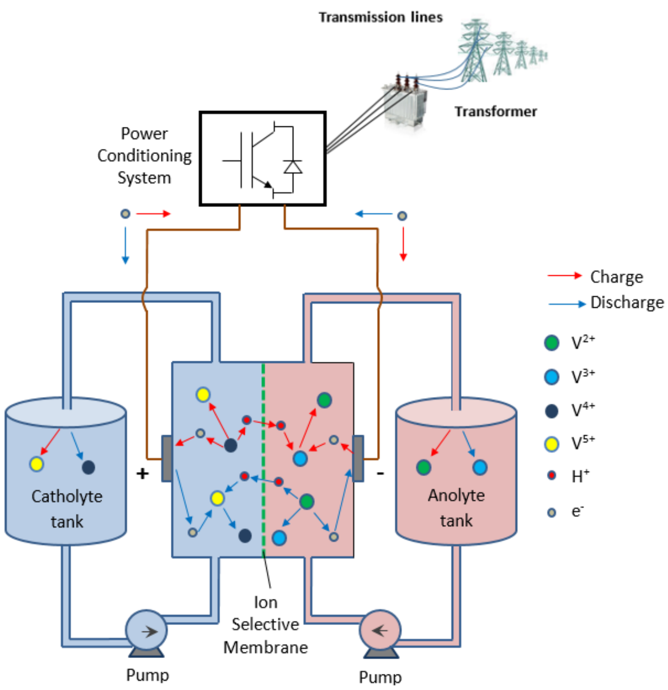

Figure 11: Schematic diagram of vanadium redox flow battery energy storage system

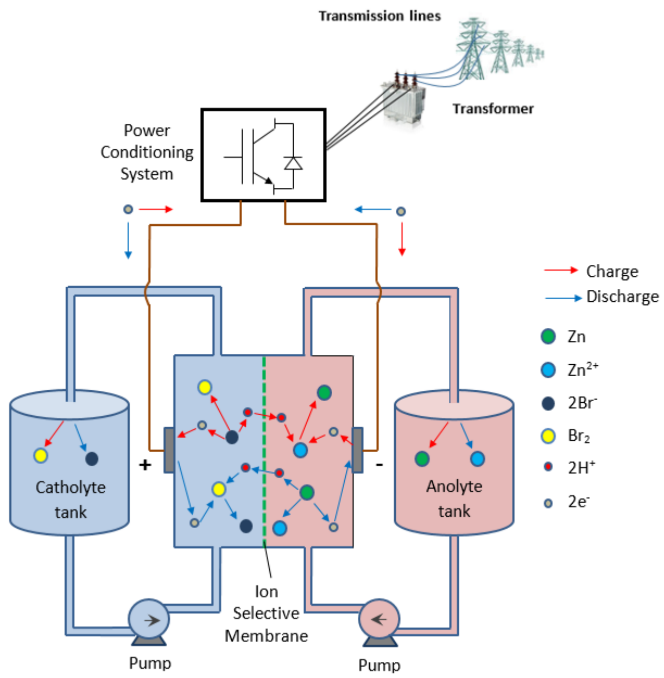

Figure 12: Schematic diagram of zinc bromine flow battery energy storage system

($NaBr_3$) and sodium polysulfide, (Na_2S_2) and it constitutes another type of redox flow battery [55]. The electrodes are electrically connected through the external circuit while the electrolytes are separated by a polymer membrane that only allows positive sodium ions (Na^+) to go through, producing a cell voltage of 1.5V [18, 53]. The electrochemical reactions occurring at the anode and cathode of the half-cells are respectively represented by equations (24) and (25).

According to Fig. 13, during the charging process the sodium bromide (NaBr) becomes sodium tribromide ($NaBr_3$) at the anode while sodium polysulfide (Na_2S_4) is converted into sodium disulfide (Na_2S_2) at the cathode. Operating within the same temperature range (0-40°C), PSB systems offer a longer lifetime (10-15 years) and a net efficiency of 75%. However, chemical handling becomes a serious issue, especially in large scale EES applications, due to environmental concerns regarding the formation of bromine and sodium sulfate crystals during operation [33]:

$$3Br^- \rightleftharpoons Br_3^- + 2e^- \tag{24}$$

$$2S_2^{2-} + 2e^- \rightleftharpoons S_4^{2-} \tag{25}$$

2.6. Regenerative fuel cell

Hydrogen is the only carbon-free fuel and possesses the highest energy content compared to any known fuel producing only water when is utilized for energy production [73–75]. It is colorless and odorless (and therefore difficult to detect). In order for 1 kg of H_2 to be stored at ambient temperature and pressure a volume of 11 m^3 is required, at the user end it is considered the most versatile fuel [4, 76]. Hence, it constitutes an electricity storage pathway through electrolysis of water, a process in which electricity splits water into its simplest components of H_2 and O_2. Electrolyzers are typically used for this method, whereas the inverse procedure of producing electricity via H_2 is realized through fuel cells, where hydrogen gas reacts with the oxygen of air, providing electricity and water which can be recycled and reused to produce more hydrogen [77–79].

A typical electrolysis unit consists of a cathode and an anode immersed in an electrolyte and, depending on the technology, water is introduced at the anode or cathode, where it is split into hydrogen ion H^+ and oxygen O_2 or hydrogen H_2 and hydroxide ion OH^- respectively, thus molecular hydrogen is always produced or remains at the cathode. A similar concept, but in reverse order, is observed in fuel cells [76, 83]. To date, the developed and commonly used electrolysis technologies are alkaline (A), proton exchange membrane (PEM) and solid oxide (SO) electrolysis cells, while the five major groups of fuel cells are alkaline (AFC), proton exchange membrane (PEMFC), solid oxide (SOFC), phosphoric acid (PAFC) and molten carbonate (MCFC) [33]. The chemical reactions that take place in the main fuel cells mentioned here are included in Table (1). The major advantage of fuel cells is their ability to convert chemical energy directly to electricity, without involving any intermediate energy-intensive steps and noisy moving parts [84]. The voltage of a FC stands below 1.5 V as it uses an aqueous technology [85].

Regenerative fuel cells are devices that combine the function of a fuel cell (FC) and electrolyzer into one device. Although all FCs can operate as regenerative FCs, they are typically optimized to perform only one function [53]. In Fig. (14), a PEMFC is demonstrated as a typical example of a regen-

Table 1: Chemical reactions of main fuel cells ([33, 80–82])

FC type	Chemical reactions at anodes and cathodes	Operating temperature, °C	Lifetime, h	Power capital cost, $/kW	Application field
PEMFC	H2 → 2H+ + 2e- 0.5O2 + 2H+ + 2e- → H2O	50-100	40,000	200	Decentralized generation
AFC	2H2 + 4OH- → 4H2O + 4e- O2 + 2H2O + 4e- → 4OH-	60-100	10,000	200	Military, space devices
SOFC	O2- + H2 → H2O + 2e- 0.5O2 +2e- → O2-	900-1000	40,000	1500	Centralized EES
PAFC	2H2 → 4H+ + 4e- O2 +4H+ +4e- → H2O	150-210	40,000	1000	Decentralized generation
MCFC	H2O + CO32- → H2O + CO2 +2e- 2H2 + 4OH- → 4H2O +4e-	600-700	40,000	1000	Centralized generation

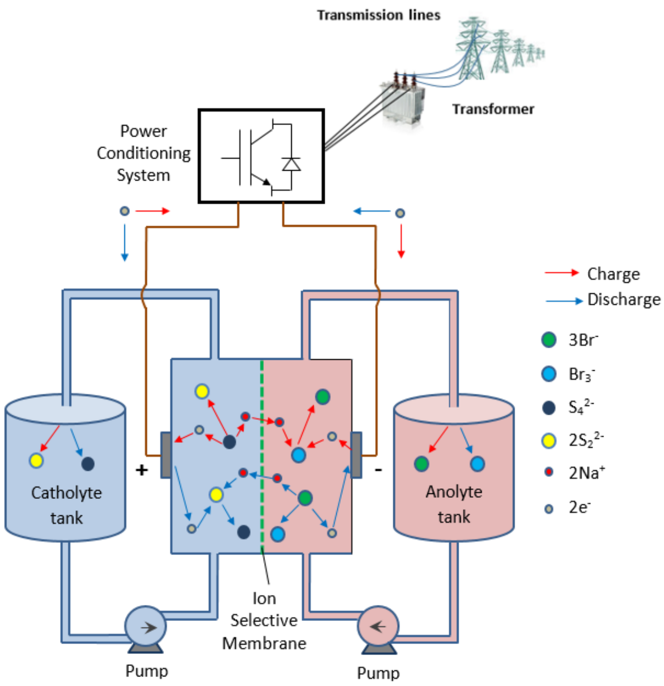

Figure 13: Schematic diagram of polysulfide bromine flow battery energy storage system

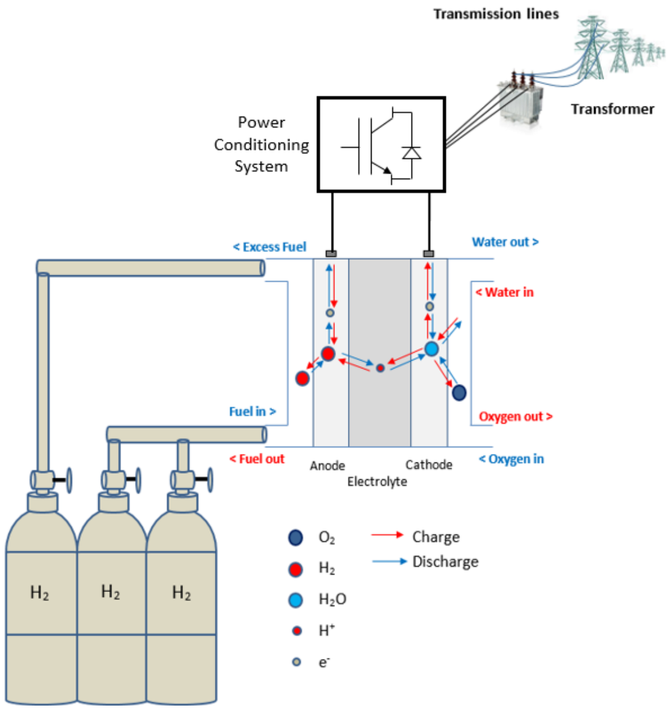

Figure 14: Schematic diagram of regenerative PEMFC energy storage system

erative FC which provides the most efficient cycle of hydrogen and electricity production. The hydrogen produced can be stored as compressed gas, cryogenic liquid or solid hydride [86–89]. In over-ground tanks or underground geological formations it is effectively stored as pressurized gas providing a daily loss of near 3% [1], while if transmitted by tracks or pipelines to where is to be used preferred storage is as a cryogenic liquid, mainly due to the reduced daily boil-off losses in the range of 0.06-0.4% [4, 76, 87]. Regenerative FCs can be characterized as long-term EES devices. They offer the highest specific energy accounted at a maximum of 1200 Wh/kg and excellent cycle capability of 20,000 cycles [33]. Their daily self-discharge is rated at 3%, the depth of discharge at 90% and the overall efficiency somewhere between 20-50% (with electrolysis being the weakest link in the chain) [18, 90]. Except for their application in the transport sector, where they could potentially replace fossil fuels for vehicles, such EES devices look promising in terms of providing both stationary and distributed power [91–93]. However, they are still in the development stage and applications are limited, relating to stand-alone renewable energy systems [94–100].

2.7. Capacitor and Supercapacitor

A capacitor consists of two conducting metal-foil electrodes separated by an insulating dielectric material normally made of ceramic, glass or plastic film. The stored energy is a result of the electric field produced by opposite charges, which occur on the electrodes' surface when a voltage is applied [33]. Already commercialized, capacitors can be charged faster and offer higher specific power than conventional batteries, but they experience a high self-discharge rate and lower energy density [18].

Supercapacitors (also named ultra-capacitors, electrochemical capacitors or electric double-layer capacitors), are energy storage devices with special features, somewhere between conventional capacitors and batteries. As illustrated

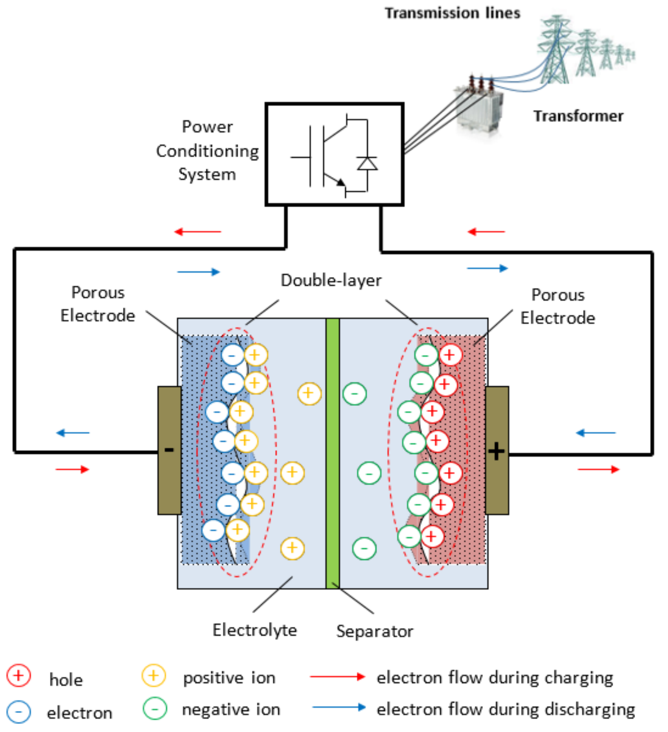

Figure 15: Schematic diagram of electrochemical double-layer capacitor

in Figure 15, their structure includes two metal electrodes with a carbon surface, separated by a porous membrane soaked in an electrolyte, which simultaneously has the role of electronic insulator and ionic conductor [101]. Their capacitance, which is determined by the effective area of the plates (A), the distance between the electrodes (d) and the dielectric constant of the separating medium (ε), is 100-1000 times greater than that of conventional capacitors ($C \propto \varepsilon A/d$). As the stored energy given by equation (26) is directly proportional to both the capacitance and the square of voltage, ultra-capacitors also offer greater energy density than capacitors [26]. The maximum voltage is dependent on the electrolyte type and is rated at 1V or 3V for aqueous or organic electrolytes respectively [45]:

$$E = \frac{1}{2}CV^2 \tag{26}$$

Supercapacitors ideally store electric energy in the electrostatic field of the electrochemical double layer, rather than perform any chemistry, thus can be cycled millions of times and have a much longer lifetime compared to batteries [102]. They achieve higher power density than batteries due to the short time constant of charging, but they provide lower energy density because of the limited surface area of the electrode [103]. Moreover, ultra-capacitors exhibit very high efficiencies up to 95% due to low resistance, which results in reduced loss of energy and can be charged/discharged faster as compared to batteries since the transport of ions in the solution to the electrode surface is rapid [101].
Although this technology is susceptible to self-discharging and is currently applied in portable electronics and the automotive industry [45], ultra-capacitors can also be used in electric or hybrid vehicles in order to supply the peak power needed during acceleration [104]. In recent years, ultra-capacitor banks have been used in power applications to provide voltage sag compensate, intermittent renewable storage and smoothing [101, 105]. Finally, through efficient use of diverse EES technologies, supercapacitors may hide their drawback of low energy density, forming a hybrid system with extended cycle life and high enough specific power to respond in pretentious applications.
A new energy storage technology that has gained interest for grid-scale applications involves electrochemical flow capacitors (EFC). Aiming to decouple the power and energy capacity, after the double layers are charged, the slurry particles together with their charged surfaces are transferred to external tanks. When required, the stored energy can be recovered by pumping these particles back through the cell. A four-tank design for such a technology is needed in order to occasionally (charging/discharging) accommodate the slurry particles of the two layers [106]. Although guidance for future EFC designs has been provided, more R&D is needed in order for such systems to become viable options for large-scale EES applications.

2.8. Superconductors

Superconducting magnetic energy storage (SMES) system is briefly composed of superconducting coil, power conversion system and cryogenically cooled refrigerator (Fig. 16). Typically, electric energy is stored in the magnetic field created by the flow of rectified current in a coil made of niobium-titanium cables of extremely low resistance [107]. In order for the superconducting state to be maintained, the device must be cooled to -264°C (9.2K), allowing current to flow permanently through the inductor [45]. The stored energy calculated by equation (27), is proportional to the wire inductance (L) and the square of direct current (I). It can be returned by discharging the coil when the network demands the excess power [18].

$$E = \frac{1}{2}LI^2 \tag{27}$$

Superconductors offer high efficiency of storage, up to 98%, due to the nearly zero resistance resulting in negligible energy losses and rapid response in comparison with other energy storage systems, as the current can be injected and extracted very quickly [107]. Moreover, these devices can be cycled almost infinitely and are capable of discharging the near totality of the stored energy [29]. The major drawbacks of the low-temperature superconducting (LTS) coils are the high cost of superconducting wire and the increased energy requirements of cooling and, as a result, they are currently used for short duration energy storage applications to improve power quality [49]. In addition, they are susceptible to daily self-discharge (10-15%) and have a negative environmental impact due to the strong electromagnetic field [18]. New, high temperature superconducting (HTS) coils are in development, reaching the superconducting state at -163°C

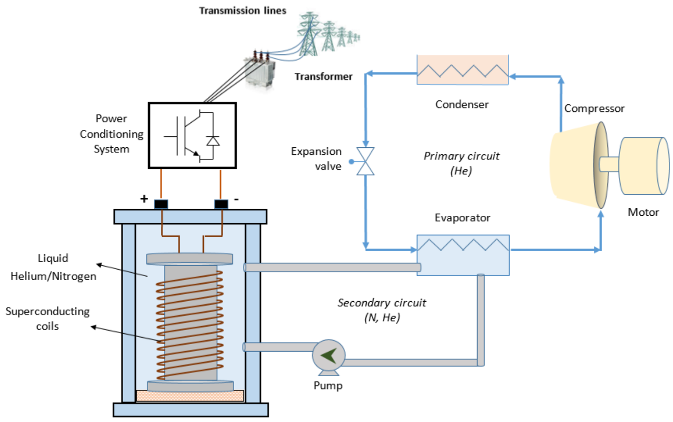

Figure 16: Schematic diagram of superconducting magnetic energy storage system

(110K) and significantly improving the economics and overall efficiency [108–110].

3. Applications of electrical energy storage technologies

Apart from the support that EES technologies offer to mobile devices, automotive vehicles, space applications and the rest of autonomous or isolated systems, EES has been attracting increasing interest for several years now, for applications in power quality regulation, bridging power and energy management applications in power system operations.

Power quality refers to the extent to which provision of power is reliable and maintains nominal voltage levels, unity power factor, nominal frequency levels (50Hz or 60Hz depending on the country's standard), and a purely sinusoidal waveform with zero harmonics and no transients [12]. Power quality regulation services are the fastest acting, enabling operation within seconds to a few minutes. The next are bridging power services, which are capable of working within minutes to an hour, constituting a bridge between the limited generation capability of energy sources and highly variable electricity demand, and assuring continuity when switching from one source to another [27, 49]. Other applications facilitate energy management and provide time-shifting in the range between hours to days or even months to decouple the timing of generation and consumption of electrical energy [111]. Several applications providing grid support and management already exist while others will emerge in the future. Table 2 presents the most important ones, based on storage duration, whereas a more detailed description of each application is set out below.

3.1. Fluctuation suppression

Fast output fluctuations from renewable sources can occur due to variations in weather conditions, in a time range of up to a minute [54, 112]. Such variations can be fatal for some power electronic, information and communication systems in the grid. In order to mitigate this recurring effect, fast-response EES capable of providing high ramp rates and cycling times can be applied [33]. The facility could be charged/discharged within a period of seconds to minutes, to smooth generation from intermittent renewable sources [18, 44, 113, 114].

3.2. Oscillation damping

Up to a certain penetration rate, the integration of renewables into the power mix can be managed by existing flexibility sources. As penetration increases, it may compromise system stability against disturbances, especially in weak or isolated grids [115]. Therefore, an EES is needed, providing fast response and high ramp rates within a one-minute timeframe, to avoid system instability and consequent brownout or blackout, by absorbing and discharging energy during sudden decreases in power output over short duration variations [112].

3.3. Frequency regulation

Frequency regulation is needed to maintain a balanced system. Although daily, weekly and seasonal patterns exist, it is impossible for power consumption to be predicted accurately, leading to generation-demand imbalances (or nominal-frequency deviations), which can cause brownouts or blackouts [116, 117]. Systems that can be used in such applications require high cycle life and fast response rates in combination with good ramp rates (i.e., 10-20 MW/s) [66, 118]. Stored energy in these applications is requested to increase or decrease the output for seconds or less, to continuously maintain the frequency within electricity network standards [49, 119].

3.4. Reactive support

Power converters used to facilitate RES integration, introduce several undesired harmonics to the system. On the other hand, some kinds of wind generators consume large amounts of reactive power, also influencing voltage degradation and synchronization with current. Devices capable of correcting the phase difference are those which provide reactive support, and include generators, loads and energy storage equipment. EES used in such applications offers

Table 2: Applications of EES technologies per value chain

Power Chain	Power Quality Regulation ≤1min	Bridging Power 1min - 1h	Energy Management 1 - 12h	hours - days	≥4 months
RES Integration	Fluctuation Suppression Oscillation Damping	Forecast Hedging Mitigation Load Following		Unit Commitment	
Generation	Frequency Regulation	Contingency Reserve Black-start	Peak Shaving Energy Arbitrage	Load Levelling	Seasonal Storage
Transmission	Reactive Support		Transmission Curtailment Transmission Deferral		
Distribution	Low Voltage Ride-Through Voltage Regulation		Distribution Curtailment Distribution Deferral		
End-user	Uninterruptible Power Supply	Emergency Back-up	Demand Shifting		

both the distinct advantage of being available even when power generation does not take place and high enough ramp rates in short time scale support [12, 66]. Regulation can be realized either mechanically or via automated generation control. It is worth noting that in both cases, the power conversion system applied plays an essential role, since both active and reactive power must be compensated from the storage device [120].

3.5. Low voltage ride-through

The low voltage ride-through, also known as fault ride-through, defines the ability of a power generator to remain connected to the grid throughout a short voltage drop or a total failure of the system. It is crucial for a power system to sustain the supply on-line, in order to avoid a possible chain event where the voltage may be caused to drop further and down far enough to force another generator to trip and so on. The integration of an EES system, with high power ability and instant response, at the point of connection with the external grid, enables the continuous connection of the power plant and reduces the risk of a network collapse [121, 122].

3.6. Voltage regulation

Apart from the frequency, stable voltage must be maintained within technical limits along the whole value chain of a power system, an issue not always guaranteed by the grid. Voltage is generally controlled by taps of transformers, but in order for modern systems to withstand the dynamic changes in active and reactive power, EES technologies could be deployed [22, 123, 124]. Fast-response EES located at the end of a heavily loaded line may improve voltage drops and rises by withdrawing or injecting electricity, respectively [33, 125, 126].

3.7. Uninterruptible power supply

Uninterruptible power supply (UPS) acts as a time-delay off-switch during interruptions, voltage peaks or flickers, and becomes crucial for some residential and commercial consumers who possess fire protection and security systems, computer, server databases and other automation systems that need to be protected or that continuously keep data recorded in memory. Since such appliances require continuity of supply, EES systems with instantaneous reaction can be deployed to improve power quality and provide back-up power during power disruptions [13, 18, 22, 127]. This application adds considerable value in cases where power quality is a concern and power outages occur frequently.

3.8. Forecast hedge mitigation

Power output from renewable sources varies according to daily or seasonal patterns and weather conditions, both of which are imperfectly predictable and uncontrollable [128, 129]. Moreover, if RES have priority in the generation mix, the net load variations (demand minus intermittent output) may fluctuate far more widely than the demand curve, giving high uncertainty to the generation units that are to be dispatched. Consequently, forecast hedging mitigation constitutes a major application, especially in systems that are highly dependent on variable renewables, so that the risk of exposure of consumers to high market prices along with financial impacts related to forecast error can be reduced [18].

3.9. Load following

Generation support and optimization involves the accurate adaptation of power output to changing demand. Depending on the flexibility needed, generators are currently dispatched upon the request of power system operators [130, 131]. However, as the penetration of renewables increases, alternative sources with good ramping capability are needed to meet the mismatches between production and consumption, and shape the energy profile [13]. This is commonly referred to as load following and includes storage devices capable of providing energy in the time frame of minutes to an hour. An EES system suitable for this purpose could offer ramp rates of 0.3-1 MW/s and sufficient stored energy and power capacity [66].

3.10. Contingency reserve

Contingency reserves are distinguished by the time needed to achieve their maximum power output into spinning, non-spinning and supplemental reserve ancillary services. Because of the rapid response needed to replace production deficit, a large fraction of primary reserve is provided by plants that are operating and synchronized (spinning) to the system and thus is referred to as spinning reserve [132]. Spinning reserves must be available within ten minutes. Then, secondary and tertiary reserves, also known as non-spinning and supplemental, respectively, that need not be operating and synchronized when called upon, can be activated by the system operator's decision. Non-spinning reserves must be available within ten minutes and operable until they are replaced by supplemental reserves [133]. The need for fast-responding, partially loaded power plants capable of providing the necessary contingency reserves results in uneconomic dispatch and increases in the capital and O&M costs, reinforcing the requirement for EES applications especially in isolated systems [112, 134–138].

3.11. Black-start

Many power plants require electrical energy from the grid to perform start-up operations, so as to build up a reference frequency for synchronization and help other units to restart [132]. This service forms an integral part in a power system and has been performed by using diesel generators or hydroelectric units to provide the initial supply needed for the power grid to restart after a full black-out. Without taking power from the grid, EES units must sit fully charged and discharge when black-start capability is demanded to assist other facilities to start-up and synchronize to the grid [13, 18, 139, 140].

3.12. Emergency Back-up

Energy storage can provide a source of back-up power that allows customers to ride-through a utility outage and continue normal operation [18]. It is operated as a substitute to an emergency diesel generator, which is typically installed and changed-over to support important users, including healthcare facilities, telecommunication services, commercial and industrial customers. For increased reliability, emergency back-up storage requires instant-to-medium response time and relatively long duration of discharge [44, 141, 142]. The rated power output and energy capacity of such applications depends on whether they are deployed to ride-through an outage until conventional back-up generator can start-up or whether they completely mitigate the event by themselves [133].

3.13. Peak shaving

If cheap energy is stored at off-peak demand periods at night, and injected into the network during periods of maximum electricity demand during the day, the economics of a power generation plant improve greatly [112, 143]. This service, also known as peak-shaving, must be operable in the time frame of 1 âĂŞ 10h, in order to meet daily peak demand and hence, to be able to de-activate expensive peak generation plants [144–150].

3.14. Energy arbitrage

Electricity prices are highly unstable, but tend to a daily pattern of low prices during night-time off-peak hours and high prices during day-time on-peak hours [133]. Energy arbitrage involves operating storage in such a manner that it consumes energy (self-produced and/or bought from others) during low market prices and releases energy when market prices are higher [12, 26, 151]. Consequently, bulk energy storage becomes advantageous in that it can provide both generation and load, allowing to arbitrage the production price of the two periods and improving the load factor of generation [18, 152].

3.15. Transmission and distribution congestion relief

In most power networks, generation is located at a distance from populated areas and electricity is delivered to the consumers with some losses. Congestion may occur either on high voltage transmission lines or more locally on the distribution system due to several reasons such as: when transmission lines cannot be enhanced in time to meet the increasing demand, in the event of an overload at the distribution equipment or due to extremely high penetration of distributed generation [12]. Where power generation or load demand exceeds the maximum delivery capacity, either excess energy must be curtailed or a system upgrade must take place to provide sufficient capacity to accommodate or meet the changes, respectively. These two constraints are usually distinguished into two individual applications in the literature and are referred to as Transmission Curtailment and Transmission & Distribution Deferral.

An EES device capable of providing energy in the time frame of 5 âĂŞ 12 h would mitigate such power delivery constraints imposed by insufficient delivery capacity [137, 153–155]. Instead of being curtailed, excess generation could be stored and injected back when the delivery capability is available again, whereas the increased demand would be treated without the additional losses burdening the transmission lines by simply shifting the delivery of generation from on-peak to off-peak periods. According to the appropriate node side at the substations where EES systems are intended for use, they could be large scale or smaller, stationary or transportable to provide supplemental energy to end-users during overload situations [13]. In this way, both transmission curtailment is reduced and investment upgrades are deferred for years, whilst improving the utilization factor of the existing network.

3.16. Demand shifting

Apart from the firm power that energy storage provides to off-grid users, grid-tied consumers may profit from a time-varying electricity price, an option often offered by power utilities. This can be therefore achieved by shifting electrical energy purchases from on-peak (with high time-of-use charges) to off-peak periods (when time-of-use charges are lower) [156]. In a similar manner, large commercial and industrial customers (whose demand charge is based on a peak load measured over a defined period) can reduce their demand charges in future bills by constantly reducing their peak load measured by the utility meter [133]. For the current requirements of a power system, EES devices with capacities of 1-10 kW and capable of providing energy in the time frame of 2-4 h would be sufficient [112]. Associated with local generation and/or in conjunction with a micro-grid formation able to be operated in island mode, power capacities may need to be increased for a time frame of 5-12 h. The feasibility of such storage systems is highly site-specific and depends on the existing incentives given by utilities [22, 55, 157, 158].

3.17. Unit commitment

Unit commitment applications contribute to appropriate scheduling of generators for certain time periods. The maximum share of RES fed to the grid is constrained by the minimum generation capacity of the conventional units being committed. As the penetration of variable renewable energy sources increases, it is more than usual for utilities to over-schedule and keep the plants partially loaded, to avoid curtailment. This implies uneconomic dispatch due to increased start-up costs and operation at inefficient output. Storage technologies are needed to provide energy in the time-frame of hours to days, in order to compensate forecast errors in the case of an under-predicted renewable source and to enhance a joint operation through efficient unit commitment [132, 145, 159].

3.18. Load levelling

Whatever the season, minimum power consumption during the day approximates to nearly one-half of the maximum peak. However, as a function of peaks, production is over-dimensioned at the expense of its economics, which are improved if it is designed to fulfil average demand [29]. Load levelling is another example of time-decoupling of generation and consumption. By charging storage during periods of low demand and discharging as needed, the gap between peak and off-peak is reduced, reducing the requirements of peaking generators to a minimum [26]. Electricity storage technologies able to provide energy for many hours to days, allow the load to become flatter, thereby improving generation efficiency, and reducing capital and O&M costs related to fuel avoidance and lighter design, respectively [22].

3.19. Seasonal storage

Systems exposed to large seasonal variations at the level of either power generation or demand, may use energy storage in a time frame of months. Such long-term electricity storage is currently limited by storing primary energy sources including coal, gas, oil, biomass or water, which can be converted to power at a later time [160]. However, EES technologies with a very large energy capacity and no self-discharge rate would be eligible, while if other quantifiable benefits (such as emissions avoidance) could be taken into account, they will become technically viable options [22, 66, 161–163].

4. Overall comparison

According to the intended eventual use of the storage devices, there are favorable or unfavorable performance characteristics to be considered, namely: scale, power and energy density, investment and whole life cost, cycle and chronological life, time of response and storage duration, technical maturity, round-trip efficiency, self-discharge rate, etc. All information found in the extensive literature is listed in Tables 3 and 4, presenting the technical and operational performance characteristics, respectively.

4.1. Comparative assessment

In this section, an attempt is taken to compare a total of 19 EES technologies based on their technical and operational characteristics. In order to effectively assess the feasibility of those systems in the power chain, the performance characteristics of interest are normalized. The ranking is selected from 0 to 10, where the range between the worst and ideal is defined accordingly. The normalization is based on 5 different functions according to the expression and which value represents the ideal. Two functions are selected to evaluate the characteristics expressed in real units, while a further two are needed for those in percentage values. The last function is typically used to quantify a special technical feature.

In this sense, lower costs (C_i) and self-discharge rates (SDR_i) show higher rankings and thus “0” represents the highest cost and “10” indicates the ideal case. To be consistent with such an assumption, equation (28) is used to give the normalized values for the real units of power capital, energy capital and O&M costs, whereas to estimate the rank of self-discharge rates equation (29) is applied:

$$Rank(C_i) = 10\,\frac{\max - C_i}{\max} \tag{28}$$

$$Rank\,(SDR_i) = 10(1 - SDR_i) \tag{29}$$

Conversely, higher potential features (F_i) including ratings, densities, and specific power and energy, cycling and lifetime, show high rankings and thus are estimated by equation (30), while efficiencies (η_i) are normalized based on equation (31) which determines a poor performance with “0” and an ideal of 100% with “10”:

$$Rank(F_i) = 10(1 - \frac{\max - F_i}{\max}) \tag{30}$$

$$Rank\,(\eta_i) = 10\,\eta_i \tag{31}$$

Finally, the special feature of technical maturity of each technology is normalized as follows: “2” corresponds to “developing” technologies, “4” to demonstration, “6” to commercializing, “8” to commercialized, and “10” to mature. The normalized values for the selected technical and operational features are provided in tables. Assumptions made here include only the costs derived from different sources but in the range of no greater than 10 years, so that the exchange rates have remained relatively stable and no present value adjustments have to take place.

Mechanical EES technologies are summarized and compared in Table 5 and Fig. 16. As can be seen, the most mature is PHES technology followed by CAES and FES, which are commercialized and commercializing, respectively. The highest power rating and energy capacity correspond to

Table 3: Technical characteristics of EES

Technology	Power Density, kW/m^3	Energy Density, kWh/m^3	Specific Power, W/kg	Specific Energy, Wh/kg	Power Rating, MW	Energy Capacity	Power Capital Cost	Energy Capital Cost	Technical Maturity
PHES	0.01-0.12 [15]	0.5-.133 [15]	0.01-0.12 [15]	0.5-1.5 [18]	100-5000 [112]	500-8000 [18]	600-2000 [18]	5-100 [18]	Mature
CAES	0.04-10 [15]	0.4-20 [15]	2.2-24 [15]	10-30 [53]	5-300 [112]	<1000 [29]	400-800 [18]	2-50 [18]	Commercialized
SS-CAES	>10 [46]	>20 [46]	-	140 [33]	0.003-3 [42]	<0.008 [42]	1400-1550 [33]	200-250 [33]	Commercializing
LAES	-	80-120 [33]	-	214 [33]	10-200 [33]	2.5 [33]	900-1900 [45]	260-530 [45]	Developing
Flywheel	40-2000 [15]	0.25-424 [15]	1000 [53]	5-100 [1]	0-0.25 [18]	0.75 [183]	250-350 [18]	1000-5000 [18]	Commercializing
Lead-acid	10-400 [15]	25-90 [15]	180 [1]	30-50 [55]	0-20 [18]	0.001-40 [184]	300-600 [18]	200-400 [18]	Mature
NiCd	38-141 [15]	15-150 [15]	140-180 [53]	35-60 [18]	0-40 [18]	6.75 [62]	500-1500 [18]	800-1500 [18]	Commercialized
NiMH	8-588 [15]	39-300 [15]	220 [53]	50-75 [18]	0.01-3 [18]	-	270-530 [17]	200-730 [17]	Mature
Zn-air	10-208 [15]	22-1673 [15]	60-225 [15]	450-650 [55]	0-0.01 [18]	-	100-250 [18]	10-60 [18]	Developing
NaS	1.3-50 [15]	150-345 [15]	150-240 [66]	120 [53]	0.05-8 [18]	0.4 [185]	>1000 [18]	300-500 [18]	Commercialized
ZEBRA	54.2-300 [15]	108-190 [15]	174 [81]	120 [66]	0-0.3 [18]	-	150-300 [18]	100-200 [18]	Commercializing
Li-ion	56-800 [15]	94-500 [15]	500-2000 [1]	100-200 [53]	0-0.1 [18]	0.004-10 [33]	1200-4000 [18]	600-2500 [18]	Commercialized
VRB	2.5-33.4 [15]	10-33 [15]	80-150 [53]	30-50 [55]	0.03-3 [18]	2 [62]	600-1500 [18]	150-1000 [18]	Commercializing
ZnBr	3-8.5 [15]	5.2-70 [15]	100 [33]	75-85 [66]	0.05-2 [18]	4 [66]	700-2500 [18]	150-1000 [18]	Demonstration
PSB	1.35-4.16 [18]	10.8-60 [18]	-	15-30 [33]	1-15 [18]	0.06 [33]	700-2500 [18]	150-1000 [18]	Developing
Reg-FC	1-300 [15]	25-770 [15]	5-50 [45]	200-1200 [45]	0-50 [18]	0.312 [33]	500 [48]	15 [48]	Developing
Capacitor	15-4500 [15]	less than SC	105 [18]	0.01-0.1 [45]	0-0.05 [18]	-	200-400 [18]	500-1000 [18]	Commercialized
S-capacitor	15-4500 [15]	1-35 [18]	500-5000 [18]	2.5-15 [18]	0-0.3 [18]	0.0005 [183]	100-300 [18]	300-2000 [18]	Developing
SMES	300-4000 [15]	0.2-13.8 [18]	500-2000 [18]	0.5-5 [18]	0.1-10 [18]	0.015 [36]	200-300 [18]	1000-10000 [18]	Commercializing

Table 4: Operational characteristics of EES

Technology	Daily self-discharge, %	Lifetime, years	Cycling times (cycles), %	Round-trip efficiency, %	DoD, %	Response time	Suitable storage duration	Autonomy at power rating	O&M cost, $/kW-year
PHES	almost 0 [53]	30-50 [57]	10000-30000 [66]	70-85 [57]	95 [90]	mins [44]	hours-months [18]	1-24h [18]	3 [33]
CAES	almost 0 [18]	30 [57]	8000-12000 [66]	42-54 [46]	100 [90]	mins [44]	hours-months [18]	1-24h [18]	19-25 [33]
SS-CAES	almost 0 [18]	23+ [42]	30000 [42]	-	100 [90]	sec-mins [44]	3h [33]	3h [33]	very low [42]
LAES	almost 0 [**?**]	25+ [**?**]	-	55-80 [**?**]	100 [90]	mins [33]	hours [**?**]	several hours [**?**]	-
Flywheel	55-100 [66]	20 [1]	105-107 [1]	90-95 [17]	100 [52]	msec [33]	secs-mins [18]	15sec-15min [33]	20 [33]
Lead-acid	0.1-0.2 [55]	5-15 [1]	200-2000 [53]	85-90 [1]	80 [55]	msec [57]	mins-days [18]	secs-hours [18]	50 [33]
NiCd	0.1-0.2 [55]	10-20 [18]	1500-3000 [1]	60-90 [53]	100 [81]	msec [57]	mins-days [18]	secs-hours [18]	20 [33]
NiMH	5-20 [59–61]	2-15 [15]	1200-1800 [1]	50-80 [53]	50 [81]	-	-	-	-
Zn-air	almost 0 [55]	0.17-30 [15]	100-300 [18]	50 [55]	-	-	hours-months [18]	secs-24h [18]	-
NaS	almost 0 [55]	10-15 [18]	1500-5000 [45]	89-92 [1]	100 [55]	msec [57]	secs-hours [18]	secs-hours [18]	80 [33]
ZEBRA	20 [18]	10-14 [18]	1000 [164]	70-85 [164]	-	-	secs-hours [18]	secs-hours [18]	-
Li-ion	0.03 [55]	5-15 [18]	3000-10000 [45]	~100 [45]	80 [66]	msec [57]	mins-days [18]	mins-hours [18]	-
VRB	almost 0 [55]	5-10 [18]	>16000 [53]	85 [55]	100 [66]	msec [57]	hours-months [18]	secs-10h [18]	70 [33]
ZnBr	almost 0 [55]	5-10 [18]	2000-3500 [57]	75 [55]	100 [66]	msec [57]	hours-months [18]	secs-10h [18]	-
PSB	almost 0 [55]	10-15 [18]	800-2000 [45]	75 [55]	100 [90]	msec [57]	hours-months [18]	secs-10h [18]	-
Reg-FC	0.06-3 [1]	5-15 [18]	20000 [33]	20-50 [18]	90 [90]	secs [44]	hours-months [18]	secs-24h [18]	0.002-0.02 [165]
Capacitor	40 [18]	~5 [18]	106 [164]	95 [164]	100 [1]	msec [66]	secs-hours [18]	secs-hours [18]	13 [33]
S-capacitor	20-40 [1]	10-12 [166]	106 [164]	85-98 [164]	100 [1]	msec [44]	secs-hours [18]	secs-hours [18]	6 [44]
SMES	10-15 [18]	20+ [18]	almost infinitely	95 [107]	100 [1]	msec [44]	âĹď30mins [33]	mins-hours [18]	18.5 [33]

Table 5: Comparisons of mechanical EES technologies

	PHES	CAES	Flywheel
Power rating	10.00	0.60	0.00
Energy capacity	10.00	1.25	0.00
Power capital cost	0.00	3.33	5.83
Energy capital cost	9.95	9.98	0.00
O&M cost	8.50	0.50	0.00
Specific power	0.00	0.24	10.00
Specific energy	0.15	3.00	10.00
Power density	0.00	0.05	10.00
Energy density	3.14	0.47	10.00
Technical maturity	10.00	8.00	6.00
Daily self-discharge	10.00	10.00	4.50
Lifetime	10.00	6.00	4.00
Cycling times	0.03	0.01	10.00
Round-trip efficiency	8.50	5.40	9.50

Table 6: Comparisons of conventional battery technologies

	Pb-acid	NiCd	NiHMe	Li-ion
Power rating	5.00	10.00	0.75	0.03
Energy capacity	10.00	1.69	0.00	2.50
Power capital cost	7.50	5.83	7.75	0.00
Energy capital cost	7.50	0.00	7.50	2.50
O&M cost	0.00	6.00	0.00	10.00
Specific power	0.90	0.90	1.10	10.00
Specific energy	2.50	3.00	3.75	10.00
Power density	5.00	1.76	7.35	10.00
Energy density	1.80	3.00	6.00	10.00
Technical maturity	10.00	8.00	10.00	8.00
Daily self-discharge	9.99	9.99	10.00	10.00
Lifetime	7.50	10.00	7.50	7.50
Cycling times	2.00	3.00	1.80	10.00
Round-trip efficiency	9.00	9.00	8.00	10.00

Table 7: Comparisons of high-energy battery and fuel cell technologies

	Zn-air	NaS	ZEBRA	Reg-FC
Power rating	0.00	1.60	0.06	10.00
Energy capacity	0.00	10.00	0.00	7.80
Power capital cost	9.00	0.00	8.50	5.00
Energy capital cost	9.67	0.00	6.67	9.5
O&M cost	0.00	0.00	10.00	10.00
Specific power	9.38	10.00	7.25	2.08
Specific energy	5.42	1.00	1.00	10.00
Power density	6.93	1.67	10.00	10.00
Energy density	10.00	2.06	1.14	4.60
Technical maturity	2.00	8.00	6.00	2.00
Daily self-discharge	0.00	10.00	8.00	9.70
Lifetime	10.00	5.00	4.67	5.00
Cycling times	0.05	2.50	0.50	10.00
Round-trip efficiency	5.00	9.20	8.50	5.00

PHES, which exhibits an advantage over the others, with FES being the last in the row. On the other hand, PHES and CAES offer quite low performance per unit mass and volume, requiring large storage reservoirs for acquiring a certain amount of power and energy. Consequently, they are disadvantaged compared to FES technology in applications where space and weight are limiting factors. The capital costs follow a reverse order per units of energy and power. The highest power capital cost concerns PHES technology, favoring FES, whereas the highest energy capital cost corresponds to FES and promotes the other two, with CAES being slightly less expensive. PHES offers the longest lifetime and the least O&M cost, while FES enjoys the highest efficiency and cycling capability. Finally, the parasitic losses are superior in a FES system resulting in even a full daily self-discharge, while PHES and CAES plants enjoy negligible losses and almost zero daily self-discharge rate.

Historically, chemical EES systems have by far spurred the greatest research interest, demonstrating many different chemistries and topologies to meet the ever increasing demand. The first conventional secondary battery, Pb-acid, was invented in 1859. Since the beginning of the 20th century (and specifically in 1915), NiCd batteries have been used commercially, followed by the introduction of NaS in the 1960s. Although the Li-ion battery was first proposed at the same time, the first ones were only produced 31 years later. In 1980, the VRB flow battery was pioneered in Australia and the basic patents were bought in 1998, whereas the ZnBr was developed in 1970 and demonstrated in 1991. ZEBRA technology was acquired by MES (Swiss) in 1999 [18]. Although many other chemical technologies, including secondary batteries, flow batteries and fuel cells, have been investigated and found technically possible, they are still under development.

The most popular chemical EES technologies, conventional, molten salt and metal-air batteries, and regenerative fuel cells, are examined and compared in Tables 6 and 7, along with Fig. 17 and 18. Pb-acid batteries account for the largest secondary battery market share in the world. The low cost and maintenance, combined with relatively high power output and efficiency, make them an attractive option for automotive, telecommunications and UPS applications. Despite the high environmental impact, this kind of battery has also been used in MW-scale stationary applications in conjunction with renewables. NiCd batteries also provide high environmental impact. With similar features such as high efficiency, specific power and moderate self-discharge, NiCd offers more cycling times and longer lifetime, higher energy density and power ratings, whereas it becomes disadvantaged in terms of capital costs and power density. Improved performance is achieved by NiHMe, which provides higher power and energy densities, lower capital costs, no self-discharge at the expense of lower efficiency, cycle capability and lifetime. For a given amount of energy, Li-ion batteries require the smallest volume and weight. Along with their higher efficiency of near 100% and extended cycle times, Li-ion batteries offer widespread uses in portable devices and promising potential in transportation and small-scale stationary applications.

High energy batteries including NaS, ZEBRA and Zn-air, together with PEM regenerative FC are summarized in Table 7 and Fig. 18. It can be seen that NaS technology enjoys the highest efficiency followed by ZEBRA, while Zn-air and regenerative FC provide the lowest of roughly 50%. Regarding energy density, Zn-air looks promising, while the regenerative FC is advantageous in specific energy. The key limitations of Zn-air are found in cycling capability and power rating, whereas the major advantages include long lifetime and low capital investment. Regenerative FCs are able to provide power density as high as ZEBRA but with lower energy capital cost, limited maintenance cost and better cycling capabil-

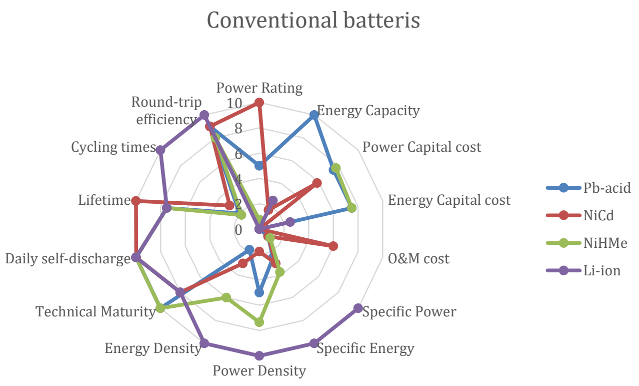

Figure 17: Potential characteristics of conventional battery technologies

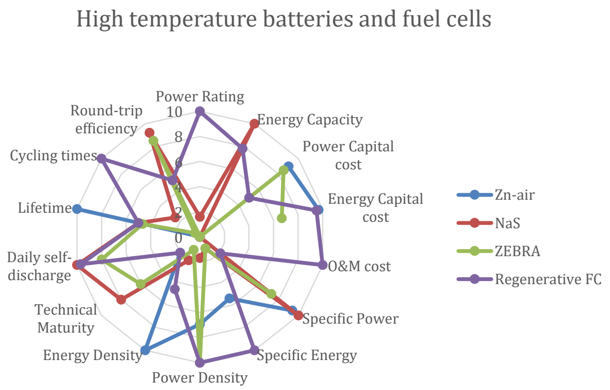

Figure 18: Potential characteristics of high-temperature battery and fuel cell technologies

ity. In addition, ZEBRA exhibits a severe self-discharge rate in contrast to the almost zero daily rate of NaS. NaS is the most expensive EES investment in the category and in order for the other technologies to become competitive, more research is needed to improve round-trip efficiency and lower costs.

VRB flow batteries outweigh the ZnBr and PSB in technical maturity, efficiency, cycling capability, specific power and power density. However, they provide moderate specific energy and the lowest energy density values, constraining their use in applications requiring bulk energy storage. All this information is presented in Table 8 and Figure 19 and as shown, with a similar capital investment such potential features can be greatly improved by a factor of two, utilizing the different topologies of ZnBr or PSB flow batteries. Hence, improvements in both cycle efficiency and lifetime are needed in order to become competitive and contribute in future power system applications.

Capacitors and inductors are appropriate for storing small quantities of energy. Recent advances have extended the use of capacitive and inductive technologies to larger scale

Table 8: Comparisons of flow battery technologies

	VRB	ZnBr	PSB
Power rating	2.00	1.33	10.00
Energy capacity	5.00	10.00	0.15
Power capital cost	1.43	0.00	0.00
Energy capital cost	0.00	0.00	0.00
O&M cost	0.00	10.00	10.00
Specific power	10.00	6.67	0.00
Specific energy	5.88	10.00	3.53
Power density	10.00	2.55	1.25
Energy density	4.71	10.00	8.57
Technical maturity	6.00	4.00	2.00
Daily self-discharge	10.00	10.00	10.00
Lifetime	6.67	6.67	10.00
Cycling times	10.00	2.19	1.25
Round-trip efficiency	8.50	7.50	7.50

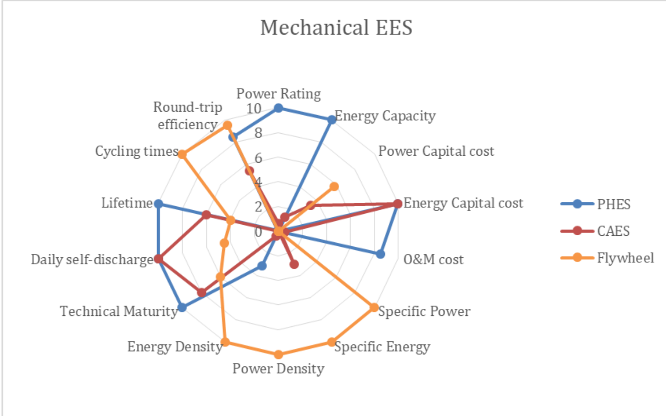

Figure 19: Potential characteristics of mechanical energy storage technologies

applications. Table 9 lists the selected potential features of capacitors, supercapacitors and superconductors, while a direct comparison is demonstrated by Fig. 21. Supercapacitors enjoy the highest efficiency and lowest investment and whole life costs. SMES can be cycled almost infinitely and provides the longest lifetime, but it is disadvantageous in terms of power and energy performance along with capital and O&M costs. Due to increased parasitic losses, electromagnetic EES technologies suffer from severe self-discharge and thus they become favorable only in high power/short duration applications. The daily self-discharge

Table 9: Comparisons of electromagnetic EES technologies

	Capacitor	Supercapacitor	SMES
Power rating	0.05	0.30	10.00
Energy capacity	0.00	0.33	10.00
Power capital cost	0.00	5.00	0.00
Energy capital cost	5.00	7.00	0.00
O&M cost	2.97	6.76	0.00
Specific power	10.00	0.50	0.20
Specific energy	0.07	10.00	3.33
Power density	10.00	10.00	8.89
Energy density	0.00	10.00	3.94
Technical maturity	8.00	2.00	6.00
Daily self-discharge	6.00	8.00	9.00
Lifetime	2.50	6.00	10.00
Cycling times	0.10	0.10	10.00
Round-trip efficiency	9.50	9.80	9.50

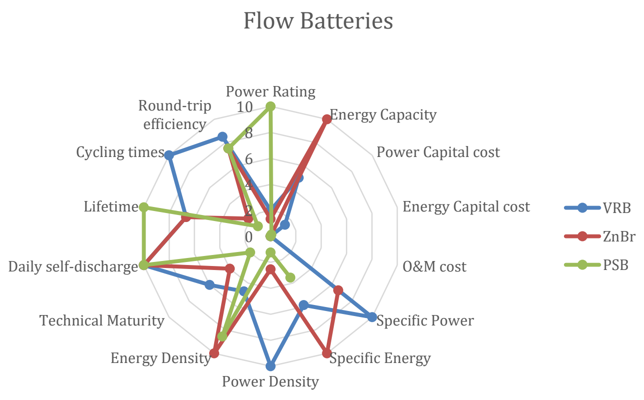

Figure 20: Potential characteristics of flow battery technologies

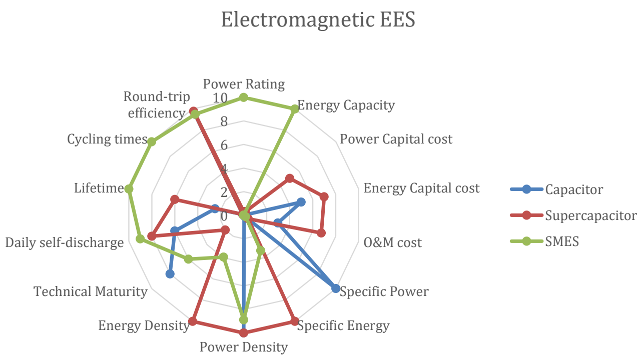

Figure 21: Potential characteristics of electromagnetic energy storage technologies

rate slightly favors SMES.

4.2. Results and discussion

A comparative assessment within the various EES categories is presented in the previous section. In this section, an overall analysis is undertaken in order to evaluate the feasibility of such systems and their future contribution, as technology-application pairs, to a sustainable energy production.

Broadly, EES systems are categorized into three types according to their power rating. PHES, CAES and LAES are suitable for large-scale applications (>100MW). Pb-acid, NiCd, PSB, SMES and regenerative FCs are suitable for medium-scale (10-100MW), while SS-CAES, flywheels, supercapacitors, NiMH, VRB, ZnBr, NaS, ZEBRA, Zn-air and Li-ion fall into small-scale applications of lower than 1-3 MW.

According to the time-scale of response, the various EES are distinguished as fast, relatively fast and not rapid. With response times within milliseconds to seconds, flywheels, supercapacitors, SMES, all kind of batteries and flow batteries, are falling into fast-response systems. Regenerative FCs together with SS-CAES provide relatively fast response in the range of seconds, whereas PHES, large-scale CAES and LAES offer slower response times of a few minutes.

Storage duration is a key element which helps distinguish EES technologies into short-term (seconds-minutes), medium-term (seconds-hours) and long-term (minutes-days). Storage duration is directly affected by the self-discharge ratio and thus short-term storage is provided by flywheels due to their very high daily energy dissipation. Medium-term is offered by electromagnetic supercapacitors and SMES due to increased parasitic losses, high-temperature/Na-based batteries because of the self-heating needs to maintain the operating temperature, SS-CAES and LAES. PHES, large-scale CAES, Pb-acid, NiCd, Li-ion, Zn-air, flow batteries and regenerative FCs are capable of providing long-term storage duration. However, Pb-acid, NiCd, and Li-ion batteries have a moderate self-discharge rate and consequently they become inappropriate for storage durations longer than the tens of days.

Related to storage capability, autonomy is an important attribute for isolated systems and micro-grids relying on intermittent renewable sources. It refers to the duration that an EES system is able to continuously supply energy. Hence, EES technologies can be classified in terms of their energy capacity (amount of stored energy) against the power they can deliver (power rating). Typically, less autonomy is expected from electromagnetic devices of supercapacitors and SMES along with flywheels. Higher autonomy is displayed by SS-CAES, conventional and high-temperature batteries while PHES, large-scale CAES, LAES, flow batteries, Zn-air and regenerative FCs are considered capable of supplying power autonomously for several hours.

Cycle or round-trip efficiency is a key element in evaluating EES options in power system applications. Very high efficiencies (>90%) appear in electromagnetic storage systems, flywheels and Li-ion batteries. Other batteries and flow batteries, SS-CAES and LAES provide high efficiencies of over 60%. Large-scale CAES, Zn-air and regenerative FC are more energy-intensive conversion processes and thus feature low efficiencies, which in the case of regenerative FCs may fall by up to 20%. It must be noted that efficiency becomes a crucial factor in some applications and even the cheapest technologies may be considered unsuitable. Such an example could be energy arbitrage where electrical energy may be purchased and sold back excluding conversion losses. In those cases, the self-discharge rate should also be considered. In addition, the efficiency of transformers and power conversion systems should be included in the estimation, since some technologies require high voltage AC to low voltage DC (and back to AC) conversions while others do not [9].

Additional factors affecting the overall investment cost are lifespan and cycle times. Electromagnetic EES devices provide extremely high cycling capability due to the absence of moving parts and chemical reactions. Mechanical components normally determine the lifetime of PHES, CAES and flywheel systems whereas all kind of chemical EES systems are deteriorated by time due to the degradation of chemical elements and electrolytes.

Apart from significant improvements in efficiency and extended lifetimes, capital and O&M costs tend to decrease when R&D efforts increase. In this sense, mature and commercialized PHES and CAES offer the lowest energy capital cost, becoming appropriate in high energy/long duration applications, followed by Zn-air and regenerative FCs which need further development to be proved as efficient. In terms of power capital cost, flywheel, supercapacitor and SMES technology are suitable for high power/short duration applications along with commercializing ZEBRA and developing Zn-air and regenerative FC. Flow batteries and Li-ion are still far too expensive, while the other conventional and high-temperature batteries sit in the middle. Regarding O&M costs, electrochemical technologies that require chemical handling are disadvantageous relative to the others, followed by technologies that need additional equipment to maintain the energy stored. However, a clearer demonstration can be achieved in [167], where both fixed and variable O&M costs along with replacement costs are examined for specific applications.

In this line of approach, it is clear that no single device can meet the requirements of a whole power system. Typically, when the discharge period is short, devices that can deliver high power are required, whereas for extended discharge periods of several hours or more, there is a requirement for devices that can store large amounts of energy. In addition, low capital cost and high O&M cost devices are more suited to short-duration applications whereas higher capital cost with low O&M costs are preferred for moving large amounts of energy over extended time periods. Finally, whether an EES system is appropriate or not depends on the exact location in the power chain where is intended for use and the requirements and preferences of the specific application discussed in Section 3. Based on the comparative assessment, the technology-application pairs identified are listed in Table 10 according to the power rating, response time and storage duration needed.

Although current trends assume small increases in fossil-fuel prices and modest penetration of renewables, to maintain economic growth whilst providing energy security and environmental protection, in the future, predictions should include higher costs of fossil fuels and consequently extended RES penetration requirements. In this regard, economics enable the storing of bulk electricity produced by intermittent sources connected to the grid, as opposed to immediate use. In medium power scales, distributed electricity may be stored locally, providing the advantage of load levelling of both the supply network and generation plant [9]. Moreover, market mechanisms may be encouraged, giving consumers an incentive to reduce usage during high demand periods when the power plants are heavily loaded and increase usage during off-peak periods [168]. Small and simpler EES units on the demand-side of the meter will then assist the possible installation of small-scale RES systems, obtaining additional benefits such as back-up power, peak shaving, load levelling, etc. [1].

Global efforts aimed at shifting towards intermittent renewable sources, reducing gaseous emissions and reliance on fossil fuels, are forcing the whole energy system to undergo dramatic change. Large-scale RES connected to the grid, highly distributed variable generation, growing penetration of plug-in hybrid electric vehicles (PHEVs) and EVs, and requirements for demand response, are some of the most important, opening up a wider field of applications which will certainly call for the active participation of EES and provide additional value [169–175]. Of vital importance too are micro grid (AC or DC) and smart grid systems, which are expected to thrive in the future, opening the pathway for a test environment for EES topology, model and device study [176].

However, alternatives to EES exist in the form of demand side management or power-to-gas processes. Demand side management involves utility control to improve the efficiency of buildings or industrial sites starts by pre-heating or pre-cooling buildings, heating water, timing the use of municipal water pumping and irrigation systems, water desalination, and so on [12, 177]. Power-to-gas appears a promising pathway to decarbonize power production and store electricity indirectly. Gas storage systems enable the process of carbon capture and storage (CCS) to be integrated and based on electrolysis, to increase both the flexibility of the power system and the share of bioenergy [167]. The various routes to hydrogen (H_2) and synthetic natural gas (SNG) are some of the major examples and could be considered viable alternatives [178, 179].

5. Conclusions

A wide variety of EES technologies and concepts are available, while others are expected to emerge in the future. In this work, a comprehensive overview of the most important EES systems has been presented. The technological progress, performance and economic aspects of 19 different EES options were discussed and evaluated. Also, the requirements and preferences relating to the potential applications across the power chain were reviewed and the technology-application pairs were identified, based on a comparative assessment. PHES is currently the most suited in large-scale energy management applications, mainly due to its technical maturity. With high power and energy per unit mass and volume, Li-ion monopolizes portable electronic devices, but are by far the most expensive and hence more difficult to be applied in larger scale, stationary EES applications. As the cheapest battery option, Pb-acid enjoys exclusivity in automotive starting, lighting and ignition applications and is considered the best choice for small-to-medium scale stationary applications of UPS and back-up power. Most of these technologies need more time to become mature and economical, and without appropriate storage opportunities their future contribution will proceed more slowly. Examples include flywheel, supercapacitor and SMES, whose applications are still focused on power quality, AA-CAES and LAES which are expected to be implemented for energy management applications in sites with favorable

Table 10: EES technology-application pairs

Power chain	Applications	Power rating (MW)	Storage duration	Response time	PHES	CAES	SS-CAES	FES	Pb-acid BES	Ni-based BES	Li-ion BES	Molten-salt BES	Metal-air BES	Flow batteries	Regenerative FC	Supercapacitor	SMES
RES Integration	Fluctuation suppression	0.2-400	âĽď1min	msecs				✓								✓	✓
	Oscillation damping	0.2-400	âĽď1min	msecs				✓								✓	✓
	Forecast hedging mitigation	0.2-400	1min-1hour	secs			✓		✓	✓		✓		✓	✓		✓
	Load following	10-1000	1min-1hour	secs					✓	✓	✓	✓		✓	✓		✓
	Unit commitment	10-1000	hours-days	mins	✓	✓								✓	✓		
Generation	Frequency regulation	1-1000	âĽď1min	msecs				✓									✓
	Spinning reserve	10-1000	âĽď1min	msecs				✓				✓					✓
	Non-spinning reserve	10-1000	1min-1hour	secs							✓	✓		✓	✓		✓
	Black-start	100-1000	1min-1hour	secs			✓								✓		
	Peak shaving	10-1000	1-10hours	mins	✓	✓			✓	✓		✓		✓	✓		
	Energy arbitrage	10-1000	5-12hours	mins	✓	✓			✓	✓		✓		✓	✓		
	Load levelling	10-1000	hours-days	mins	✓	✓								✓	✓		
	Seasonal storage	10-1000	âĽĕ4 months	mins	✓	✓							✓	✓	✓		
Transmission	Reactive support	0.002-10	âĽď1min	msecs				✓				✓				✓	✓
	Transmission congestion relief	0.25-100	5-12hours	mins	✓	✓			✓	✓		✓		✓	✓		
Distribution	Low voltage ride-through	0.002-10	âĽď1min	msecs				✓								✓	✓
	Voltage regulation	10-100	âĽď1min	msecs								✓					✓
	Distribution congestion relief	0.25-10	5-12hours	mins					✓	✓	✓			✓	✓		
End-user	Uninterruptible power supply	0.002-10	âĽď1min	msecs				✓	✓	✓						✓	
	Emergency back-up	0.002-10	1min-1hour	secs			✓		✓	✓					✓		
	Demand shifting	0.001-0.01	2-4hours	mins					✓	✓	✓			✓			

geology and metal-air as environmentally benign technologies. In the near term, the various types of FC are expected to be used mainly in vehicles while in the long term, their use as CHP facilities may be extended to both residential and industrial applications. Two possible modes for their participation in a sustainable development exist, for either direct or indirect EES, and must be considered viable. Although the increasing dependence on variable renewable energy sources has kickstarted the widespread use of EES, the lack of sufficient algorithms and tools capable of capturing the whole range of benefits potentially offered by them (such as RES integration, emissions avoidance, power plants cost savings, asset deferral, etc.), along with the lack of market mechanisms and regulatory structures, discourage utilities, consumers and other industry stakeholders from making investments. It is clear that market rules and policy developments from the side of the regulators, system operators and decision makers will help technology developers, analysts and planners improve EES' cost-effectiveness and vice versa.

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