

Today, Tomorrow, and the Future of Energy Storage Materials for Solar Energy

Dawar Ali¹, Mehmet Fatih Kaya^{2*}, Levent Şendoğdular³

ABSTRACT

Increasing global energy demand and environmental concerns due to the emissions of greenhouse gases as by-products of fossil fuel consumption have led to the exploration of the potential of renewable energy sources such as solar, biofuel, hydrothermal energy etc. Among these, solar thermal energy is becoming a highly desirable source of renewable energy because of the widespread availability of solar radiations and the progress achieved in its efficiency and effectiveness.

Different forms of thermal storage especially thermochemical storage (TCS), latent heat storage (LHS), and sensible heat storage (SHS) have been reported so far. Likewise, there are studies in the literature which also focus on the main mechanical energy storage systems. In addition, electrochemical energy storage devices like batteries are increasingly gaining popularity due to their highly efficient energy conversion values. Recently investigated materials for various solar storage forms show great potential as the future storage materials since theoretical limits are not reached yet; however, they are still in the experimental stage and this paper presents glimpse of those potential studies.

Keywords: Solar energy, storage materials, batteries, thermal energy

Güneş Enerjisi Depolama Malzemelerinin Bugünü, Yarını ve Geleceği

ÖZ

Fosil yakıtların tükenmeye başlaması ve bu yakıtların yan ürünleri olarak ortaya çıkan sera gazı salınımları, bunun yanı sıra artan küresel enerji talebi ve çevresel endişeler, güneş, biyoyakıt, hidrotermal enerji gibi yenilenebilir enerji kaynaklarının potansiyelinin daha da detaylı araştırılmasına yol açmıştır. Bunlar arasında termal güneş enerjisi sistemleri yenilenebilir enerji sistemleri içerisinde güneş ışığına kolay erişilebilir olması, elde edilen verimlilik değerleri ve etkili bir enerji dönüşümü sağlanması sebebiyle çok yaygın olarak tercih edilen sistemler haline gelmiştir. Şimdiye kadar farklı termal depolama biçimleri, özellikle termokimyasal depolama (TCS), artık ısı depolama (LHS) ve hissedilir ısı depolaması (SHS) ilgili kapsamlı çalışmalar yapılmıştır. Bunların yanı sıra literatürde de ana enerji depolama sistemleri olarak mekanik depolama sistemlerine de odaklanan çalışmalar bulunmaktadır. Ek olarak, bataryalar gibi elektrokimyasal enerji depolama sistemleri yüksek enerji dönüşüm verimleri sayesinde giderek daha fazla popülerlik kazanmaktadır. Çeşitli güneş depolama yöntemleri için yakın zamanda araştırılan malzemeler, teorik sınırlara henüz ulaşılmadığı için güneş enerjisi depolama malzemeleri konusu araştırmacılar için büyük bir potansiyel göstermektedir. Ancak bu çalışmaların çoğu halen deneysel aşamada olup bu değerlendirme çalışmasında güneş enerjisi depolaması ile ilgili malzeme temelli bu potansiyel çalışmalara bir bakış açısı sunulması sağlanmıştır.

Anahtar Kelimeler: Güneş Enerjisi, depolama malzemeleri, bataryalar, termal enerji.

* İletişim Yazarı

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¹ Erciyes Üniversitesi, Mühendislik Fakültesi, Malzeme Bilimi ve Mühendisliği, Melikgazi, Kayseri
dawar1424@gmail.com, ORCID: 0000-0002-1432-5557

² Erciyes Üniversitesi, Mühendislik Fakültesi, Enerji Sistemleri Mühendisliği, Melikgazi, Kayseri
kayamehmetfatih@erciyes.edu.tr, ORCID: 0000-0002-2444-0583

³ Erciyes Üniversitesi, Mühendislik Fakültesi, Malzeme Bilimi ve Mühendisliği, Melikgazi, Kayseri
lsendogdular@erciyes.edu.tr, ORCID: 0000-0002-6364-0932

1. INTRODUCTION

In this era, energy shortage and environmental issues need to be addressed urgently and globally [1-3]. As compared to 2017, the energy consumption in 2018 increased 1.5% worldwide [4]. A statistical study by British Petroleum shows that global energy demand is continuously increasing and fossil fuel share has almost reached to 87% of the total consumption [1]. Nuclear energy causes less greenhouse emissions and therefore seems to be a promising candidate in terms of environmentally friendly energy source, but it has security problems based on infrastructure and is also very expensive to maintain [3]. Greenhouse gas emissions can only be reduced or at least avoided by consuming renewable energy and therefore, many countries have taken initiatives in this regard [5-11].

Although renewable energy sources cannot be adopted widely because of geographical limitations, economic and atmospheric conditions; they have low environmental damage, produce almost insignificant pollution, and their derivatives are widely available. Among the many other renewable energy sources like wind, biogas, hydrothermal etc., Sun is the major source of clean energy worldwide. Solar energy can be converted to electrical power by both concentrated solar power (CSP) systems and photovoltaics (PVs) [4, 12]. PV cells usually convert solar energy to chemical energy which can be stored in batteries and can be converted into electrical current when needed while CSP systems help to store solar energy as heat to be used as electricity after all [13].

The fundamental parts of any solar thermal system are those which store and collect energy. Solar collectors either transform solar energy into electrical energy using PV methods or into thermal energy of a storage material [14, 15]. PV, solar thermal, and PV/T (photovoltaic/thermal) are the three main solar collectors [6]. PV technology gained massive interest in the last decade in the form of both domestic and remote installations [16] whereas the solar thermal technology has relatively been employed in the housing sector for around half a century now [10]. Thermal energy is further categorized as latent heat, sensible heat and thermochemical heat storage.

Latent heat storage or phase change materials in other words although has low thermal conductivity [7], is considered better than sensible storage due to its high storage density and limited phase transition range [17]. Latent and sensible heat storage do not have the potential to store energy for longer periods of time like from one season to another, instead they can only store energy for a few hours. Therefore, TCS is viable as it solves the issue of longer period energy storage [8]. In this review, the main energy storage materials, or systems like thermal, mechanical, and electrical are considered. Moreover, the potential future storage materials are also presented briefly.



2. THERMAL STORAGE MATERIALS

The flow chart in Figure 1 summarizes the main types of energy storage systems used for solar radiation. Among these thermal, mechanical and electrochemical storage are mainly and widely used systems. Based on the storage mechanism, TES materials can be simply divided into sensible (SHS), thermochemical (TCS), and latent heat storage (LHS) materials [19].

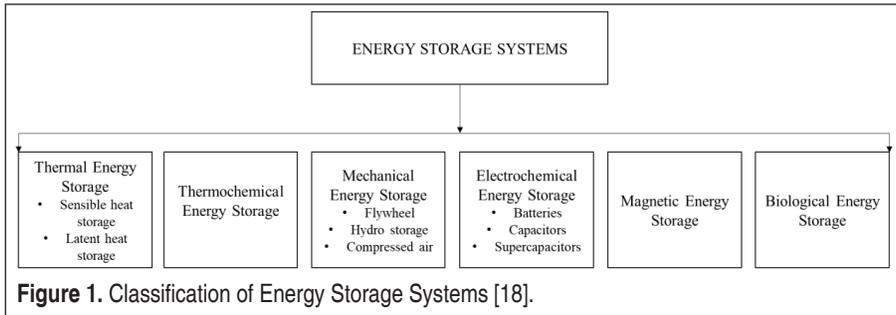


Figure 1. Classification of Energy Storage Systems [18].

2.1 Sensible Heat Storage

The SHS materials do not have to go through a phase change process to store the thermal energy. The extent of thermal energy stored depends on the thermophysical characteristics of the storage material and can be expressed in the form of relationship (1):

$$Q = m \cdot C_p \cdot \Delta T = m \cdot C_p \cdot (T_2 - T_1) \quad (1)$$

Where Q is the thermal energy as sensible heat, m is the mass of the storage material in kg, C_p is the specific heat capacity in kJ/kg.K; and T_1 and T_2 are the initial and final temperatures in K [20]. The materials for sensible heat storage can be solids or fluids.

2.1.1 Liquid Storage

Also called as an active system, a liquid storage material can easily circulate and transport the heat. Such kind of system is named as active system. Another major advantage of liquids is that they create a thermal gradient between the hot and the cold fluid. As a result, the density of the storage fluid changes causing the hotter part of the fluid to rise up naturally [21].

2.1.1.1 Water

With a working temperature range between 25-90 °C for low temperature applications, water is the best storage material in this range [22]. The best usage of water is in the form of hot water supply as in residential heating. Materials like aluminium, steel, fiberglass, and reinforced concrete are used for water tanks and heat insulated with polyurethane, wool, or mineral wool.

Hot water mixed with sand gravels in underground can serve as a seasonal large-scale facility for energy storage. This kind of system significantly reduces the water tank construction costs [23].

2.1.1.2 Mineral Oil

Mineral oil is mostly chosen as cooling or heating fluid in the concentrated solar power plants passing through the receiver, collecting heat, and providing it to the boiler for the production of steam for turbine [24]. Mineral oil is less volatile than water and can bear temperatures up to 400 °C without evaporating, allowing it to operate at higher temperatures. The only condition affecting their performance is that they degrade with time and beyond a certain limiting temperature [25].

2.1.1.3 Molten Salts

Molten salts are cheaper, have higher energy storage density and a reduced vapor pressure as compared to water enabling them to work up to 400 °C. For those reasons, they are in high demand in CSP plants as thermal energy storage materials [26]. The most commonly used molten salts remain in the liquid phase throughout the operation even at nights without the need of an antifreeze. Salt composites are used to keep the liquid between 100-500 °C [26]. In addition, Zhao and Wu [19] reported a variety of ternary salt mixtures with melting temperatures less than 100 °C. Those LiNO_3 , $\text{Ca}(\text{NO}_3)_2$, and KNO_3 mixtures can operate around 500 °C with viscosities 80% lower than their commercial counterparts. Moreover, they are corrosive at higher temperatures since they have an oxidizing nature [27].

2.1.1.4 Molten Metals and Alloys

Metals and alloys in the pure form have a higher thermal conductivity, low vapor pressure, higher maximum operating temperature. Therefore, metals and alloys with melting points above 300 °C can be used as a storage media for sensible heat. In the literature Zn/Mg (53.7/46.3), Zn/Al (96/4), Al/Cu/Si/Mg (64.6/28/5.2/2.2), Mg/Ca (84/16), Si/Al (86/12) can be used commonly as molten metals and their alloys [28]. However, they are also corrosive [22].

2.1.2 Solid Storage Medium

Solid materials like rocks, bricks, concrete, sand, and metals can be used for all types of energy storage since they do not boil and freeze. They do not have limitations of liquids, but they have a limitation of circulation as well. Therefore, they can be utilized for passive storage only where air normally transfers the heat. Thus, they are better for applications that need low temperature like space heating and recovery of industrial waste heat. Among all the solid materials pebbles and rock piles are the most preferred since they are cheaper [22].



2.1.2.1 Rocks

Rocks around 5 cm are used together with air or a mineral oil which serve as heat transfer fluids in sand-rock-mineral combinations. In the rock heat storage, heated air passes through the holes between rocks charging them, in the same way cold air circulates through the rocks and gets heated. Rocks are easily available, cheap, non-flammable, and non-toxic, whereas they also face the issues like reduced pressure drops and low air mass flow rates [29]. As an example, appropriate amount is around 300-500 kg rock/m² for thermal energy storage required in space heating.

2.1.2.2 Concrete

Because of its high mechanical strength, the concrete is easily applicable as an SHS material and hence, a container is not required. By circulating the heat transfer fluid (HTF) through the pipes fixed inside a concrete block, heat exchange between concrete and an HTF can occur. In high-temperature applications, its probability to crack under repeated thermal contraction and expansion cycles might be a drawback but research is underway to establish the best suited mixing method to improve chemical-physical characteristics and durability at elevated temperatures [30]. Practical applications have proved that 400 kWh of energy can be stored in 20 m³ of concrete.

2.1.2.3 Sand

Thermal energy can easily be stored in the fine grained gravel and silica sand. Air as an HTF can perform heat transfer within sand grain beds with 0.2 - 0.5 mm diameter. Those beds have been measured up to a storage capacity of 550 °C [31]. The packing density is determined by the fineness of the sand. Finer sand has a greater density of packing. Gravels have grains of 0.4 mm. diameter. To use as solar thermal energy storage options, basalt gravels can be used directly for the solar systems. The gravels fall under gravity absorbing solar energy in the receiver. The Rankine cycle power plant is driven by the steam which is produced by the sand at 700-1000 °C at the bottom of the receiver.

2.1.2.4 Bricks

To reduce the space heating electricity cost, building wall bricks can store thermal energy [22]. During the off-peak hours at night, bricks are heated and store heat. During the day, the heat is extracted by convection or radiation. During the peak hours the stored heat is utilized to keep the buildings warm and this saves the cost of electricity [32].

2.2 Thermochemical Heat Storage

In the thermochemical heat storage systems, reversible chemical reaction is employed to store solar-thermal energy [33]. The heat energy stored equals the enthalpy of the reaction. The storage process occurs with the conversion of reactant (A) to products

(B and C) at the end of the reaction. The backward reaction (exothermic) also generates the A and releases stored heat during the chemical discharge process. Both endothermic and exothermic reaction products can be stored at ambient or working temperatures. Thermal energy stored in thermochemical material can be calculated by:

$$Q = n.H \tag{2}$$

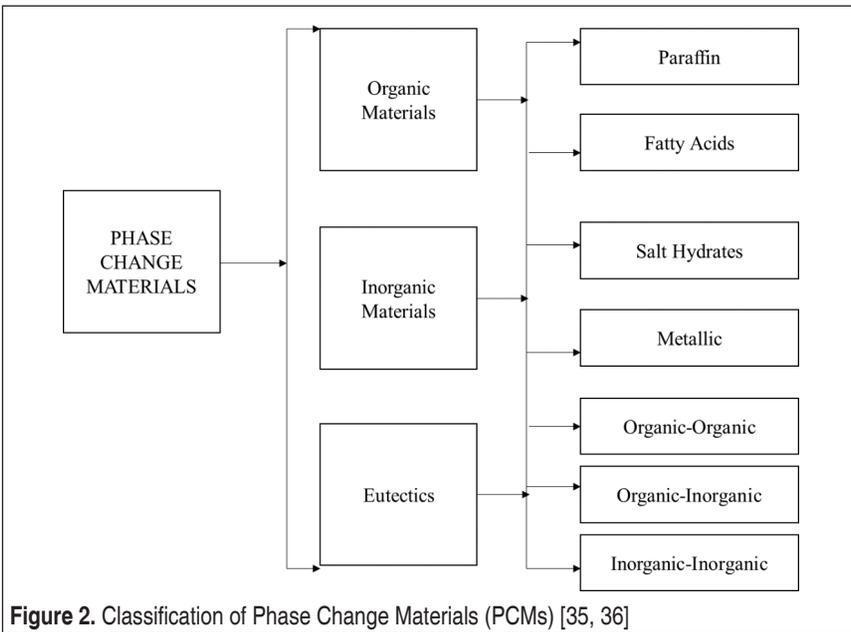
Where n represents the reactants' mol number (mol) and ΔH is the reaction enthalpy (kJ mol^{-1}). Unfortunately, thermochemical energy storage studies are still in laboratory scale, but sensible and latent heat storage studies are in the industrial level. Thermochemical energy storage provides about 6 times the energy density of latent heat storage and 15 times that of sensible heat storage [8, 34]. Thus, this proves how efficient this system can be compared to others.

2.3 Latent Heat Storage

During the melting, phase change materials (PCM) are usually called as “latent fusion fuel”. Phase change reaction occurs during the thermal energy absorption and the temperature fluctuation is very insignificant. Materials store thermal energy as the phase change with the equation below;

$$Q = m.H \tag{3}$$

Here, mass m is in kg and the latent heat of fusion, H is in kJ.kg^{-1} . Usually, phase change occurs between solid and liquid phases [28]. This method is very common





in industrial applications in the last ten years. The Figure 2 below presents the main types of phase change materials; organic, inorganic and eutectics which can be further categorized. All the PCMs are discussed in detail in the following sections.

2.3.1 Organic Materials

For many residential and commercial applications, CHO based latent heat materials (organics) and the mixtures of these organic based materials have proven to be successful and have been used in space heating applications for homes, air conditioning systems, electronic equipment, solar/water heating systems, food, automobiles, textiles, and space industries [12]. Organic PCMs have low melting temperatures restricting their use in power plants as they require high temperatures.

2.3.1.1 Paraffin

Paraffin waxes are members of n-alkanes group ($\text{CH}_3\text{-(CH}_2\text{)}_n\text{-CH}_3$) by their simple chains [37]. Due to the high cost of paraffin purity, professional quality paraffin waxes are used for these storage studies. Commercially used paraffin is the product of distillation of crude oil. Mostly, paraffins which have saturated carbon are more suitable for PCMs. They have different carbon atoms in their molecules. In these applications, the paraffin wax is used as the PCM and filled inside the tubes. The heat exchange takes place between paraffin and water through heat exchangers.

2.3.1.2 Fatty acids, Esters, Alcohols and Glycols

Fatty acids of ($\text{CH}_3\text{(CH}_2\text{)}_n\text{-COOH}$) type are the perfect fit as low temperature latent heat storage materials with the best thermophysical properties. They are more expensive than paraffins of professional quality, slightly corrosive and have an unpleasant odour. They are naturally combustible [37].

Esters consist of one group of hydroxyls and alkyls. In the small temperature range, esters exhibit solid-liquid phase change [38].

Polyalcohol or sugar alcohol are called medium temperature PCMs suitable between 90 °C and 200 °C. In the last 40 years, alcohols have been considered as potential PCMs. Although not much research has been done since then, some studies indicated that xylitol, mannitol, and erythritol have almost 300 kJ/kg latent heat due to fusion reactions [39]. This potential has been recorded as the highest value up to which other alternative materials could not reach.

Polyethylene glycol (PEG) is known as polyoxyethylene (POE) and polyethylene oxide (PEO). PEG is located in hydroxyl group and it has dimethyl ether chains with a formula of $\text{HO-CH}_2\text{-(CH}_2\text{-O-CH}_2\text{)}_n\text{-CH}_2\text{-OH}$. It can dissolve in water and organic compounds. PEGs have also different grades such as PEG600, PEG400 etc. In literature, there exists some earlier studies focused on those materials [40]. They are chemically heat resistant, non-toxic, non-flammable, inexpensive, and non-corrosive.

The PEGs' latent heat of fusion and melting point is directly proportional to the molecular weight [41]. Like other organic PCMs, PEG also has low thermal conductivity.

2.3.2 Inorganic Materials

Inorganic PCMs typically have a heat storage capacity twice that of organic materials per unit volume. The latent heat density is around 350 MJ/m³. They also exceed organic PCMs by having superior thermal conductivities, lower operating temperatures and costs [26]. They are corrosive, which ensures that the devices that contain them have shorter service lives, which raise their costs.

2.3.2.1 Salt Hydrates

Salt hydrates are usually used in the range of 30-50°C at low operating temperatures. They are denoted by a general formula of AB.nH₂O. This can somehow be considered as the representation of water of crystallization of inorganic salt compounds. During the phase change, salt dehydrates and stores the energy. This could be either in the form of a salt with less water or an anhydrous salt [42].

2.3.2.2 Salts

Salts with lower melting temperatures store liquids as a sensible medium. Yet, they can store heat as high as 100°C for high temperature applications. They can be divided into many material types such as carbonates, nitrates, chlorides, and hydroxides, having a wide melting temperature range [43, 44]

2.3.2.3 Metals and Their Alloys

It is well-known that metals have very good thermal conductivity and stability. Moreover, they have good mechanical strength and they can be used again and again for thermal storage without deteriorating their properties at high temperatures [38] Among all materials, metals exhibit the highest phase transfer heat per unit mass or unit volume. Hence, their energy storage potential is very high. Volume change after phase transition is also insignificant. The vapor pressure is also very low. However, they are competitors of salts when volume is important [28].

2.3.3 Eutectic

Eutectics have organic – inorganic, organic – organic, and inorganic – inorganic components. They change their phase in agreement with each other. Eutectics have fixed solidification and liquefaction temperatures. They transform crystal components during the crystallization reactions. Eutectics usually freeze and melt congruently and do not undergo separation.

Alnaimat et al. [45] studied the thermal energy storage systems for solar energy in detail. In Table 1, a summary of different energy storage systems can be seen. Different thermal energy storage systems based on different criteria are also compared in Table



1. The heat losses are the lowest in thermo-chemical while the storage duration is the longest as compared to the other two systems. However, the easiest system to operate among those three is the sensible energy storage.

Table 1. Comparison of Different Energy Storage Systems [45]

Criteria	Sensible Energy Storage System	Latent Energy Storage System	Thermo-chemical Energy Storage System
Operation	Easy	Medium	Hard
Density	Too low	Medium	High
Heat losses	Too High	Medium	No heat loss
Technological Level	In Industrial Use	Preliminary work is still in progress	Only with some demonstrations
Storage time	Couple of hours	Couple of hours	More than a month
Temperature of heat storage	A temperature range	Temperature of phase transition	Ambient temperatures

3. MECHANICAL STORAGE MATERIALS

Considering the cost, environmental footprint, and sustainability, mechanical energy storage systems are much better than others and attract great attention. Mechanical energy storage can be normally divided into flywheel energy storage (FES), pumped hydropower storage (PHS) and compressed-air energy storage (CAES) [46-48].

3.1 Flywheel Energy Storage System (FESS)

In a flywheel energy storage (FESS) system [49] a rotating mass stores energy as kinetic energy for a short-term [50] as shown in Equation (4). They are one of the most effective, fast response storage systems in terms of economic aspects [51].

Flywheels are available in various shapes; laval disc, thick ring, solid disc, and thin ring [52]. Each flywheel features a shape factor (K) reflecting material utilization. Equation (5) represents the specific energy per unit mass which is proportional to K. These equations help to calculate the effect of speed, shape, and inertia on the energy stored by the flywheel [53].

$$E = \frac{1}{2} IW^2 \quad (4)$$

$$\frac{E}{m} = K \sigma_{max} / \rho \quad (5)$$

Where E represents the energy stored, W is the rotational speed, I is the moment of inertia, m is the mass, ρ is the density of the flywheel, and σ_{max} is the maximum stress.

As shown in Figure 3, rotating weight, frequency inverter, and motor-generator are the main parts of the FESS. The design of each component affects the overall efficiency, and one of the main targets is to reduce losses due to power transmission that are determined by the kind of bearing; magnetic bearings proved to be the best selection [54]. In addition to the energy storage, it also increases the battery life [55] in conjunction with renewable sources due to intermittent character.

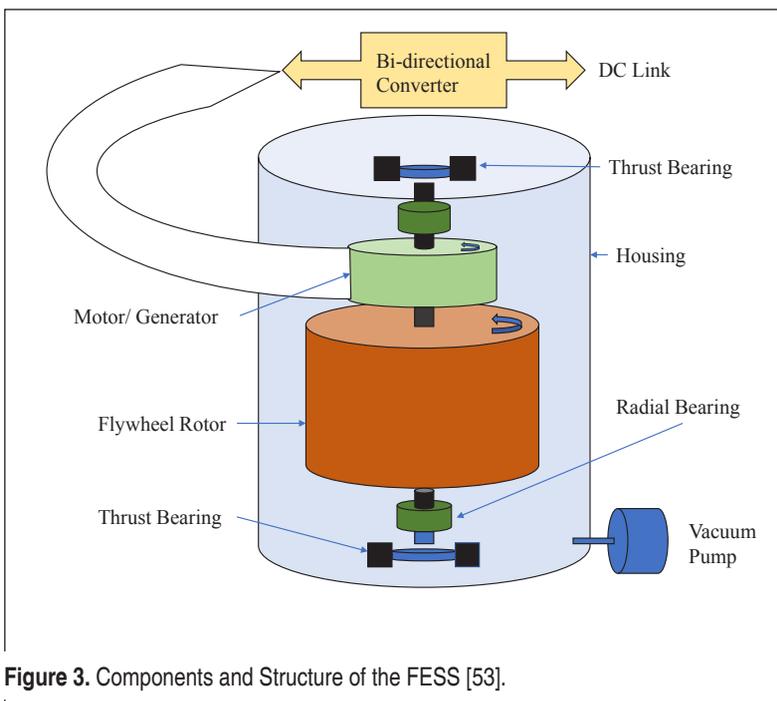


Figure 3. Components and Structure of the FESS [53].

3.2 Pumped Hydro Energy Storage (PHESS)

Another type of mechanical energy storage is the pumped hydro energy storage having features such as flexibility, long-life cycle, and low maintenance cost. It is composed of a pumping system, upper reservoir, and hydro turbine [56]. The excess energy containing water is pumped to the upper reservoir and used when needed.

Photo-voltaic power fluctuations can be avoided by solar-PHESS. The Figure 4 shows the working mechanism of the system in day and night. During the day, the heated

water is pumped to the upper reservoir as storage of energy using the motor, while the same heated water passes to the lower reservoir rotating the turbine to generate the power for use at night [57]. The optimized PHESS reduces the operating costs and is employed in remote areas having no grid supply [58].

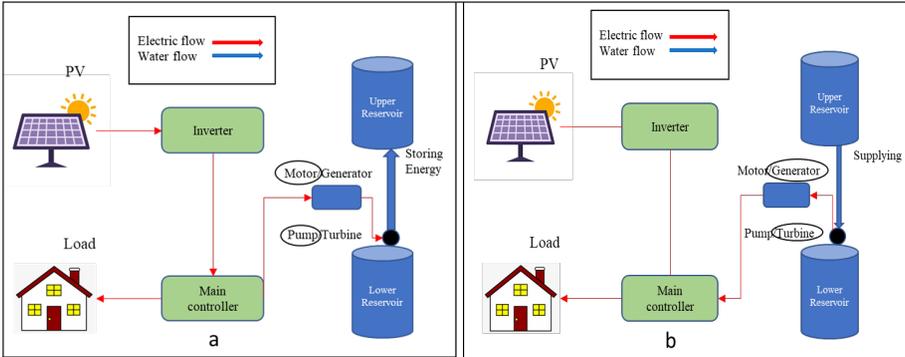


Figure 4. Solar Energy Connected with PHESS (a) Storage; (b) Power Supply [53].

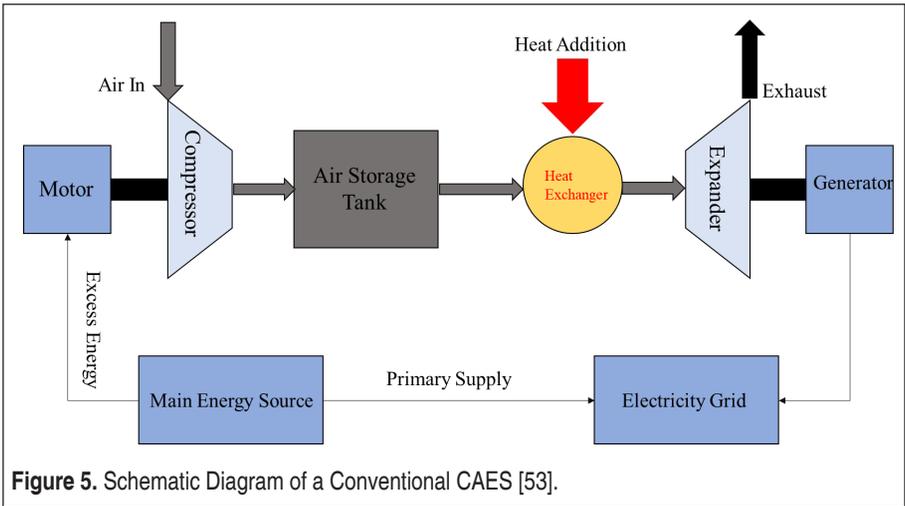


Figure 5. Schematic Diagram of a Conventional CAES [53].

4. ELECTROMAGNETIC ENERGY STORAGE

In 1970, superconductive magnetic energy storage, consisting of a liquid nitrogen cooling system and a superconducting coil, was first introduced. In this method, the coil is charged and discharged for energy storage and consumption. The energy storage efficiency of SMES is >97% and is prompt. The solar and wind power stabilization, improvement in the quality of electrical power supply, voltage stability, and improvement in the power of industrial sectors are all the benefits of this system. The major



drawback of SMES as compared to other systems is the high cost of the superconductors, and maintenance cost of cryogenic temperatures. High temperature superconducting materials are expected to lower the cost of a SMES system [60].

5. ELECTROCHEMICAL ENERGY STORAGE

Batteries and capacitors are the main sources of electrochemical energy storage. A battery stores electrical energy as chemical energy while a capacitor stores energy as surface charge. Another hybrid form is the supercapacitor exhibiting both the characteristics of batteries and capacitors. Lead-acid, nickel-cadmium, zinc-air, sodium-sulphur, and Li-ion batteries are all the battery types based on the component of the electrodes [61].

Electrochemical energy storage is highly efficient, versatile, and flexible as compared to other energy storage technologies. Among the various rechargeable battery types, Lithium-ion batteries (LIBs) are the most widely utilized as they provide high voltage, long cycling life, high reliability, low toxicity, and low self-discharge.

The LIB was commercialized during the early 1990s and since then has gained worldwide acceptance. It consists of a positive cathode, a negative anode, an electrolyte, and a separator. Mainly lithium cobalt oxide or lithium manganese oxide are cathode materials. The anode materials are carbon, iron oxides, cobalt oxides, Si, Sn, and nickel oxides [60].

6. FUTURE OF THE STORAGE MATERIALS

6.1 Mechanical Energy Storage

The energy density of a FES system is linearly dependent on the square of the angular velocity of the flywheel and its mass. Since the material of the flywheel determines the energy density, the faster the rotating speed, the higher the energy density. In this regard, Carbon-fiber reinforced composites having a high strength can serve the purpose. Moreover, carbon nanotubes could prove to be a promising candidate since they have very high tensile strength and young's modulus [62-64].

6.2 Electrochemical Energy Storage

Among all the battery systems LIBs have gained popularity over the last thirty years. If pure lithium could be used as an anode or if pure chalcogen could be used as the cathode, the volumetric storage capacity could be enhanced to a considerable extent. Likewise, the energy density could be doubled if the lithium-air cell becomes operable. Apart from the lithium, sodium or magnesium-based batteries could also be considered but the sodium has safety concerns. Sodium reversibly intercalates into



the chevrel phases, MxMo_6S_8 ; it gives a range of phases by intercalating into the chalcogenides and layered oxides [61, 65].

6.2.1 Iodine-Based Solar Batteries

The first triiodide/iodide (I_3^-/I^-) redox based solar battery was prepared by Hauch and Orel et al. in 2002 [66] which was influenced by the iodine-based electrolyte usage in dye-sensitized solar cells [67, 68].

However, the insufficient concentration of the Li^+ in the electrolyte restricts the capacity of the battery and the device performed better in low light making it useful for indoor systems. The colour shifts between WO_3 and Li_xWO_3 making the possibility of the device as photo-electrochromic system [69].

6.2.2 Vanadium-Based Solar Batteries

The fast kinetics of vanadium based redox flow batteries (RFB), aqueous species, and rich redox chemistry makes them the most widely used RFB systems on the commercial scale in terms of the stationary electrical storage facilities [70-73].

The TiO_2 photoelectrode was merged with the vanadium RFB solar cell in 2012 proposing the new vanadium-based solar battery. In this system, during the charging process electron-hole pairs are generated when the incident light is absorbed by the TiO_2 photoelectrode. During the night, the discharging process occurs in the same way as before where the V_2^+ is oxidized in the anolyte and the VO_2^+ is reduced in the catholyte [74].

Although the TiO_2 showed an efficiency of 12% at 350nm of incident photon-to-electron conversion in an acidic environment. However, the device could not absorb light in the shorter wavelength of the light spectrum due to the large (3.2 eV) bandwidth [75, 76].

6.2.3 Selenium and Bromine-Based Solar Batteries.

For solar batteries, n- $\text{MoSe}_2|\text{Br}_2\text{Br}^-$ and n- $\text{GaSAs}|\text{Se}_2^{2-}/\text{Se}^{2-}$ were researched as PE-catholyte combinations in solar batteries. The device with these material combinations achieved a current of around 20 mA/cm^2 and a Voc of 400-500mV which was much higher than the similar $\text{CdSe}|\text{S}/\text{S}^{2-}$ combination. It was believed that the design with flowing electrolyte instead of the static one may help achieve better performance of the device [77].

6.2.4 The Iodine-Based Lithium–Oxygen Solar Batteries

A new concept of integration of TiO_2 photoelectrode with air electrode using I_3^-/I^- redox couple was applied to the normal $\text{Li}-\text{O}_2$ battery in 2014 [78]. The absorbed solar energy reduces the charging potential of the battery by pumping the electrons to the

higher energy level. The device was photocharged to a much lower value of external voltage (2.8 V) than the normal lithium-oxygen battery. The dye-sensitized TiO₂ photoelectrode is recently replaced by g-C₃N₄ photocatalyst [79]. However, the major drawback of such system was the inability to be fully charged and a need of a power input for the charging [80].

6.3 Thermal Energy Storage (PCMS)

The recently developed phase change materials could be the potential future storage materials which are represented below in Table 2. The NaNO₃ : KNO₃ mixture has the highest heat capacity per Kg.K while the latent heat is the highest in Al-Si eutectic.

Table 2. Summary of New PCM Material Properties

Material	Heat Capacity (KJ/Kg.K)	Latent Heat (kJ/ Kg.K)	Volumetric Energy Density (MJ/m ³)	Operating Temperatures Melting	Operating Temperatures Solidification	Thermal Efficiency (%)
NaNO ₃ :K-NO ₃ =60:40 (molar ratios) with 1% CuO [81]	1.68–1.93	122.5–178.87	NA	216–218.21°C	NA	NA
NaNO ₃ :K-NO ₃ =60:40 (molar ratios) [81]	1.24–1.5	107.03	NA	219 °C	NA	NA
Aluminium–silicon eutectic [82]	1.04–1.74	470	NA	577 °C	NA	NA
Ternary carbonates [83]	1.22–1.34	247	NA	405 °C	387°C	NA

6.4 Thermochemical Energy Storage

Table 3 below compares some of the newly developed thermo-chemical energy storage materials. Among all these, the CaO/SiO₂ composite has the highest thermal efficiency of 95.7%.

**Table 3.** Summary of New Thermo-Chemical Energy Storage Materials

Reactants	Operational Suitability	Energy Density (MJ/m ³)	Operating T (°C) Charging	Operating T (°C) Discharging	Thermal Efficiency (%)
Hydroxide looping with Sr(OH) ₂ /SrO [84]	Rankine cycle with subcritical steam	97.09	600	525	7.09
Hydroxide looping with Ca(OH) ₂ /CaO [84]	Rankine cycle with subcritical steam	101.97	700	505	4.78
Redox with BaO ₂ /BaO [84]	supercritical CO ₂ cycle combined	46.09	980	690	23.93
CaO/SiO ₂ composites [85, 86]	NA	NA	950	650	95.7

7. CONCLUSION

Solar energy has the capacity to fulfil the global demand of energy but the major limitation to accomplishing this potential is inherent intermittency. To get around the problem, many newly developed materials for all the storage systems are being researched and tested. Although thermal energy storage is commercially available, electrochemical storage systems like batteries also seem to be a promising choice for continuous flow of power generation and moving peak sunlight hours of solar energy to peak utilization hours in the near future. Moreover, the newly developed materials for the electrochemical batteries in the solar cells, as discussed in the article, although still in the experimental phase, also seem to offer a better storage capacity. All in all, it can be concluded that the development of new materials will boost the stability and performance of energy storage systems.

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