Overview on recent developments in energy storage: Mechanical, electrochemical and hydrogen technologies

OVERVIEW ON RECENT DEVELOPMENTS IN ENERGY STORAGE: MECHANICAL, ELECTROCHEMICAL AND HYDROGEN TECHNOLOGIES

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Abstract

Energy production is changing in the world because of the need to reduce greenhouse gas emissions, to reduce the dependence on carbon/fossil sources and to introduce renewable energy sources. Despite the great amount of scientific efforts, great care to energy storage systems is necessary to overcome the discontinuity in the renewable production. A wide variety of options and complex characteristic matrices make it difficult and so in this paper the authors show a clear picture of the available state-of-the-art technologies. The paper provides an overview of mechanical, electrochemical and hydrogen technologies, explaining operation principles, performing technical and economic features. Finally a schematic comparison among the potential utilizations of energy storage systems is presented.

Keywords: Energy storage; Power system; Technical and economic performance features; Renewable energy systems

1. Introduction

"Energy" can be considered a prerequisite of the countries development and one of the most important factor to increase people wellness. For this reason the world energy diet shows a steady growth (+56% from 1990 until 2015) in the last years mainly due to the Asian continent (see scenario of Figure 1), while North America and European Union slightly decrease energy demand from 2008 due to the economic crisis. Fortunately, in the last 20 years, energy production from renewable sources has risen continuously (see Figure 2). The Italy scenario is a good further example of energy production due to the great amount of energy plants for renewables production. In fact, Figure 3 shows the Italy trend of energy production in the 2005-2015 interval (data provided by national energy services manager, GSE). The slight decrease in renewables production in 2015 (vs 2014) is due to a minor rainfall in this last year.

The reasons that explained this increase of attention about renewables are the lack of carbons and the necessity to offer a best future to 4,5 billion of people who today have a limited access to energy resources, and this also matches the international environment treaties to reduce world pollution, i.e., Kyoto Protocol, EU 2020. Despite this trend, renewable sources are still unable to overcome the other energy sources for mass energy production because of their random behaviour [1–3]. For instance, the biogas production from biomass relies on the performance of a cultivation, but in a more general way, on the employed "digestion" processes [4–6]**.** Eolic and solar generations are characterized by the greatest availability, but are considered to be unpredictable. An additional important aspect that should be considered is that generally the load curves almost never follow the energy availability curves. Consequently, the direct consumption of energy produced from renewable sources can be very inefficient and inadequate because a large amount of energy is over-produced and then most commonly wasted, as well as, is not directly recovered in other cases (e.g., thermal conversion). This asynchronous production against energy demand can represent a limiting factor to the further development of renewables. The only solution to continue improving renewables is the energy storage. For these reasons the increase in scientific research into energy storage systems is highly desirable. The use of an Energy Storage System (ESS) can raise the energy production efficiency [7,8]. It is charged with energy surplus coming from the production phase, while when the production is insufficient or absent, the needed amount of energy is withdrawn by its discharging. Moreover, such system allows separating, both in space and time, the power production from its consumption.

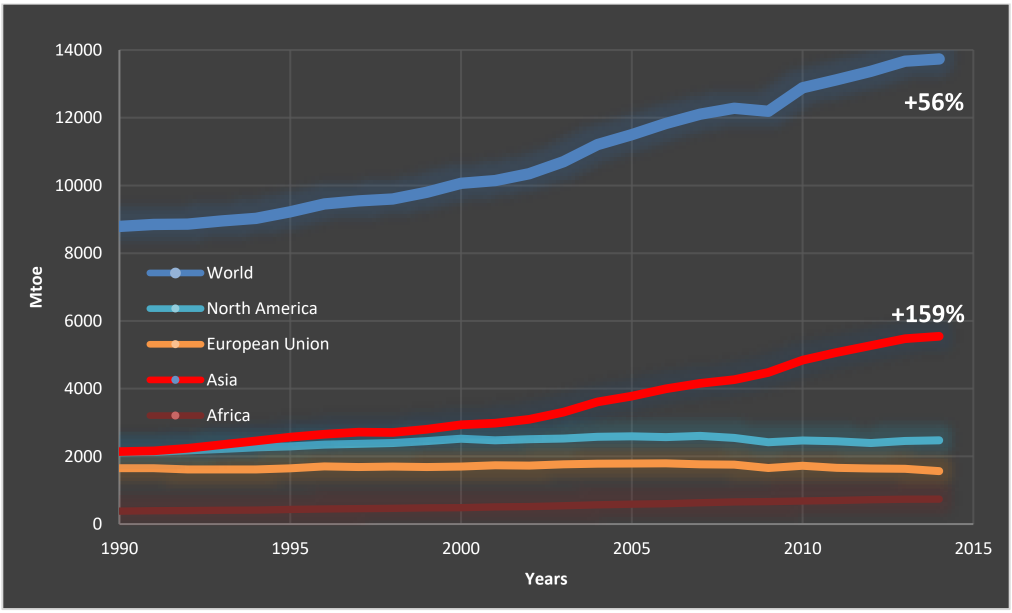

Figure 1 - World energy diet (Mtoe), adapted from ENERGY DATA - Global Energy Statistical Yearbook 2015

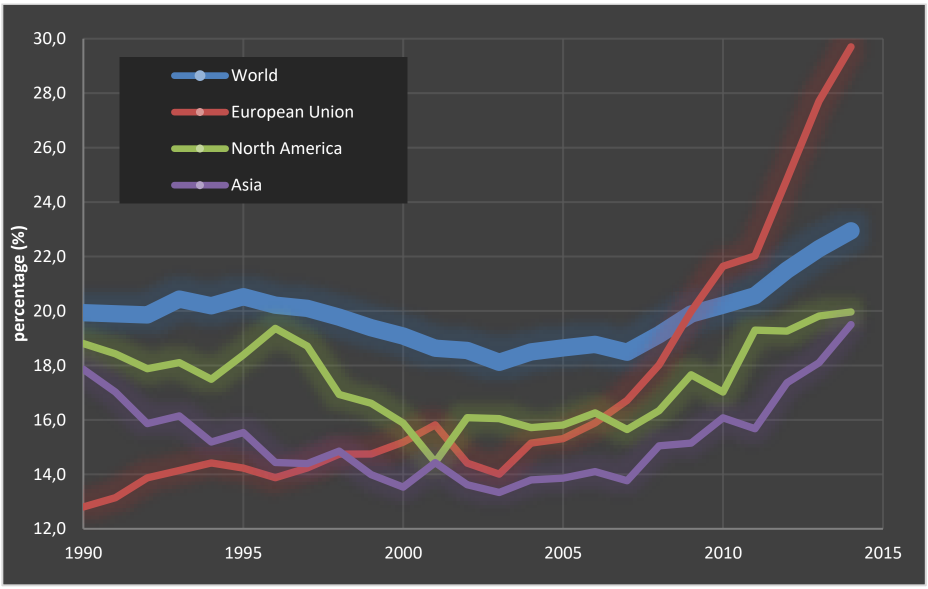

Figure 2 - Renewables to ELECTRICITY production, ENERGY DATA - Global Energy Statistical Yearbook 2015

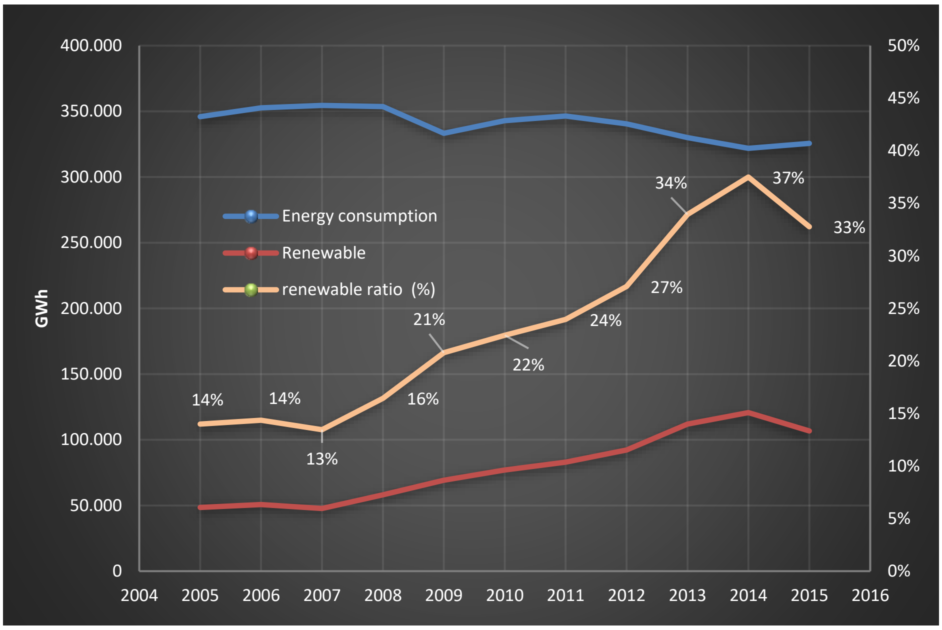

Figure 3 – Italy electric energy demand, GSE data 2015

In this way, it would be possible to achieve the transition from a localized energy production (few big power plants) to a grid energy production (more and smaller power plants). This change would increase the global efficiency of the whole energy production-distribution system, reducing the losses in the Transmission and Distribution (T&D) process and being much more environmental friendly due to the lower fossil fuel consumption and pollution emissions [4].

A huge variety of energy storage systems is available. Usually, it is possible to provide a classification based on the energy conversion mode. Therefore, they can be divided as follows:

- Mechanical Systems: Compressed Air Energy Storage (CAES), Pumped Hydroelectric Storage (PHS) and Flywheel Energy Storage (FES);

- Electric Systems: supercapacitors and Superconducting Magnetic Energy Storage (SMES);
- Electrochemical Systems: Lithium-ion battery and flow battery;
- Hydrogen storage, based on electricity conversion in hydrogen in charge phase and vice versa.

The present work aims to provide an extensive review on mechanical, hydrogen and electrochemical storage systems, which appear to be the most promising and appealing technologies in a long time prospective. In particular, the mechanical systems represent the longest studied storage technology, while the battery storage is largely considered as the technology that today attracts the most profitable investments, both in static applications and automotive field. The hydrogen storage represents one of the most remarkable alternative to the fossil fuels. Starting from the physical principle on which they are based, a detailed analysis on the most recent developments and applications is therefore reported for each of the storage solutions considered in the present work.

2. Mechanical Systems

Pumped hydro storage

In Pumped Hydro (PH) stations, water is pumped to a higher reservoir, during the charging phase, using over-produced energy. During the discharging phase, water flows downfall through the turbine producing energy. A schematic is reported in Figure 4.

Usually, the hydraulic machine is a “pump as turbine” (PaT), a reversible machine that can act both as pump and as turbine. PaTs are connected to reversible electrical reversible machines (Alternator-Motor). In the charging phase, external energy is employed to pump water from the lower reservoir to the upper one. When the power demand in high, the discharge phase starts and the water flows downward through the turbine generating electrical energy. The charge and the discharge powers depend mainly on the hydraulic head (namely from the height difference between the reservoirs), while the amount of energy stored is function of the capacity of the reservoirs [7,9].

Pumped hydroelectric storage is a mature technology that offers a long storage period, high efficiency, relatively low capital cost per unit of energy and fast response time.

The typical rating is between 1000 and 3000 MW. The discharge period takes hours or days and the response time is less than 1 minute. The lifetime is about 40 years while the power and energy capital cost value amount respectively to 500-1500 €/kW and 10-20 €/kWh [9–11].

If the losses within the pipeline are neglected, the efficiency depends directly on the machine's efficiency and a typical value is comprised between 70% and 80%. The most performing systems reach an efficiency of 87% [10].

The main drawbacks are represented by the geological structure reliance, the low energy density (0,3 kWh/m^3), the long construction time (about 10 years), the high capital cost (millions of euros), together with some environmental issues linked to the building of the reservoirs [12–14]. Moreover, evaporation losses are significant and they increase the costs in the hot climate [7,13].

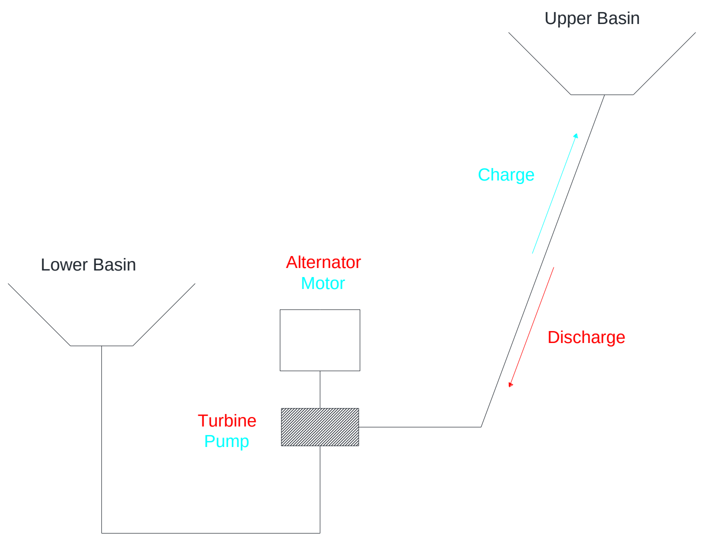

Figure 4 - A pumped hydro storage system [11]**.**

PHS represent the oldest storage technology: in Alpine region hydroelectric systems were built since 90s of XIX century. In 1950s reversible pumps-turbines were introduced. Nowadays, PHS stores about 127 GW worldwide (more than 76 GW were installed just in 2014), which corresponds to 3% of the global energy storage capacity. About 99% of the stored energy is ”packed” in water [10,11]. Moreover, PHS results suitable for balancing intermittent energy generation from wind or photovoltaic plants. Especially in isolated realities, as Canary Islands or Ikaria Islands, PHS coupled with wind power represents the best solution if containing costs is a main purpose [10,12,15–17]. In such contexts the sea is used as lower reservoir, saving part of the construction costs. As side effect, more attention preventing corrosion is needed [16,18–20].

Recently, Sarasúa et al. [21] provided an example about the importance that hydropower plants can have in the grid integration of increasing levels of intermittent energy sources. They studied the dynamic response and governor tuning of a long penstock pumped-storage hydropower plant (PSHP) equipped with a pump-turbine and a DFIG, which was connected to a small isolated power system with thermal generation, and which provided load–frequency control under the orders of an automatic generation control (AGC) system. Three different criteria were investigated for tuning the unit's governor. The first two criteria (DCP and FDR) were based on the root locus analysis of a linearized 4th order model of the unit's speed control loop. The third criterion was based on a Pareto approach using the non-linear model. They found that FDR tuning criterion managed to significantly damping the oscillations of both the hydraulic and mechanical variables of the PSHP, which may result in an extension of the plant's lifetime. By contrast, it gave rise to a higher overshoot in the unit's speed, what is not likely to affect the output power of the PSHP or the system frequency. With the DCP tuning criterion, the dynamic response of the PSHP was poorly damped. The Pareto-based tuning criterion showed an intermediate behaviour in terms of both the damping and overshoot of the hydraulic and mechanical variables of the PSHP.

However, the influence of different values of the reference unit speed, should be so studied too, in order to verify the adequacy of the governor tuning criteria for variable-speed operating conditions.

Talking about photovoltaic and wind systems used in rural electrification, the great part of the works, in which to find an efficient way of storing energy is the main topic, have not considered other ways of storing energy except for conventional battery storage systems. Kusakana [17], showed as a hybrid system consisting of a photovoltaic unit, a wind unit, a pumped hydro storage system and a diesel generator can be an attractive solution. In such study, an energy dispatch model that satisfies the load demand, taking into account the intermittent nature of the solar and wind energy sources and variations in demand, is presented, with the aim to minimize the hybrid system's operation cost while optimizing the system's power flow considering the different component's operational constraints.

The integration of wind or solar farms and pump storage plants is instead increasing. More and more large-scale renewable energy integration systems are taking shape gradually. As a consequence, optimized control has become a great challenge to these systems. Reversible design and "S" characteristic area of the PSHU are the basic obstacles [22,23]. Operating along the S-shaped curve can lead to intense oscillations of rotational speed in the start-up process making it is so unstable that it may cause difficulties with synchronization. An accurate care is needed to control systems applied to renewable energy plants to avoid the so called "voltage dips" to the grids. Thus, this scenario might be attractive for a research field that takes into account innovative controlling techniques. An example could be the proposal of that used a Fuzzy logic rules as a control for turbo-gas technology [24]. Recently, Xu et al. [25] studied this problem and proposed an adaptively fast fuzzy fractional order PID (AFFFOPID) control method for PSHU. In their work an improved stochastic search algorithm, namely BCGSA, and the time domain optima tuning function are proposed for the parameter selection of PSHURS. And, by means a comparative

analysis among the AFFFOPID, PID and FOPID method of the novel PSHURS (which could fully reflect the nonlinear in 'S' area) Thy showed that AFFFOPID could effectively restrain the oscillation of rotational speed in 'S' area of PSHU and has high robustness and stability.
Conversely, the introduction of Hydrokinetic micro-turbines lowered the PHS target size, allowing the construction of smaller plants with lower capacity. As a result, this energy storage system became suitable also for grid application as well as for little realities [17,20].

Compressed air energy storage

In the Compressed Air Energy Storage (CAES) systems, the energy is stored in form of pressure energy, by means of a compression of a gas (usually air) into a reservoir. When energy is required, the gas is expanded in a turbine and the energy stored in the gas is converted in mechanical energy available at the turbine shaft. A possible system configuration is depicted in Figure 5.A usual plant arrangement is composed of a multistage compressor equipped with both an intercooler and an aftercooler, a multi-shaft gas turbine, a motor/generator with a clutch, which allows to act the compressor and the turbine in different moments, an underground storage for the compressed air and other equipment controls and auxiliaries, such as a fuel tank and a heat exchanger [1–3,5–7,10].
In the charging phase, the exceeding energy is used to compress air in the underground storage (up to 70-100 bar). In the discharging phase, the air is drawn from the storage, heated (burning natural gas or using recovered/recycled heat) [1,3], and then expanded through the turbine train [4,9,13,14].

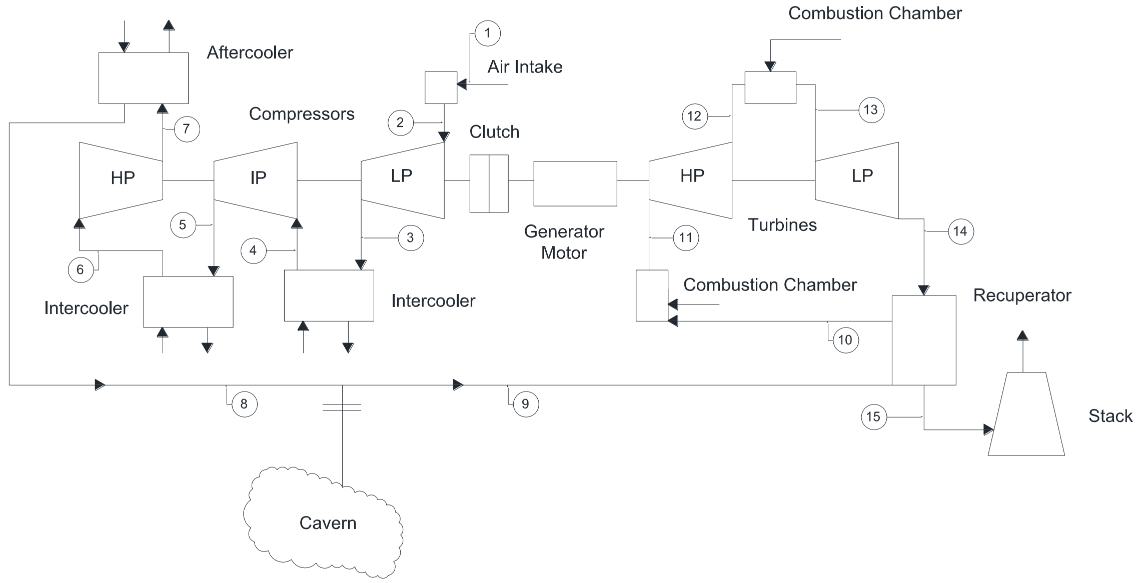

Figure 5 - Schematic diagram of a CAES plant, adapted from [20]

CAES is suitable for large-scale power, i.e., hundreds of MW. T storage period can be greater than a year. The efficiency varies between 70% and 89% since it is correlated to the compressor and turbine efficiencies and it is decreased by low self-discharge ability that is typical of this system. Other peculiarity are a fast start-up (9 minutes for an emergency start, 12 in normal conditions), an energy density counts about 12 kWh/m^3, a lifetime approximately of 40 years (comparable to PHS) and a power capital costs that range from 400 €/kW to 800 €/kW (since the presence of underground storage conditions)[9,11–13].

Thanks to these features, CAES results suitable for energy management applications as load shifting, peak shaving, frequency and voltage control [9].

Furthermore, for adiabatic CAES, heat usually cannot be efficiently utilized and the low inlet temperature of turbine in an adiabatic-CAES (A-CAES) usually leads to low discharge efficiency. To address these problems, Yao et al. [26] recently proposed a novel combined cooling, heating and power system (CCHP) based on small-scale CAES. In particular, a gas engine was employed to boost the power output, while the tri-generation aimed at using heat, particularly low-grade heat in a cascade way. They performed a sensitivity analysis that showed that the air temperature and pressure at the turbine inlet, as well as the effectiveness of the heat exchangers have great influence on the system's thermodynamic performance. In such study, the trade-off between the thermodynamic and economic performances was also investigated by an evolutionary multi-objective algorithm. The results they showed reported that the total investment cost per output power of the Pareto solutions does not increase significantly when increasing exergy efficiency below 51%, indicating the solutions with an exergy efficiency of around 51% are promising for practical designs.

The most important drawback of CAES technology is represented by the difficulty in finding appropriate geographical sites with underground natural caves. Moreover, fossil fuel are burned within the system and this raises concerns about the well know problems relate to pollutant emissions [12,27].

Therefore, in order to deal with these issues, Advanced Adiabatic CAES (AA-CAES) systems have been developed. Referring to Figure 6, the thermal energy is drawn from the compressed air, stored in the thermal storages, and released before the expansion, without requiring any combustion process and therefore involving no fuel consumption. The compressed air is stored in stainless steel vessels in place of natural caves [27–30]. In this way it was also possible to implement the so called Sm CAES (SS-CAES) since they generate smaller power, namely less than 10 MW [7,28]. SS-CAES plants are also built using external reservoirs instead of natural caves.

Furthermore, it may be possible to recover a greater part of the wasted heat, by using a Kalina cycle enhancing the cycle efficiency by 4% [29]. The Kalina cycle is a combined cycle that employs a two phase solution of two fluids with different boiling points. Since the solution boils over a range of temperature more of the heat can be extracted from the source than with a pre working fluid and different level of heat sources can be used in the same system. Such cycle requires, however, a more complex plant.

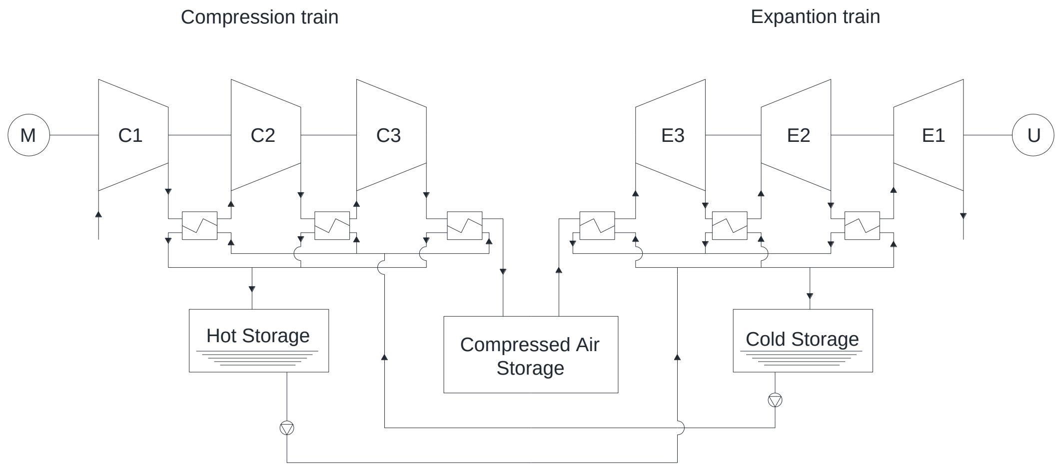

Figure 6 - CAES-TES plant, adapted form [21]

The oldest CAES plant was built in Hundorf, Germany, in 1978. It was designed to meet the energy demand peak and allowing a nuclear power plant to maintain a constant capacity factor. The plant used two salt dome caverns as underground storage (300000 m^3 at 50°C and 46-66 bar) and developed 290 MW [28–30]. The MacIntosh plants, built in 1991 in Alabama with 110 MW of energy storage, improved the Hundorf's technology by using a heat recovery system to recycle part of the heat that the gas still has once it left the turbine [28,29].

A variant of CAES is represented by the Liquid Air Energy Storage (LAES). In that system an air flow is liquefied and then stored at atmospheric pressure in an insulated vessels [28]. The use of an external reservoirs, instead of that of an underground caves, for large scale CAES reduces significantly the pressure losses due to the rocks natural permeability, increasing the global efficiency of the system [31].

Furthermore, CAES systems are suitable for being integrated with wind turbines both in on-shore [30] and in isolated areas [31,32] and in off-shore [33] plants as well. It is also possible to combine PHS with CAES systems, allowing to overcome the respective drawbacks and consequently producing an increase of the energy density as well as an increase of the efficiency of the plant [33,34].

The most recent innovations in this field include the use of either supercritical compressed air [35] or compressed CO2 energy storage system under supercritical and transcritical conditions [36].

are represented by Another solution is represented by supercritical compressed air energy storage (SC-CAES) which possesses the advantages of high efficiency by employing the special properties of supercritical air. Recently, Guo et al. [35], targeting the problems of conventional CAES, investigated the performance of a novel SC-CAES. They provided an exergy analysis of the system and concluded that the processes of the larger exergy destruction include compression, expansion, cold storage/heat exchange and throttle.

The efficiency of SC-CAES is expected to reach about 67.41% when energy storage pressure and energy releasing pressure are 120 bar and 95.01 bar, respectively. At the same time, the energy density is 18 times larger than that of conventional CAES [35].

Liu at al. [36] proposed the use of a two-reservoir of compressed CO2 energy storage system under supercritical and transcritical conditions. Results showed that the transcritical compressed CO2 energy storage system has higher round-trip efficiency and exergy efficiency, and larger energy storage density than the supercritical compressed CO2 energy storage. However, the configuration of supercritical compressed CO2 energy storage is simpler, and the energy storage densities of the two systems are both higher than that of CAES, which is advantageous in terms of storage volume for a given power rating.

FLYWHEELS

In the Flywheel Energy Storage (FES) systems (Figure 7), it is possible to store the exceeding energy by means a conversion into a kinetic energy of a spinning mass. FES systems are composed of a steel or composite rotating mass (the flywheel) matched up with an electrical motor/generator for charge/discharge phases, two magnetic bearings that avoid mechanical friction and a vacuum chamber able to reduce the aerodynamic losses [11,12].

During the charge phase, the flywheel is accelerated by the electric motor; when the energy demand in high, the flywheel slows down and the energy transfer to the generator is realized by electromagnetic induction [9,12].

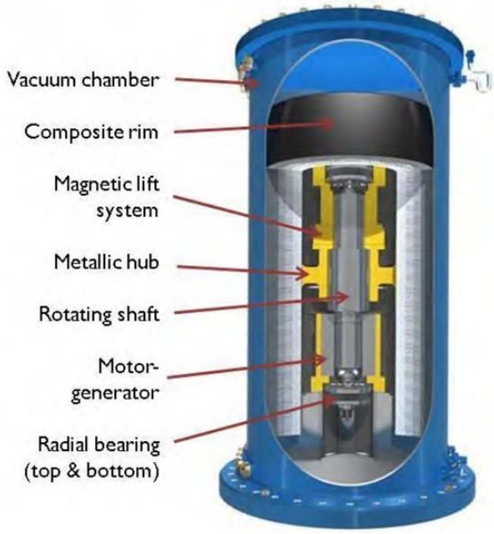

Figure 7 - A typical flywheel configuration-Beacon Power

The stored energy depends on the moment of inertia of the spinning mass, as well as of the rotational speed. Therefore, in order to increase the available energy, it is possible either by increasing the moment of inertia or by using composite materials to build the flywheels that can allow to overcome 10^5 rpm. In fact, the first strategy is typically adopted in low speed applications (speed lower than $6*10^3$) while advanced materials are used to perform high speed FES [9,37].

In particular, in order to obtain higher flywheel energy densities, a search for a higher strength and lower density composite for the constant stress portion is required. Recently, Conteh and Nsofor [38] studied lamina and laminate mechanical properties of several composite materials suitable for flywheel energy storage. Design and stress analysis were used to determine the maximum energy density and shape factor for the flywheel. They found that a hybrid composite of M46J/epoxy–T1000G/epoxy for the flywheel exhibited higher energy density when compared to known existing flywheel hybrid composite materials such as boron/epoxy–graphite/epoxy.

These systems can be compared with electrochemical batteries, since they show high efficiency (90-95%), long lifetime (20 years) with low maintenance, no depth-of-discharge effects, no environmental issues deriving from no use of toxic materials, fast response time and short recharge time. Moreover, the flywheels are able to be connected in parallel, increasing the specific energy from low (5 Wh/kg) to high speed (100 Wh/kg) [9,13,14,37].

A critical aspect of this technology is represented by the high self-discharge tendency: frictions and aerodynamic losses can reach about 20% of the stored capacity per hour [11].

FESs find applications both in stationary and vehicular fields. On one hand, flywheels are often coupled with wind-diesel or PV-diesel plants, like UPS units, in order to contain cost and downsize the diesel generator reducing fuel consumption and emissions; moreover FES systems provide backup power, improve power quality, generate high voltage and supply both active and reactive power to compensate frequency and voltage [37,39]. On the other hand, flywheels are often part of hybrid energy storage systems, especially in automotive applications. In these configurations, FES are coupled with batteries: the flywheel represents the power source for transients while the battery provides the main energy storage. Furthermore, KERS (Kinetic Energy Recovery System) relies on FES plant: braking action makes flywheel spin at almost 60000 rpm, providing the engine stop and allowing a 25% reduction in fuel consumption [7,40–42].

Recent developments regards innovative electric motors [43] and magnetic bearings based on REBCO (Rare Earth Barium Copper Oxide) HTS magnet, which allow 7-10 tons flywheels spinning at 6000-9000 rpm and providing about 1000 kW of power output and about 300 kWh of stored energy [44].

Other innovations regard control strategies. Based on the use of a homopolar synchronous machine in a FES, Amodeo et al. [45] developed a high performance model-based power flow control law using the feedback linearization methodology, which is based on the voltage space vector reference frame machine model. The result is a high-performance sensorless control that uses a load angle observer that can be implemented without major hardware modifications or cost increase. Hamzaoui et al. [46] analysed two control techniques DTC (direct torque control) and DPC (Direct power control) dedicated to a variable speed wind turbine based on a double fed induction generator with storage in order to achieve better performance. They showed that the command DTC applied to the DFIG (Doubly Fed Induction Generator) and FES, presented a high performance torque control and a very important dynamic, while keeping good accuracy of control.

3. Electric and electrochemical systems

Supercapacitors and magnetic field energy storage

Supercapacitors Energy Storage (SES) power plants employ high energy density capacitors to store electricity. Thanks to their fast response, such systems are often employed in power leveling or power balancing installations. An interesting application of SC is given in the work by Zhang et al. [47]. A system to produce electric energy from vibrating railroad is presented: Supercapacitors are employed to store the electricity produced by the generator. Thanks to their fast response, SC are the only devices able to handle a so high power rate. The overall efficiency of the system is about 55%, which is an impressive value. Despite the high cycling life, over 10^5 complete cycles, and high efficiency , 84% ÷ 97%, the self-discharge rate (up to 40%/day) and costs (6000 $/kWh) make this technology still un-able for spread. Research is focused on the development of low cost multi-layer supercapacitors employing new materials like Carbon[9],[48], Graphene [49] or Paper [50] .

Hybrid configuration and molecular engineering are also employed. Varying the carbon activation process or the carbon nano tubes (CNTs) orientation, different results are obtained. With random CNTs orientation, a 102 F/g capacitance is obtained; vertically aligning CNTs through a CVD process, the specific capacitance enhances to 365 F/g. Electrode production with chemically activated Carbon gives a specific capacity of 135 F/g while employing a laser, a value of 276 F/g is obtained [51].

Hybrid configuration are considered when the major object is pseudocapacitance enhancing. An electrode made of a MnO_2 coated Carbon fiber fabric is presented by Cakici et al. [52].Results are quite interesting, sicne they showed that capacitor achieved a specific capacitance of 467 F/g with a capacitance retention of 99.7% after 5k cycles. The energy density was 20 Wh/kg. The coulombic efficiency kept around 97% during the 5k cycles of testing. Due to the low cost and the excellent energy density, they concluded that represented a good starting point for new hi-capacity portable energy device.

Superconducting Magnetic Energy Storage (SMES) is based on a magnetic field obtained by current circulation in a superconducting wire. A simple scheme is showed in Figure 8

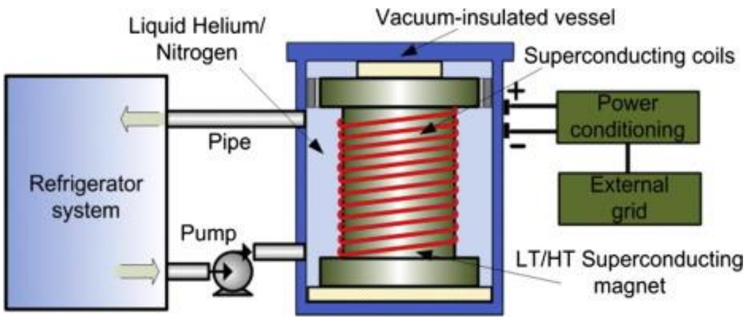

Figure 8 - A typical SMES layout [9]

Electricity come to the coil passing through a power conditioning system (usually an AC to DC converter), then is converted to magnetic field. When discharging, the electric current runs from the coil to the grid converted by a DC to AC converter.

To reduce ohmic losses, the wire is kept under it is superconductive temperature. Now a class-based distinction can be made:

High Temperature SMES' coil works at ~70K while in Low Temperature SMES coil is kept at ~7 K.

Such systems can achieve high energy densities (up to 4kW/l), very high efficiencies (95% ÷ 98%), fast response times (milliseconds) and very good lifetime (up to 30 years). They can even be fully discharged without reporting significant deterioration, despite almost all batteries. Moreover, high shunt currents are supported so high powers can be handled (for short times) without damages. However, the cost are still forbidding, being around 10.000 $/kWh, due to the cooling system and coil's materials. Environmental issues rises from high concentrated magnetic field employing [9].

SMES and Supercapacitors can be used in hybrid configuration with Batteries in contests where power demand often changes respect the power production (e.g. Wind and Photovoltaic farms), combining the high power density of SMES and SES with the high energy density and reliability of batteries [53–55]. Introducing a Proportional-Integral (PI) controller, Prakash et al. obtained a lower frequency variation in various hybrid configurations, even in absence of storage systems. The lowest frequency variations are obtained employing fast response EE systems such as Flywheels and Supercapacitors. Moreover, it's exposed that systems' response is faster when energy is transferred to employers by a High Voltage Alternated Current link, which is optimal for distances lower than 50 km. In this case (FESS+SES) the Integral Square Error of the frequency variation – in the worst condition analysed (wind turbines + fuel cell + photovoltaic + diesel generation)- decreases from 0.2360 to 0.0194. Even in High Voltage Continuous Current link the PI controller introduction strongly reduces the system's response time [56]. Another application of a PI controller is given in [57]. A STATCOM controller is employed to guarantee the grid stability against the reactive power variation due to the variating speed of wind turbines and variable torque request of induction machines. The bidirectional AC/DC converter (STATCOM) connected to the grid and coupled with a supercapacitor is able to achieve the requested reactive power in order to maintain stable the whole grid. Moreover, the Supercapacitor achieve the controller the ability to satisfy the active power request in transient stages. It can be seen that the storage system is not the only entity involved in a micro-grid structure. The energy management policy plays a crucial role too.

Redox flow battery

Redox Flow Batteries (RFB) are a new generation of power accumulation units. Their biggest advantage is that the power density is detached by the battery's capacity, allowing the easy upgrading of existing RFB supplies and various configurations depending on specific requests. Despite standard batteries, the redox reaction is performed through an ion-permeable membrane dividing the positive and negative electrolyte. The electrolytes are stored in separate tanks. They are pumped into the cell and the proton exchange between anode and cathode generates the electric power circulation. The tank capacity is directly related to the battery's capacity while the number and materials of cells influences the battery power capabilities.

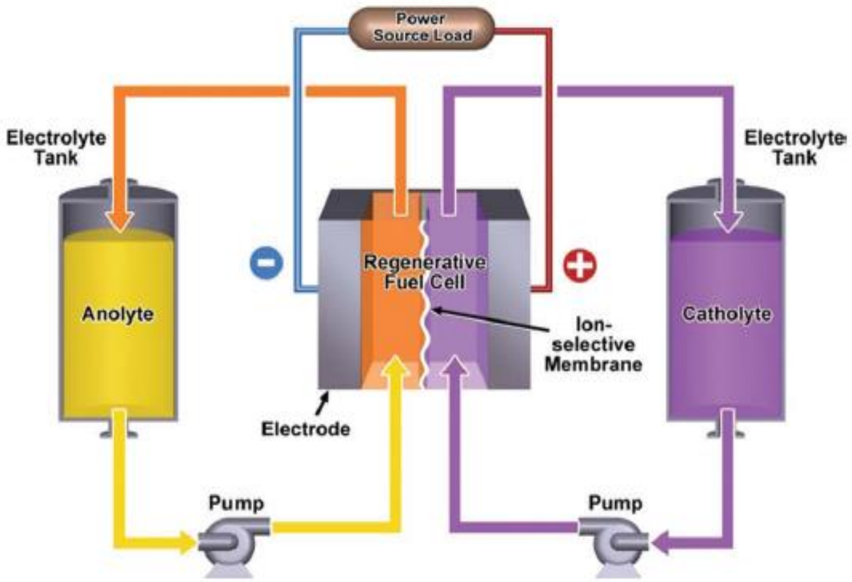

Figure 9 - A standard RFB configuration

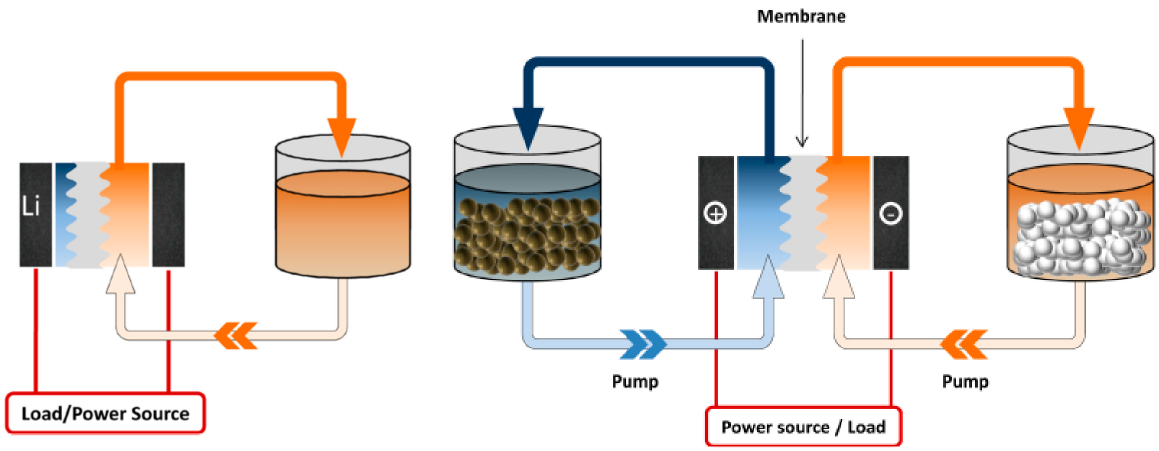

Figure 10 - Hybrid configurations: left is with a solid electrolyte (Lithium typically) right a semi-solid configuration (the solid material, Lithium, is stored in tanks with the liquid electrolyte).

Basic operative parameters are the usual of common batteries like Energy (or equally Power) Density (ED), the various efficiencies (Coulombic, Voltmetric and Energetic) and of course Capacity and life (expressed in terms of time or cycles).One of the most important differences between RFBs and common electro-chemical power accumulator units is the relationship between Depth of Discharge (DoD) and life-time. Liquid RFB's life is generally not influenced by the Depth of Discharge (DoD) (full Vanadium and Zinc-Bromine RFB, for instance, can achieve a 100% DoD without losing life-cycles or Efficiency). It should be pointed out that cell's life and efficiency depends on various factors like the operating temperature and the discharging current [58].

An ideal battery should have high Energy Density (or equally high Power Density) to reduce the overall dimensions (and\or weight), of course great Capacity and high Energy Efficiency. Output voltage and\or current is not so important because cells may, however, be connected to achieve higher Current gain (e.g. parallel connection) or higher Voltage Output (e.g. in series connection). The second choice is less typical due to fast electrodes degradation phenomena.

Depending on battery type, typical energy density values are in the order of 45-90 Wh/l (full Vanadium RFB) [59].

The major cons in RFB are the low specific energy density and high costs. To enhance energy density and overall efficiency, different approaches have been followed. New redox species have been tested, including Lithium, Sulfur and Quinones. Moreover, molecular engineering has been applied to create organic specific molecules and ligands (Metal or organic complexes) to avoid toxicity or corrosion related troubles and to improve energy density. The introduction of Carbon Nano Tubes (CNT) yielded higher efficiency and higher capacity, due to lower electrode's ohmic losses [59]. Electrode material, form and coating has a general heavy impact on battery's performances.

Treating standard electrodes in a partial oxygen environment (42% of Oxygen, 58% Nitrogen) decreased the activation over potential of 140 mV, moreover an aerial increase was obtained. The Energetic Efficiency (EE) raised from 63% to 76% and the usable capacity at 200 mA\cm2 has almost doubled. So doing, system cost has been reduced of about 20% (at constant stored energy) [60].

Employing Nitrogen-Doped Carbon Nanotubes as electrodes, the EE increase up to ≈ 76% while the discharge capacity raises from 25 to 33 Ah/l (@40 mA/cm2)[61].

Electrodes (Graphite felts) modified with atmospheric pressure plasma jet can achieve a 22% EE improvement [62].

A coconut shell derived mesoporous electrode is presented by Ulaganathan et al. Such electrode provides an extra electron couple reaction in the cell (V^{3+}/V^{4+}) bringing the cell EE to 85% after 100 cycles [63].

In flow-by configuration, the employment of perforated carbon paper electrodes yielded higher power and current densities, with a general performance increase up to 31%, with a global lower pressure drop (4÷14 %) [64].

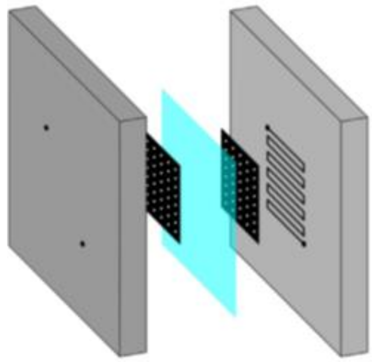

Figure 11 - The cell used in [64]

Membranes too are elements of research. Jia et all. introduces an innovative (and low cost) Sulfonated Poly(Ether Ether Ketone) (SPEEK) membrane embedded with the short-carboxylic multi-walled carbon nanotube (shortly SPEEK/SCCT membrane) claiming an overall performance increase (7% higher Coulombic Efficiency -CE-, 6% higher EE but lower capacity loss in comparison with the one with Nafion 212)[65].

In Xi et al.'s work the SPEEK membrane is analyzed varying the Degree of Sulfonation (DS) and casting solvent showing interesting results [66]:

- with a 67% DS the ion selectivity is optimal;

- N,N' -dimethylformamide (DMF) is the optimum casting solvent due to polymer (membrane itself)-solvent interaction .

CE increases by 5,4% and EE by 6,6% respect the Nafion 212 [66].

The employment of a hybrid membranes (SPI/ZGO) composed of Sulfonated PolyImide (SPI) and Zwitterionic polymerfunctionalized Graphene Oxide (ZGO) shows a higher cell performance (CE: 92-98%, EE: 65-79%) compared with commercial Nafion 117 membrane (CE: 89-94%, EE: 59-70%) at 30-80 mA/cm^2[67].

A Diels Alder Poly(Phenylene) (DAPP) membrane is instead analyzed by Pezeshki et al. [68] that showed as, depending on the functionalization group, DAPP could be used as anion exchange membrane or cation exchange membrane. Energy Efficiency raised to 85 % while CE is slightly above 95% .

Sol–gel-derived Nafion/SiO_2 hybrid membrane lowers vanadium ions permeability and increases Coulombic and Energy efficiencies compared to pure Nafion membrane. The pore size and pore-size distribution of Poly(Ether Sulfone) (PES)/silica composite porous membranes can be controlled by the amount of silica gels inside the pores to reach a Coulombic Efficiency of 97% [69].

A pump-less solution, based on a hybrid electrolyte, has also been tested (Lithium-Polysulfide) [70] with up to ≈400 Wh/kg Energy ED [70]. A membrane-less battery (Lithium-Ferrocene) is proposed in [71]; ED is about 40Wh/l . A general description of new conception RFB and redox species can be found in [59,72]. Currently, Lithium is the principal candidate to enhance RFBs' Energy Density, with the anode degradation phenomena. One interesting application is reported in [73] where a very cheap and durable RFB is presented. Although the low ED (10 Wh\l) the battery life is high (10k cycles).

A solar-driven chargeable Lithium–Sulphur battery can be obtained with a Pt-modified CdS photocatalyst. Sulphur is oxidized to Polysulphide in aqueous solution, so doing electro-chemical energy and Hydrogen is produced. Battery can deliver a specific capacity of 792 mAh g−1 during 2 h photocharging process with a discharge potential of around 2.53 V versus Li+/Li. Charging can be performed at direct sunlight [74].

Despite the high number of publications regarding RFBs, the major adopted are still the full Vanadium, Zinc-Bromine and Iron-Chromium RFBs. In the following Table 1, Table 2 and Table 3 the estimated costs are expressed [75]. Zinc-Iron too is an emerging technology in wide energy application (ViZn projects). A target cost of 100 $/kWh is achieved by a combination of inexpensive redox materials (i.e., zinc and iron) and high cell performance (e.g., 676 mW/cm^2 power density) [76].

Table 1 - Main cost items of VRFB systems - [a] Including BOP costs approximately 25€/kWh; [b] Mainly for MW-scale systems with rated DoD of 80%, used for bulk energy storage and T&D support (discharge time 4h); [c] Every 8 years for the mentioned application (365-500 cycles per year).

Cost item	Average	Middle fifty range, IQR	Range
PCS[a] (€/kW)	490	478-518	472-527
Storage section[b] (€/kWh)	467	440-536	433-640
Fixed O&M (€/kWh-yr)	8,5	4,3-16,1	3,4-17,3
Variable O&M (€/MWh)	0,9	0,5-1,2	0,2-2,8
Replacement costs[c] (€/kW)	130	114-165	111-192

Table 2 - Main cost items of zinc-bromine (Zn-Br) battery systems - [a] Including BOP costs approximately 25€/kWh; [b] Mainly for MW-scale systems with rated DoD of 80%, used for bulk energy storage and T&D support (discharge time 2-5h); [c] Every 15 years for the mentioned application (365 cycles per year).

Cost item	Average	Middle fifty range, IQR	Range
PCS[a] (€/kW)	444	343-470	151-595
Storage section[b] (€/kWh)	195	178-314	178-530
Fixed O&M (€/kWh-yr)	4,3	3,6-5,4	3,2-6,9

Variable O&M (€/MWh)	0,6	0,4-1,0	0,3-2,0
Replacement costs[c] (€/kW)	195	148-198	101-201

Table 3 - Main cost items of iron-chrome (Fe-Cr) battery systems - [a] Including BOP costs approximately 25€/kWh; [b] Mainly for MW-scale systems with rated DoD of 80%, used for bulk energy storage and T&D support (discharge time 2-5h); [c] Every 15 years for the mentioned application (365 cycles per year).

Cost item	Average	Middle fifty range, IQR	Range
PCS[a] (€/kW)	362	333-393	326-525
Storage section[b] (€/kWh)	145	126-152	64-156
Fixed O&M (€/kWh-yr)	3.3	2,8-4,0	2,7-6,9
Variable O&M (€/MWh)	0,4	0,2-0,6	0,1-1,0
Replacement costs[c] (€/kW)	29	24-33	14-38

Lithium battery

Lithium-ion battery is a market widespread technology, especially for low power portable application since the first steps of the development in the early 1990s [13,77].

Nowadays, this kind of battery is available also for higher power applications, both for automotive and stationary purpose [9].

Generally, two electrodes and an organic electrolyte compose a Lithium battery. The cathode is made of Lithium metal oxide, i.e. $LiCoO_2$, the anode is a graphitic carbon cell and the electrolyte can be a non-aqueous solution made of an organic solvent and a dissolved lithium salt or a solid polymer [9].

The introduction of carbon cell as anode (Li_xC_6) prevents incidents caused by excessive heating and melting of traditional anode: lithiated carbon has a higher melting point (180°C) [78].

During the charging phase, lithium ions are pushed out from the lithium metal oxide (LiMO) and are absorbed by the carbon anode (LiC_6); the vice versa occurs in the discharging phase.

The first phase is called "Intercalation" while the second is named "De-Intercalation" [9]. The Electrolyte does not take part in the reaction, it only ensures and facilitates the exchange of ions during the two phases [77]. Typically, the charging (leftward) and discharging (rightward) reactions, respectively at positive and negative electrode, are [9] :

$$Li_{1-y}MO + yLi^{+} + y\,e^{-} \rightleftarrows LiMO$$

$$Li_{n}C \rightleftarrows n\,Li^{+} + ne^{-} + C$$

The reasons why this technology is considered the best frontier of energy storage are: high energy density (160 ÷200 Wh/kg) [9,77], fast response time (milliseconds) [9], low self-discharge rate (5% per mount) [11] and high efficiency (up to 97%) [9,79]. Cons regard lifetime and Depth of Discharge. Both are temperature dependent. Aging effect is enhanced by high temperature [12,13,80] **.** Moreover, this battery requests a complex management system, usually called Battery

Management System (BMS). It is an electronic platform which monitors and estimates the battery State of Health (SoH) in real time: it controls the aging effect, checks the performances and detects the End of Life at cell level, in order to prevent cell fail and predict components substitution [77][81][82][83]. This system also protects the battery against overheating, low temperature, overcharge and discharge and provides optimal working conditions (like charging/discharging current and voltage) [78,80,81]. Obviously, such equipment increases the battery's cost.

A huge cost decrease in the latest years is highlighted: while in 2009 unit cost was estimated between 900 and 1300 $/kWh [13], it was reduced to about 600 $/kWh in 2012 [11] and it ranges between 225 and 800 $/kWh [84] .

This trend is due to latest developments in battery design: over the above-mentioned thermal management [80], research proceeds to enhance power capability by adopting nanoscale materials and to increase specific energy by studying innovative materials for electrode and electrolyte [85–88]. A concrete application of a Lithium-iron-phosphate ($LiFePO_4$) battery is reported in [89]. Batteries are employed to reduce the fuel consumption of the diesel generators in an oil drilling rig. In this specific case, a major attention is focused on the reactive power: a parallel connected capacitor (the so-called DC-link) is placed between the battery pack and the power inverter, making the battery able to handle both Active and Reactive power. A 175,000 EUR total investment plus 11,400 EUR/year for maintenance has been considered. Employing a proportional State of Charge based energy controller (for generator/battery switch on/off), up to 17.69 m^3 of diesel can be saved. The return-of-investment period has been estimated between 1 and 2 years (battery life is rated to be 10 years). CO_2 reduction is about 5000t in magnitude. Such results demonstrate how mature this technology is. Moreover, the importance of a good energy management policy is, again, high lined.

Lithium-Sulfur battery is emerging as a credible alternative for common lithium ion battery due to high specific energy, low cost, raw material abundance, safety and low environmental impact[85,90].

Selenium (Se), which is the congener of Sulfur, has been studied in order to introduce an innovative carbon-based material doped with SeS_x. The composite material, called SeS_x/NCPAN, should replace the traditional cathode, increasing capacity and lifetime [87] .

Dimethylsulfoxide (DMSO) replaces the carbonated based electrolyte in a Lithium-air battery to enhance cycling performances, reducing anode's fast deterioration. A higher (>20%) coulombic efficiency, despite standard Li-air technology, is obtained [86].

A new generation of Li-ion battery employs a solid-state electrolyte, composed of garnet-type metal borohydrides, which can improve of seven orders of magnitude the ion exchange due to microcrystalline geometry [88].

4. Hydrogen storage

In the hydrogen storage technique, the hydrogen is produced using the exceeding energy, then it is stored and eventually the energy is recovered from the stored Hydrogen. The last phase consists in a electrical energy production by using either a traditional internal combustion engine or a fuel cell [7,9,91].

Hydrogen has remarkable features as a fuel. It has a High Heating Value (HHV) of 141,8 MJ/kg, which is more than double in comparison to methane. In addition, the fact that it burns in stoichiometric conditions with an air-to-fuel ratio equal to 34.33, coupled with its very wide flammability limits, allows a combustion with a very low fuel consumption. The main drawback emerges considering its density in STP condition, which is very low, namely 0,084 kg/m^3. This affects the energy density value, which, despite the great HHV [91]. This factor is crucial, since it marks the difficulty in storing hydrogen by using traditional methods, such as gas compression or liquefaction, and suggests the use of fuel cells in place of internal combustion engine, if a more efficient process is the desired target [9,91].

Hydrogen has been object of several studies concerning its applicability as fuel in power plant [92]. For instance, in the engine field it has always been considered an attractive "additive", either for diesel or natural gas, able to increase engine performance and, more important, to reduce gaseous and soot emissions [93–95]. These features, together with the development of innovative combustion control techniques [96,97], and the use of various after-treatment devices [98], are essential for meeting the newest emission standards [99].

About 95% of the worldwide hydrogen production involves non-renewable resources. Hydrogen is extracted from natural gas by means of an endothermic process at high temperature (800÷1000°C) in presence of a catalyst. In such technique, called Steam Reforming, natural gas acts both as raw material for hydrogen production and as fuel, since it is burned to increase the temperature of the process. A natural gas amount comprised between 3 and 20% is used to keep alive the reaction. For each ton of hydrogen produced, 2.5 ton of CO_2 are released [91].

Hydrogen extraction from coal has been widely investigated. Such a process has a heavier environmental impact in comparison to the extraction from NG (5 Tons of CO2 are released for each ton of H2 produced). To contain the environmental impact, either the Pressure Swing Adsorption (PSA) or the Carbon Capture System (CCS) techniques have been developed. CCS enabled plants have higher (22%) Hydrogen cost. To reduce overall H2 cost, electricity co-production (by gasified coal) has been considered [91].

In a relative new technique hydrogen is produced starting from gasoline and diesel fuels. This process, called Partial DeHyrogenation (PDH), leads to a high purity hydrogen (up to 99%) and allows the recover the original fuels. The reaction acts in presence of a catalyst, like Platinum, at 400°C and at 0.1 MPa. About 1800 Nl/h and 3500 Nl/h of Hydrogen for kilogram of catalyst mass are produced respectively form gasoline and diesel. The catalyst life is about 300 hours for gasoline and 29 hours for diesel [100].

Hydrogen productions by using water electrolysis and biomass amount to, respectively, the 4% and the 1% of the total production [91]. In Water electrolysis electricity is employed to brake the water molecule bonds, generating oxygen and hydrogen atoms. The production rate is higher in presence of an electrolyte, commonly KOH (which is reusable). The efficiency of this kind of process is high (up to 75%) [91,101] and the purity of the produced hydrogen can reach 99,9% [101,102]. However, its costs are high because of the electricity consumption (about 4.49 kWh/m^3 are required) and the expensive coated electrodes (Platinum) required in the process. The introduction of a Cobalt phosphate catalyst allowed to decrease the costs [91]. Further development concerned the cathode material: instead of Platinum and other expensive materials, Microbial Electrolysis Cell (MEC) can be used, which employed a macro-porous nickel foam-graphene (NF-graphene) cathode, which provides the diffusion of the respiring bacteria for hydrogen production [103]. Renewable and sustainable resources has to be preferred also because of the energy related cost reduction; micro and small wind turbines (<50 kW) can be used in grid system to feed the electrolyser [102].

Furthermore, the solar energy can be involved in the hydrogen production. Four different techniques are usually adopted, namely photovoltaic panels, to feed electrolyser; photo-electrolysis, to split water by photons energy; solar thermal, to exploit thermochemical reactions for thermolysis process; and photobiological generation to provide decomposition of water by microalgae and cyanobacteria activated by solar light [91,101].

Recently, Khalilnejad and. Riahy [104] designed a hybrid wind–photovoltaic system for the purpose of hydrogen production through water electrolysis. They analysed three different conditions, consisting respectively in using just wind turbine (WT), photovoltaic (PV) array, and combination of them as power source. The results showed that the combination of WT and PV array was the best choice. The average hydrogen production rate of combined system was 0.0173 mol/s (26.2% and 127% more than the other two solutions respectively). On the other hand, average unused power production of combined system was 0.183 kW, namely 3.8% less than the first solution, and 55% more than the second one.

The energy management strategy (EMS) to control hybrid system is a crucial aspect that have heavily influence on the overall efficiency and costs. Cau et al. [105] give a practical example with their study about an isolated micro grid powered by a photovoltaic array and a wind turbine and equipped with two different energy storage systems, namely electric batteries and a hydrogen production and storage system. They proposed an EMS that considered the uncertainty due to the intermittent nature of renewable resources and electricity demand. Starting from forecasts of weather conditions and load requirements, the optimal generation scheduling to minimize operating costs and maximize system efficiency with a stochastic approach was proposed. The results showed a reduction of utilization costs of about 15% in comparison to conventional EMS based on the state-of-charge (SOC) of batteries and an increase of the average energy storage efficiency.

As well as for fossil fuel, the hydrogen production processes from biomass rely on thermochemical or biological reactions [91,106–108]. Glycerol, which is a product of biodiesel industries, is often used to produce hydrogen by various techniques: steam reforming (SR) -comparable to the fossil fuel case, partial oxidation reforming (POR) , autothermal reforming (ATR), aqueous phase reforming (APR) and supercritical water reforming (SCWR) [91,106]. Moreover, microalgae are often preferred to cultivation biomasses due to the higher growth rate, a more efficient solar energy conversion, the higher nutrient acquisition, and the ability to grow under severe conditions [91,107].

Hydrogen can be also produced from bio-oil too. The process is based on the sorption enhanced steam reforming (SESR) of acetic acid, a bio-oil compound, and by using dolomite as CO_2 sorbent. The resulting H_2 has a 99.8% purity and it is suitable for cell application without further purifications [108].

The traditional methods in gas storing consist in compression and liquefaction. The production of pressurized hydrogen at 200 bar is the most commonly employed technique. Despite the high storage pressure, the energy content per weight remain low, since the very low density. Therefore, in order to enhance the hydrogen quantity, the storing pressure is usually increased up to 700 bar, but the adoption of more resistant tanks is not the only side effect. Unfortunately, the compression cost also increases proportionally. In comparison, the liquefaction process guarantees a better storage in terms of energy density, but this technique needs a cryogenic system, since in order to keep the hydrogen in liquid state it is necessary to reach a temperature of 20.4 K. Obviously, such a process is quite inefficient due to the unavoidable thermal losses and the high cost for the cryogenic system [13,109].

Zhang et al. [110] provided a comprehensive evaluation of the performance of a grid-tied microgrid, consisting of a PV system, a hydrogen fuel cell stack, a PEM electrolyzer, and a hydrogen tank. The surplus electricity was stored as hydrogen, which was supplied to the fuel cell stack to generate heat and power as needed. They found that the emission and the service quality were higher when the fuel cell stack was employed.

Another example concerning hybrid renewable energy-based power plants with hydrogen as the intermediate energy storage medium is provided by Valverde et al. [111]. In their study, six operation modes were defined according to plant topology and the possibility of operating electrolyzer and fuel cell at steady-power or partial load, allowing to conclude that certain modes resulted more appropriate from technical and practical standpoints when they are implemented in a real plant. In particular, modes operating the fuel cell and electrolyzer at variable power showed better efficiency indicators but at higher cost, sometimes inadmissibly high. In contrast, modes working at steady power had reduced degradation costs, with the drawback of lower efficiency.

An innovative way for the hydrogen storage is based on the chemisorption ability of Metal hydrides [112]. Metal hydrides are alloys of cerium, lanthanum and nickel (Ce-La-Ni) [113], magnesium borohydride $Mg(BH4)_2$ [114], magnesium hydride with zirconium oxide and single-walled carbon nanotubes [115]. The storage process consists in thermochemical reactions that occur between the gaseous hydrogen and the solid materials, which are able to change its crystalline structure during the adsorption and the desorption phases. Specifically, the adsorption reaction is exothermic, while the desorption is endothermic, so a thermal control system is required [13]. The whole process depends on the activation energy, the thermal conductivity, the pressure and the temperature [113–115]. In comparison with traditional methods, this technology is safer, requires lower service costs, is more compact, has greater energy content per weight and guarantees higher efficiency, while the reactions kinetic is very fast provides rapid hydrogen release and fast response. However, metal hydrides have some drawbacks: apart the aforementioned thermal management, their cost is high and the hydrogen content per weight, even if it is greater than that obtainable from the traditional methods, is still low.

In order to reduce the influence of the thermal management, metal hydrides can be ~~endowed~~ coupled with a thermic storage based on phase change material (PCM) which exploits ~~the~~ material latent heat in place of external heat sources [116]. Rhodium-silver alloys (Ag_xRh_{x-1} with $0 \leq x \leq 1$) show important properties in hydrogen storing where the adsorption potential depends on alloy composition and electronic structure configuration [117].

Natural clay porous Nano-material is cheap, biocompatible, very durable and has a high hydrogen storage capability. An example of natural clay is represented by the acid treated hallo site clay nanotubes (A-HNTs) doped with hexagonal boron nitride nanoparticles (h-BN): up to 0.22% hydrogen in weight can be stored in pristine nanotubes; increasing nanoparticles up to 5% the stored hydrogen quantity can reach 2.88wt.% [112].

Clathrate hydrates are solid compound whose crystalline structure is made of water molecules. The particular shape of crystals guarantees the presence of cavities, which can be filled with particular gases, called gas hydrates: these gases have low molecular weight comparable to methane, carbon dioxide and hydrogen. The clathrate can resist at high pressure at room temperature in solid state.- The efficiency relies on cavities size [118].

5. Assessment and comparison

Among the treated systems there are several differences regarding the characterizing parameters of an ESS such as the energy capacity, the power rating, the efficiency, the lifetime, the discharge the time, the maturity and the cost.

A comparison between the various systems described above is provided with the aim to better clarify the fundamental differences existing among them. The analysis focuses, for each storage system, on the aforementioned characteristics and, at last, resumes them in the Table 4 obtaining a useful and simple overview. In this section, the hydrogen energy storage is neglected because of its great number of alternative techniques, with remarkable differences in terms of approaches and features.

Power and energy

The Power rating represents the maximum power that the system can handle during the charge and discharge phases, while the energy is often associated to the system capacity.

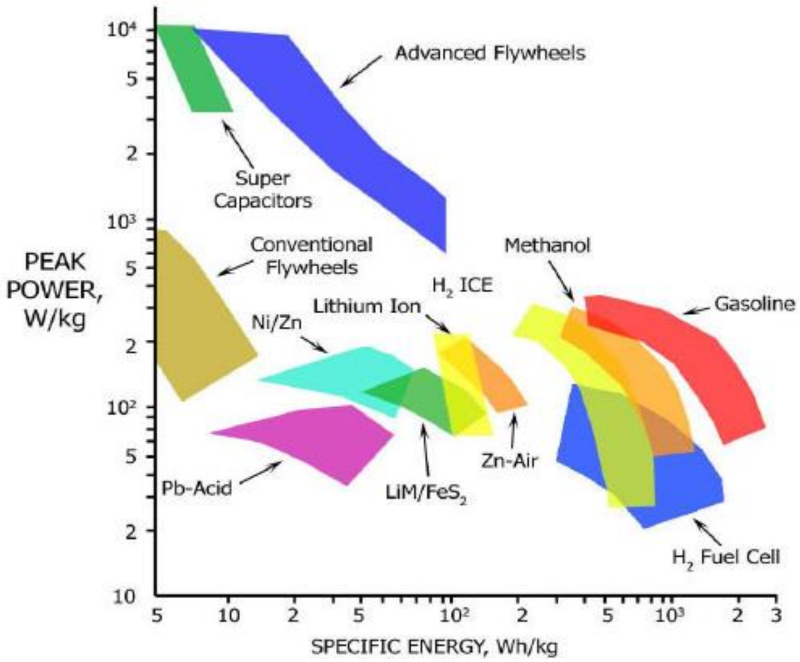

Figure 12 - Power rating, Ragone Chart [119]

Usually, the specific power and energy are used to compare different technologies. Plotting the specific energy versus the specific power, the Ragone Chart is obtained and it is reported in Figure 12. Both the axes use logarithmic scale and each area refers to a particular storage system. The devices with a faster response, such as the supercapacitors or the flywheels, have a great specific power and a low specific energy while fuels, fossil or renewable, which have a lower response time, presents a higher specific energy but a lower specific power.

Efficiency

The cycle efficiency is defined as the ratio between the discharged energy (supplied to loads) and the energy needed to restore the initial state of the charge. The efficiency takes into account the various losses typical of each system, either mechanical losses for PH, CAES and FES or ohmic and chemical-related losses for BES.

Discharge time

ESSs have discharge times varying from few milliseconds to many hours. Consequently, it is possible to sort the storage systems:

- Short discharge time: less than 1 hour, typical value for flywheels and supercapacitors;
- Medium discharge time: up to 10 hour, involving small-scale CAES and batteries;
- Long discharge time: greater than 10 hours, usually for PHS and large-scale CAES.

Lifetime

This parameter refers to the number of charge-discharge cycles that the system can handle without considerably losing its power, energy and efficiency capabilities. Generally, mechanical storage systems have longer lifetime, while other systems are affected by chemical deterioration and even temperature-dependent phenomena.

Cost

The cost comprehends both the installation and the ordinance and maintenance cost. Many technologies have low capital cost but require many maintenance during lifetime. The unit costs are often used in the analysis: in particular power [$/kW] and energy cost [$/kWh]. In fact, specific power and energy can be quite different, as shown in Ragone Chart, so, energy and power cost can be different as well.

Technical Maturity

The maturity is referred to the experience acquired in the use of a specific technology, to the level of commercialization, the technical risks and the related economic benefits. It is then possible to divide the ESSs in:

- Mature technologies: PHS find application in energy storage since XX century;
- Developed technologies: mature technologies from the technical point of view and commercially available, but large-scale applications are not widespread, such as lithium-ion battery or flywheel;
- Developing technologies: technologies under development and not commercially mature.

A comparison among different energy storage systems is reported in Table 4.

Table 4 Comparison among different energy storage systems

Technology	**Specific Power [W/kg]**	**Specific Energy [Wh/kg]**	**Power Rating [MW]**	**Efficiency [%]**	**Discharge Time**	**Lifetime [years]**	**Power Cost [$/kW]**	**Energy Cost [$/kWh]**	**Technical Maturity**
PHS	-	*0.5 ÷ 1.5* [9]	*4100* [10] *<3000* [9]	*Up to 87%* [10,11]	*1÷24+ h* [10,11]	*40* [9]	*500-1500* [10]	*10-20* [10]	*Mature* [12], [11]
CAES	-	*30 ÷ 60* [9]	*10 ÷ 110, 290* [28]	*42%* [9] *70%* [28]	*1÷24+ h* [28]	*40* [11]	*400÷1500* [11], [28]	*2÷120* [28] *2÷50* [12]	*Mature for large app* [28]
FES	*400 ÷ 1500* [9,12]	*5÷100*[13] *10÷80* [9] *100÷130* [41]	*0.25* [9] [37] *0.5* [14]	*90%* [13,14]	*Milliseconds÷15 min* [12] *15 s ÷ 15 min* [9]	*>20*[11] *15* [12]	*250÷350* [9] [12]	*1000÷5000* [9] , [12]	*Mature for low speed* [37]
Flow Battery	*150 ÷ 160* [9]	*10÷30* [11]	*0.5÷100* [11]	*85%*[11]	*2÷12 h* [9] *Seconds ÷ 10 h*	*5÷10* [11] *5÷15* [12]	*600÷1500*[11]	*100* [64] *150÷1000* [12]	*Developing* [11]
Lithium Battery	*150 ÷ 315* [9]	*160 ÷200* [9][77]	*0.1÷100* [9] *0.5* [79]	*up to 97%* [9][79]	*Minutes ÷ Hours* [9]	*5÷15* [12] *28* [79]	*4000* [9] [11]	*350÷700* [80]	*Developed* [80] [81]

6. Conclusions

In the recent past, little is being done to create and develop the research sector and the industrial sector about energy storage. On the contrary, these topics are the most important to radically change the way in which the energy production sector could be organised. So a long term planning to promote research is desirable in every Government of the nations and it should ensure that energy storage is seen as a key ingredient in the energy policy landscape and is very much part of the policy roadmap of every country. For example given, in the Obama age, energy storage industry is now an active in US with an estimated annual investment of over 500 Million of dollars. Energy storage systems (ESSs) are a fundamental requirement for innovative, and future, energy production by means of renewable resources. This scenario should become part of an emerging "global industry" with a potential business approximatively of a trillion dollar.

So this paper has provided an overview of the most promising ESSs, performing technical and economic features, with the purpose of providing the state of the art and promoting the research in this field. The always rising energy demand with the greenhouse gasses reduction goal makes renewable sources the new frontier of energy production. However, the behaviour of such sources is often unpredictable and, in the most general case, the availability almost never satisfies the demand. Moreover, a transition to a "grid" energy system is expected to come, enhancing the efficiency of the distribution process. This explains why an ESS that can significantly increase the global efficiency of the system is duplicable. Therefore, ESS represents a crucial device for the future of the energy production.

In this paper the most spread and promising technologies have been reviewed. A detailed description of their characteristics together with an extensive analysis of the state of the art was provided. Finally, a comparison between all the different solutions considered throughout the present analysis was reported.

A storage system that is at the same time mature, durable, efficient, cheap, with a wide power range can only be obtained by matching different technologies, i.e., flywheels and batteries often find application in automotive or stationary plants while PHS or CAES are usually employed for large size energy storage.

The analysis of the value of the specific power and energy provides a useful comparison. In fact, the systems with huge capacity and power rating and long discharge time, like PHS and CAES, have low values of specific energy. Conversely, FESs, which have fast discharge time, provide high power, but can store a low quantity of energy. Flow batteries represent an important in-perspective solution because they are composed of numerous modules: capacity and power rating can be adjusted varying the number and dimension of such modules. Unfortunately, this versatile technology is still in the developing phase. Hydrogen energy storage relies on different techniques and solutions, and the great part of them is still in a developing phase, such as carbon nanotubes or clathrate hydrates, while others, such as metal hydrides, are more mature, but they need to be optimized before being commercially available. The traditional compression systems of the hydrogen are still the more commonly adopted technology, in particular when matched with electrolyser or fuel cell systems. Finally, lithium batteries showed a decisive development in the last few years in a way that their power rating has been enhanced, their lifetime has got longer, their efficiency has been increased and their costs has been reduced.

Nomenclature

BESs	*Battery Energy Storage system*
BMS	*Battery Management System*
CAES	*Compressed Air Energy Storage*
CNT	*Carbon Nano Tubes*
DoD	*Depth of Discharge*
ED	*Energy Density*
EE	*Energetic Efficiency*
ESS	*Energy Storage system*
FES	*Flywheel Energy Storage*
PaT	*Pump as Turbine*
PH(S)	*Pumped Hydroelectric (Storage)*
RFB	*Redox Flow Battery*
SES	*Supercapacitor Energy Storage*
SMES	*Superconducting Magnetic Energy Storage*
SoH	*State of Health*
T&D	*Transmission and Distribution*
Mtoe	*Million Tonnes of Oil Equivalent*

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