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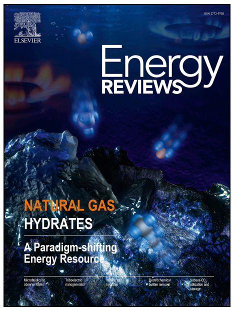

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An Overview of Application-oriented Multifunctional Large-scale Stationary Battery and Hydrogen Hybrid Energy Storage System

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Abstract: The imperative to address traditional energy crises and environmental concerns has accelerated the need for energy structure transformation. However, the variable nature of renewable energy poses challenges in meeting complex practical energy requirements. To address this issue, the construction of a multifunctional large-scale stationary energy storage system is considered an effective solution. This paper critically examines the battery and hydrogen hybrid energy storage systems. Both technologies face limitations hindering them from fully meeting future energy storage needs, such as large storage capacity in limited space, frequent storage with rapid response, and continuous storage without loss. Batteries, with their rapid response (<1 s) and high efficiency (>90%), excel in frequent short-duration energy storage. However, limitations such as a self-discharge rate (>1%) and capacity loss (~20%) restrict their use for long-duration energy storage. Hydrogen, as a potential energy carrier, is suitable for large-scale, long-duration energy storage due to its high energy density, steady state, and low loss. Nevertheless, it is less efficient for frequent energy storage due to its low storage efficiency (~50%). Ongoing research suggests that a battery and hydrogen hybrid energy storage system could combine the strengths of both technologies to meet the growing demand for large-scale, long-duration energy storage. To assess their applied potentials, this paper provides a detailed analysis of the research status of both energy storage technologies using proposed key performance indices. Additionally, application-oriented future directions and challenges of the battery and hydrogen hybrid energy storage system are outlined from multiple perspectives, offering guidance for the development of advanced energy storage systems.

Highlights:

- Application-oriented energy storage systems are reviewed for battery and hydrogen hybrid energy storage system.
- A series of key performance indices are proposed for advanced energy storage systems.
- Battery and hydrogen hybrid energy storage system (0.626 \$/kWh) is more cost competitive compared to battery energy storage system (2.68 \$/kWh) in a renewable energy storage case.
- Challenges of multifunctional large-scale stationary battery and hydrogen hybrid energy storage system are summarized.

Keywords: hybrid energy storage system, battery, hydrogen, stationary, large-scale, multifunctional.

List of abbreviations including units and nomenclature:

Abbreviation	
AHEAD	Advanced Hydrogen Energy Chain Association for Technology Development
AI	Artificial Intelligence
B&H HESS	Battery and Hydrogen Hybrid Storage System
BEMS	Building Energy Management System
BESS	Battery Energy Storage System
CcH2	Cryo-compressed Hydrogen
CE	Coulombic Efficiency
China Datang	China Datang Corporation Limited.
China Huadian	China Huadian Corporation Limited.
China Huaneng	China Huaneng Corporation Limited.
CHN ENERGY	China Energy Investment Corporation
CSIRO	Commonwealth Scientific and Industrial Research Organization
DoD	Depth of Discharge
EE	Energy Efficiency
EnWG	Energiewirtschaftsgesetz
ESS	Energy Storage System
FC	Fuel Cell
H$_0$LOHC	Unload LOHC
HESS	Hybrid Energy Storage System
HGMs	Hollow Glass Microspheres
H$_n$LOHC	Loaded LOHC
HOMER	Hybrid Optimization Model for Electric Renewables
HPLT	High Pressure and Low Temperature
HPNT	High Pressure and Normal Temperature
HSS	Hydrogen Storage System
LDES	Long Duration Energy Storage
LLNL	Lawrence Livermore National Laboratory
LOHC	Liquid Organic Hydrogen Carrier
MGF	Metal Graphene Framework
MH	Metal Hydride
MLI	Multilayer Insulation
MOF	Metal-organic Framework
NASA	National Aeronautics and Space Administration
NPLT	Normal Pressure and Low Temperature
NPT	Normal Pressure and Temperature
PEM	Proton Exchange Membrane
SB	Senate Bill
SCE	Southern California Edison Company
SDES	Short Duration Energy Storage
SGSS	Smart Grid Stabilization System
SOC	State of Charge
SPIC	State Power Investment Corporation Limited
UHS	Underground Hydrogen Storage
UHVAC/DC	Ultra-high Voltage Alternating Current and Direct Current
VCS	Vapor Cold Shield
VE	Voltage Efficiency
VRB	Vanadium Redox Flow Battery
ZBB	Zinc-bromine Flow Battery

Nomenclature	
C	Cost, \$
E	Energy capacity, kWh
e	Energy density
e_v	Volume energy density, kWh/m^3
e_m	Mass energy density, kWh/kg
P	Power, W
t	Service life, year
λ	Coefficient, the ratio of storage power and maximum collecting power
η	Energy transformation ratio
Δt_{reg}	Response time, s

Contents

1 Background

As the social economy and technology advance, there is a growing demand for electricity. Fig. 1 presents data from the National Bureau of Statistics of China, which illustrates the increase in electricity generating capacity from 2012 to 2021. Over this decade, the capacity has risen from 49,875.5 GW to 85,342.5 GW, with an average growth rate of 6.15% [1]. An analysis of the energy structure reveals that approximately 70% of electricity is supplied by fossil-fired power stations. Since the establishment of the first coal-fired power station by Edison in 1882, named Holborn Viaduct in London [2], coal-fired power stations have developed for about 140 years. The increasing consumption of fossil fuels for daily life and production has led to significant atmospheric pollution. In response to environmental challenges, China, currently the largest carbon emitter in the world, has formally introduced carbon peaking and carbon neutrality goals during the 75th United Nations General Assembly. To meet these goals, the electric-power industry bears the responsibility to expedite the transition toward a green-oriented energy structure [3]. China has implemented policies and measures focused on the development and utilization of renewable energy sources, including hydropower, solar energy, wind energy, nuclear energy, and more [4].

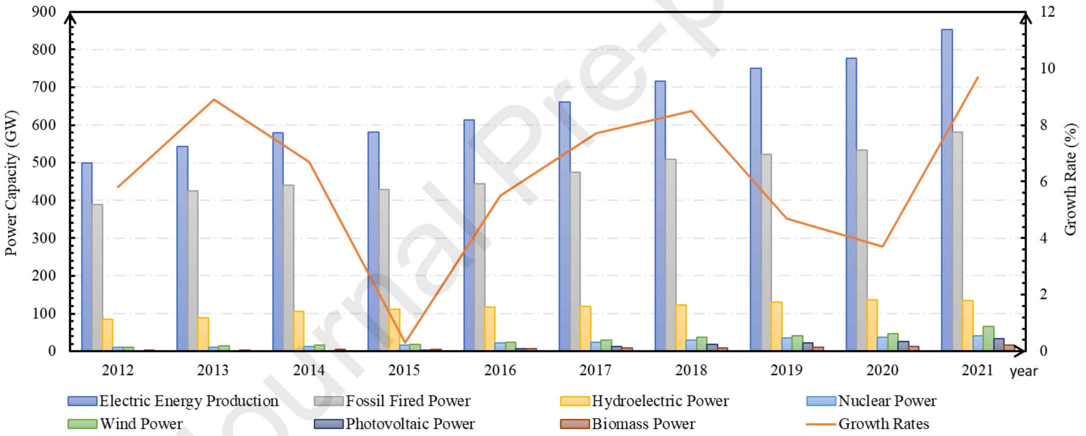


Fig. 1. Data of electric energy generation and growth rates in China from 2012 to 2021

As pivotal national industries, five power generation groups have actively established new power systems (Table 1) [5-9]. By the year 2021, China Energy Investment Corporation (CHN ENERGY) had an installed wind power capacity of 49.99 GW, while the State Power Investment Corporation Limited (SPIC) boasted an installed solar power capacity of 41.13 GW, both of which ranked as the world's largest. However, in 2022, the abandonment ratios for wind and solar energy generation were 3% and 2%, respectively, due to the challenges posed by the randomness and fluctuations in the power grid [10]. Consequently, renewable energy generation systems require compatible storage systems to mitigate these abandonment rates [11]. Fig. 2 illustrates various categories of energy storage systems (ESSs) supported by different technologies, reflecting their diverse performances. The research on ESS is a key and promising technology that has garnered widespread attention, leading to the implementation of practical installations worldwide. The choice of an ESS depends on multiple factors, including capacity, cost, and area. Certain ESSs, such as flywheels and batteries, are well-suited for short-duration energy storage (SDES), characterized by frequent charge/discharge cycles within a brief timeframe. These systems excel in rapid response and high power density, catering to the specific requirements and fluctuations of energy sources. However, their limitations lie in short cycle lifetimes and high energy losses, making them less practical for long-duration energy storage (LDES). The extension of storage times in LDES inevitably dissipates a significant amount of stored energy in the form of heat, which is challenging to re-utilize. Large extra energy consumption accumulated through storage/release cycles results in reduced efficiency and increased unit cost over time. Furthermore, applying these systems as large-scale ESSs would require impractical amounts of space due to their low storage density. Conversely, ESSs designed for LDES should ideally not be used for SDES due to their lower energy transfer efficiency and larger extra energy consumption during the energy storage process.

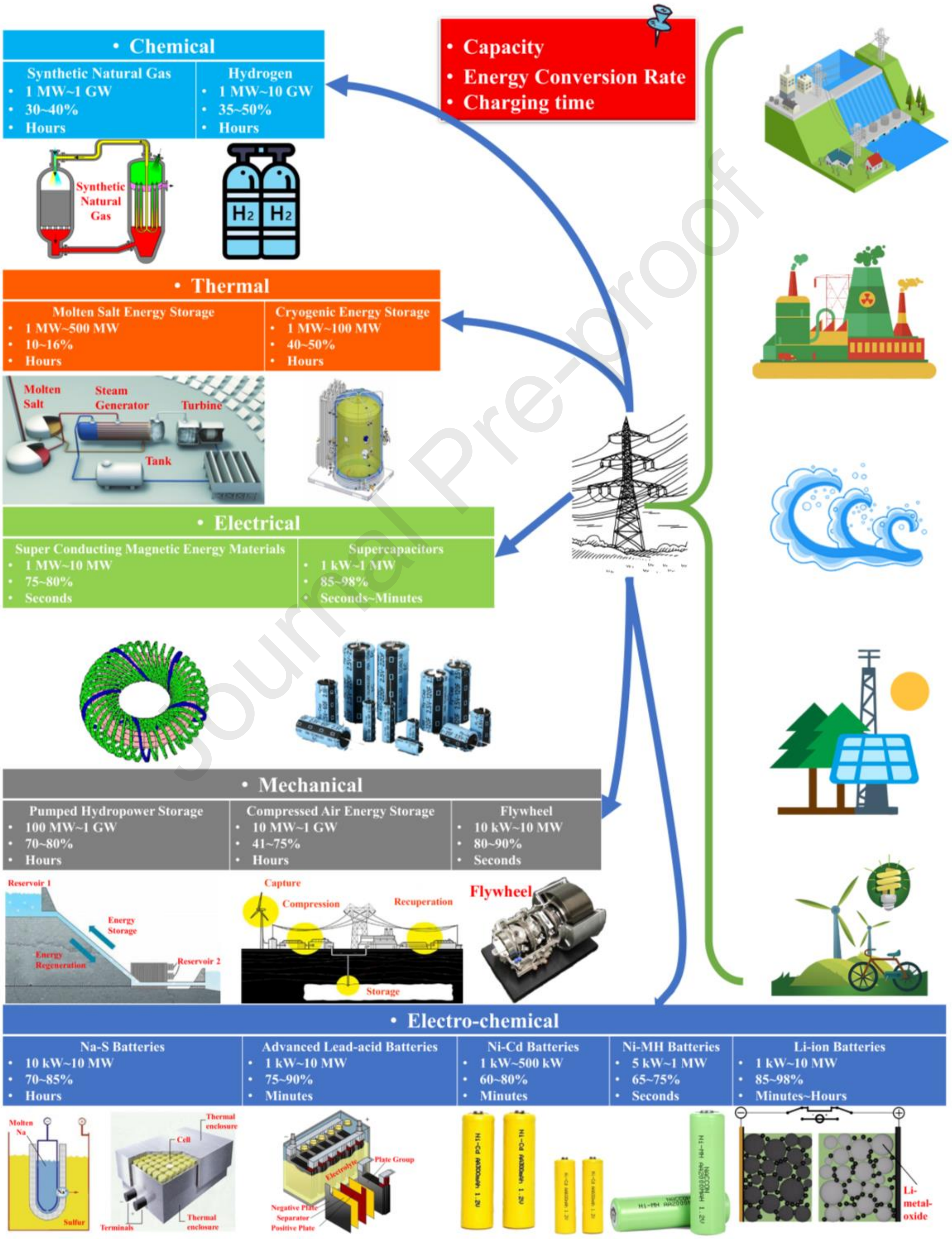


Fig. 2. Categorization of electricity ESSs.

Table 1

The cumulative installed renewable energy capacity of five power generation groups in 2021

Five Power Generation Groups	**Wind (10 MW)**	**Photovoltaic (10 MW)**	**Nuclear (10 MW)**	**Hydroelectric (10 MW)**	**Clean Energy (GW)**
China Huaneng	2917	912	N/A*	2756	78.49
SPIC	3823	4113	809.4	2465	120
China Datang	2545.14	534.76	N/A	2716.33	64.08
CHN ENERGY	4999	860	N/A	1869	78.05
China Huadian	N/A	N/A	N/A	2741	71.38

*N/A: not available

To address these limitations, researchers have dedicated efforts to enhance energy storage in different fields. Governments globally actively construct energy storage systems, and researchers contribute to the advancement of technologies with improved efficiency, larger capacity, and lower costs. California utilities planned to acquire nearly 1500 MW of electricity storage systems for the coupling of solar and wind energy with battery storage [12]. Beacon Power, for instance, manufactures a 250-kWh flywheel system used for stabilizing wind power generation by Fuji Electric [13]. In a study by Kose et al. [14], the Alibeyhuyugu region was chosen for simulating a comprehensive wind-pumped hydropower system. The researchers analyzed the system's electricity storage capacity and financial advantages. Kubo et al. [15] designed a large metal hydride (MH) tank system filled with the Mm-Ni-Mn-Co alloy to store hydrogen produced by renewable energy-derived electricity. Experiments demonstrated the system's ability to store up to 1000 Nm^3 of hydrogen with maximum absorption and desorption rates of 70 Nm^3/h. In an assessment by Bilich et al. [16], the life cycle inventory data of a Lithium-ion battery used in a PV microgrid system was analyzed. While some characteristics approached the standards for large-scale storage, such as 112-Wh/kg energy density, a 20-year lifetime, and 7300-cycle times, it exhibited an inevitable parasitic loss factor of 1%, resulting in substantial energy loss. Additionally, numerous other ESSs suitable for various scales exist. The challenge of realizing an ESS with excellent performance in all aspects, serving both SDES and LDES supported by a single energy storage technology, continues to impede practical applications.

The combination of various ESSs has the potential to address complex energy storage challenges and create multifunctional large-scale stationary ESS with high energy storage density, frequent storage with rapid response, and continuous storage without losses. A Hybrid Energy Storage System (HESS), incorporating more than two energy storage technologies, can efficiently manage different storage tasks, often dividing functions into SDES and LDES. Intelligent control systems are designed to regulate the entire HESS for efficient operation. Fig. 3 summarizes the normal rate, scale, application, and efficiency of several energy storage technologies. The combination of battery and hydrogen emerges as an attractive direction for developing multifunctional large-scale HESS. Batteries, extensively researched, offer diverse performance and can be combined with other ESSs. Most batteries used for energy storage like lithium-ion battery exhibit high energy efficiency and rapid response, making Battery Energy Storage Systems (BESSs) suitable for SDES, with numerous BESS implementations worldwide. Hydrogen storage, gaining attention for its zero-emission advantage, has become a research hotspot [17,18]. Hydrogen, a highly potential energy form, has diverse practical applications. Converting electricity to hydrogen enhances stable, long-term energy storage, presenting a promising approach for seasonal energy storage.

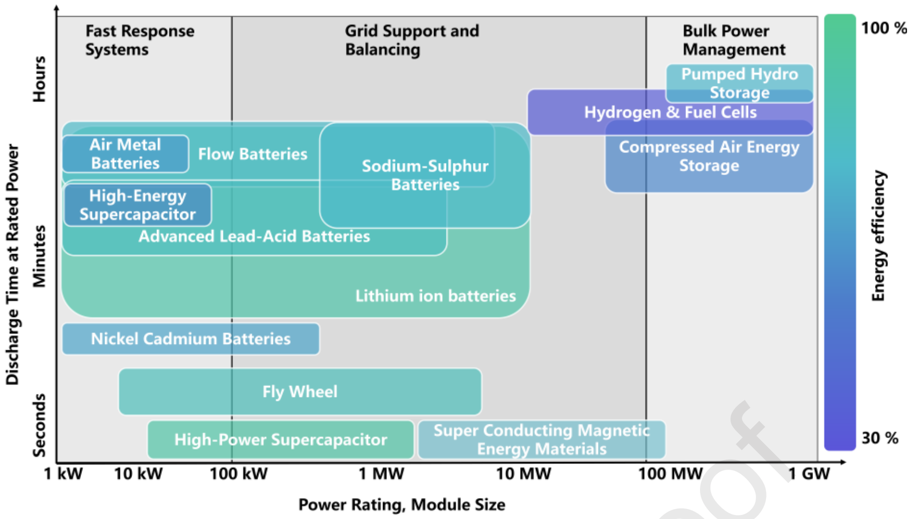


Fig. 3. Discharge time, power rating, and energy efficiency of energy storage technologies

Initially, energy harvested from natural sources is stored in battery stacks. The battery adapts to different charge/discharge power requirements by controlling the number of operational stacks, enabling high-response energy transfer. This facilitates efficient storage and utilization of energy in short durations. For LDES, addressing the inhomogeneity of renewable energy and the mismatch between energy consumption and production, electricity undergoes electrolysis to convert to hydrogen, which is stored in hydrogen form. Although the transformation process incurs minimal energy consumption, hydrogen storage proves advantageous due to its ability to be stored for an extended period with relatively low energy loss compared to electric energy storage. Additionally, the volume of a hydrogen energy storage system is reasonable, given its higher volume energy density compared to batteries. Fig. 4, illustrates that BESS and hydrogen storage systems (HSS) form a complementary solution for multifunctional energy storage. The combination of Battery and Hydrogen Energy Storage (B&H HESS), utilizing both mature battery technology and the potential of hydrogen as an energy form, presents a transitional yet appealing concept for multifunctional large-scale stationary ESS. Scaling each ESS regulates the overall HESS performance, accommodating variable energy storage demands. Therefore, researching B&H HESS holds significance.

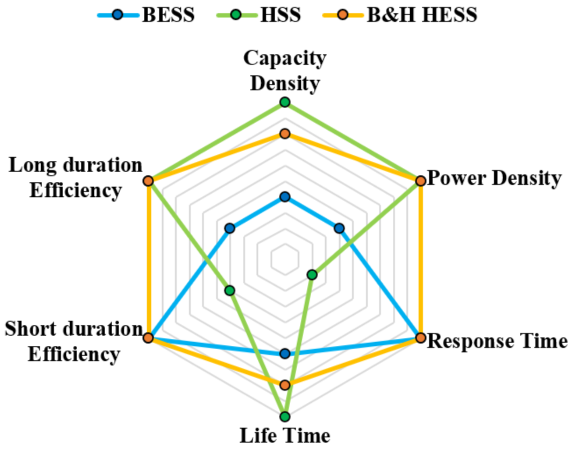


Fig. 4. Performance comparison of BESS, HSS, and B&H HESS

This study reviews the combination of short-duration BESS and long-duration HSS in the context of B&H HESS. It covers the research status, specific performance, practical applications, prospects, and challenges associated with this hybrid system. The second section introduces a set of indices for analyzing and comparing various ESS systems, providing clarity on current situations and future directions. In the third and fourth sections, battery and hydrogen energy storage technologies are evaluated across different performance fields using the proposed indices. The analysis includes a review of practical and commercial ESSs, exposing the current development status and existing challenges. The fifth section presents existing and emerging B&H HESSs, outlining future improvement targets and progress in each property. This section highlights potential application-oriented research directions. The sixth section discusses the prospects and challenges of B&H HESS in the field of renewable energy storage, considering policy and technical support. The paper aims to offer guidance and potential directions for developing high-performance, multifunctional, large-scale stationary B&H HESS, contributing to the transformation of the future energy structure.

2 Performance indices

The appropriate indices for the evaluation of ESSs' performance are decisive. Normally, a few of the most concerned properties mainly include capacity, efficiency, and lifetime. Under some restrictions like limited space and precise control, some other indices are required like storage density and response time. For practical application, the cost is an influential factor for system's construction. So, a series of indices are summarized as followings:

2.1 Capacity and energy density

Energy capacity (E_{tot}) is the maximum amount of energy ESS can store described by Equation (1), and energy storage density (e) is the unit capacity. Energy capacity determines the scale of storage and could be expanded by installing extra storage facilities. Usually, ESS is designed based on the amount of energy input from upstream energy generation industries. However, energy capacity is not fitted for diverse ESSs in terms of a universal evaluation index because of their different demands of renewable energy storage. So, another index, energy density, may be more reasonable than capacity in comparison. Energy density contains mass energy density (e_m) and volume energy density (e_v), which are energy storage capacity per unit mass and volume, described by Equations (2) and (3), respectively. Mostly, for stationary ESS, the total volume is more important than weight of installation due to limited space. Normally, high energy density is much more attractive and competitive for any ESSs in technical aspect.

Overall energy capacity is described as follows,

$$E_{\text{tot}} \tag{1}$$

where, E is the energy capacity of the ESS, and subscript *tot* is the whole system.

Energy mass density is described as follows,

$$e_m = \frac{E_{tot}}{M_{tot}} \tag{2}$$

where, e and M is the energy density and mass of an ESS, and subscript m is the mass of whole system.

Volume energy density is described as follows,

$$e_v = \frac{E_{tot}}{V_{tot}} \tag{3}$$

where, V is the volume of the ESS, and subscript *v* is the volume of the whole system.

2.2 Response and Power

Response time (Δt_{reg}) described by Equation (4) is the time interval between receiving changing signal and responding. Power (*P*) is the amount of energy input/output per unit time and reflects energy transport velocity. As early said, renewable energy fluctuates all the time which means the power of storage changes and it may be an extremely high charging power in a short period accordingly. The energy demand from downstream users is unsteady requiring changeable storage power accordingly. So, a design of large-scale ESS should not only focus on the whole amount of energy, but also concern on the power matching of generation and storage to ensure a high response and storage rate in a SDES process. Generally, the whole range of renewable energy could be stored if the ESS is designed according to the maximum value. However, the more the quantity of energy is stored, the lower the grade of energy is. It's worthless to manufacture a high-power ESS for a little renewable energy which exists within a short time. So, an evaluation of appropriate maximum power for storing a large proportion of renewable energy with a relatively high efficiency and a relatively low cost is reasonable. A coefficient, λ, which is the ratio of storage power (P_{in}) and maximum colleting power (P_c) is defined by Equation (5). It's different for various regions and changeable based on climate forecast for matching the fluctuating power of renewable energy. The higher release power (P_{out}) should match to the power demand (P_{d}) described by Equation (6).

Response time to regulation is described as follows,

$$\Delta t_{\text{reg}} \tag{4}$$

where, Δt is the response time to regulation, and subscript reg is the regulatory process.

Storage power is described as follows,

$$P_{\text{in}} = \lambda \cdot \max(P_{\text{c}}) \tag{5}$$

where, P and λ are the power and a coefficient, respectively, and subscripts in and c are the input process and collecting process, respectively.

Release power is described as follows,

$$P_{\text{out}} = P_{\text{d}} \tag{6}$$

where, subscript *out* and *d* are the output process and demand, respectively.

2.3 Energy transformation ratio

Energy transformation ratio (η) is a ratio of practical output to input energy after a series process like long duration storage, transformation of energy forms, and so on. According to the first law of thermodynamics, the form of energy would be changed, and the quantity of available energy would be lost during the process of transmission and transformation. Besides, there is another loss caused by the downgrade of available energy. The ability of doing work may decrease in the whole process. So, these energy loss in quantity and grade is inevitable, and the actual amount of stored energy is lower in practical. In another aspect, through the process of transformation and transportation, auxiliary equipment worked for renewable energy storage is bound to consume energy for the stable and normal operation. The energy stored practically equals to the total storage minus the consumption of transfer included doing work, heat emission, and others. Energy transformation ratio could be used to describe the real storage ability of an ESS. The proportion of renewable energy which is stored and transformed to available energy is the product of overall processing energy transfer ratios as written in Equation (8) and Equation (9). To achieve the maximization of energy utilization, a high energy transformation ratio of close to 80% even 90% is favored.

Overall energy transformation ratio is described as follows,

$$\eta_{\mathrm{tot}} \tag{7}$$

where, η is the energy transformation ratio.

Energy transformation ratio of ith process is described as follows,

$$\eta_i = \frac{E_{\mathrm{out},i}}{E_{\mathrm{in},i}} \tag{8}$$

where, subscript i is the ith energy transformation process.

Energy transformation ratio of multiple processes is described as follows,

$$\eta_n = \eta_i^n \tag{9}$$

where, subscript n is the number of energy transformation processes.

2.4 Service life

Service life is a period (t_e), in which equipment is in service efficiently, described by Equation (10) or normally (t_w) described by Equation (11). Service life is also a key index to evaluate an ESS because it is always related with cost. According to actual energy storage demands, diverse energy storage tasks will be faced possibly. Some ESSs are responsible for frequent SDES and some ESSs are stored in fully charged state for LDES. For the multifunctional large-scale stationary ESS, a large quantity of energy is transported through the mediums and transformed to other forms frequently with unstable input/output power. Extreme operating conditions exacerbate device degradation even scrapping. That means the damage of equipment is further intensified, and the service life of systems is influenced more seriously. Normally, the service life is quite different, which depends on technologies and operational modes. Different ESSs differ in the service life from days to years. Extending efficient service life based on service life extension is research's goal all along.

Service life is described as follows,

$$t_w(\text{with an operational capability}) \tag{10}$$

Efficient service life is described as follows,

$$t_e(\text{with a rewarding efficiency}) \tag{11}$$

where, t is the service life, and subscripts w and e are the working capability and efficient capability.

2.5 Overall cost

Overall cost (C_{tot}) is the economic consumption of a storage system in the whole constructing and operational process described by Equation (12). It contains initial investment (C_{ini}) and total operating cost (C_{oper}) which are described by Equation (13) and Equation (14) respectively. Initial investment usually refers to the purchase and installation of infrastructures and it’s always quite different for various ESSs. For example, photo thermal power technology utilizes most of facilities powering in traditional coal-fired power station, so it will save a portion of cost in powering. But for other ESSs like HSSs, all the facilities which work for energy production, storage and reutilization need to be purchased, constructed, and installed at first. In addition, total operating cost is attributed to creating and maintaining operational conditions. Stable energy storage capacity and changeable energy storage rate are achieved by assistant equipment. The maturity of energy storage technologies is discrepant so that their overall cost for application is quite different. In general, price is always the factor which people concern mostly for the practical application of ESS. So, it's also a pivotal index to evaluate a system. Lower cost is a comprehensive objective of ESS and breakthrough in low-cost energy storage are desiderated to be achieved.

Overall cost is described as follows,

$$C_{\mathrm{tot}} = C_{\mathrm{ini}} + C_{\mathrm{oper}} \tag{12}$$

where, C is the cost, and subscripts *ini* and *oper* are the initial and operational stages, respectively. Initial investment is described as follows,

$$C_{\mathrm{ini}} = (\mathrm{purchase} + \mathrm{contruction} + \mathrm{installation} \ldots) \tag{13}$$

Operating cost is described as follows,

$$C_{\mathrm{oper}} = (\mathrm{regulation} + \mathrm{maintenance} \ldots) \tag{14}$$

2.6 Geographical conditions

Geographical conditions are the topographic conditions and regional distribution required for ESS installation. China is a country boasting a vast territory. Diverse climate of different regions causes a significant heterogeneity in the distribution of renewable energy sources. Moreover, the standards of energy consumption are quite related to the level of urban development. It's commonly seen that the regional imbalance of energy production is one of the most critical problems influencing energy utilization. Cities providing large area for the building of renewable ESSs is usually with a low energy consumption capacity. Partial energy consumed by over long-distance transport and over long duration storage is one of the most striking contradictions.

Besides, some ESSs rely on the natural environment like hydrogen stored in salt cavern. These actual demands require that the site selection of ESS should adjust to local conditions. Various factors of geographical conditions need to be considered in detail like renewable energy production, energy consumption, cycle lifetime of energy storage, and so on. Finally, a profitable complete regional industrial chain including efficient storage of abundant renewable energy and full utilization of stored energy will be formed.

2.7 Safety

Safety is one of the properties which reflects the accident possibility and potential damage. Depending on the characteristics and operating conditions, ESSs can be divided into several levels of risk. Safety is affected in many aspects. Some ESSs are manufactured by polluted even toxic materials, and some are operated under extreme reaction conditions to acquire a better storage performance. In addition, fluctuation of power is possible to cause damage to key units and trigger serious accidents. The overall goal is lowering down dangerous factor and improving safety in terms of precaution, control, and management.

2.8 Section summary

Fig.5 shows the indices above mentioned to evaluate the performance of ESS. These indices reveal the necessary characteristics and specify the developing aim for ESS. Single improvement is not suitable for synthetical demand of energy storage. Although an ESS with excellent properties in all aspects is still hard to developed, multi-objective optimization of ESS is what researchers focus on. A specific series of indices are quite helpful for this. Awareness of ESS is restricted by research progress, and development is influenced by these indices possibly. Mining new indices and broadening the scope of optimization are two future goals for the realization of perfect ESS.

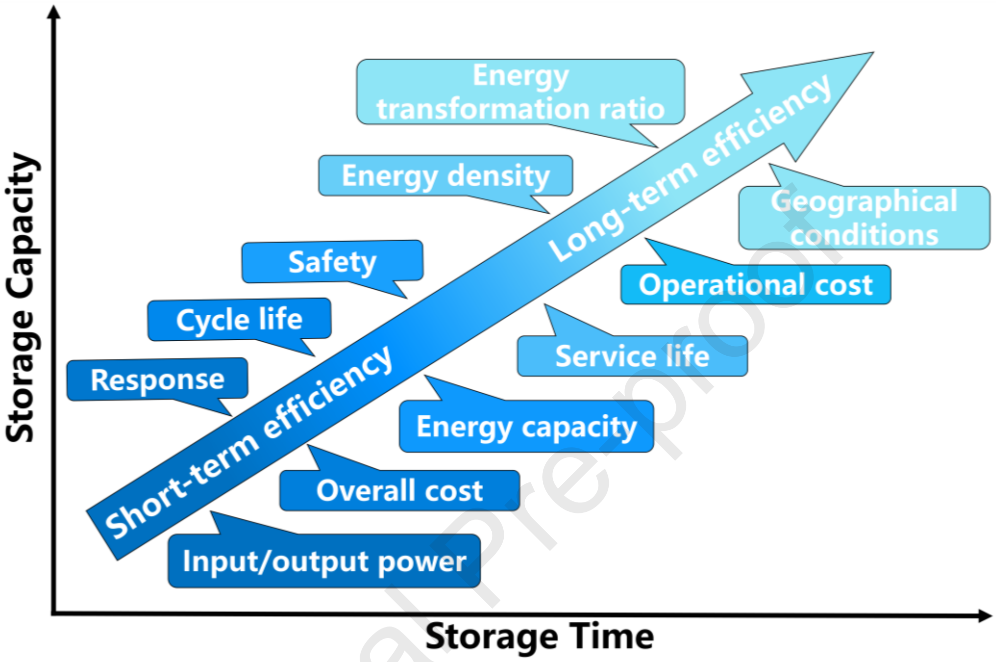


Fig. 5. Key indices to evaluate the performance of ESS

3 Battery energy storage system

BESS utilizes the conversion between electric energy and chemical energy to realize the electric energy storage. BESS is one of the most profitable and maturest energy storage technique. Generally, batteries include lead-acid battery, Lithium-ion (Li-ion) battery, flow battery, molten sodium (Na) battery, Nickel-Cadmium (Ni-Cd) battery, and some advanced batteries [19]. These batteries show their specific advantages and shortcomings in practical applications. Meanwhile, researchers have made some efforts on advanced batteries for better properties.

3.1 Lead-acid battery

Lead-acid battery is the oldest and the maturest type of rechargeable battery. Its highlights are the lowest cost and the maturest technology. However, it shows the apparent shortcomings of the slow rate of charge, the low density of energy and power, the limited cycle lifetime, the high self-discharge rates which means low energy transfer ratio, and the seriously toxic material caused environmental hazards. Typically, it has energy conversion efficiency of around 75%~80% with an expected lifetime of 5~15 years or 1,200~1,800 cycle lifetime [19-21].

To improve performance, many works have been reported. Japanese scientists found that adding more carbon to the battery would increase performance and lifetime dramatically in 1997. Their work was confirmed by Australia Commonwealth Scientific and Industrial Research

Organization (CSIRO). CSIRO developed an advanced lead-carbon battery technology named Ultrabattery which is a hybrid energy storage device combined by a lead-acid battery and an asymmetric supercapacitor through the carbon addition into negative plate. Although the cost of production is much higher, the improvement of lifetime, efficiency and operability of partial state-of-charge are acquired [22]. The electrode is still in a healthy condition after 5000 charge/discharge cycles [23]. So, advanced lead-carbon battery is a potential candidate chosen as the ESS for several projects.

In addition, there have been applications of renewable energy generation and storage which take lead-acid BESS as ESS. Nortrees project, a wind farm system, resolved the intermittency of wind power system through a 36 MW/24 MWh lead-acid BESS combined by several 1 MW lead-acid battery units produced by Xtreme Power Inc [24]. However, due to the inherent problems of low energy density (40~60 Wh/kg) and pollution in the production process, more progress in the improvement of battery properties and development of eco-chemical industry should be made for lead-acid BESS.

3.2 Li-ion battery

Li-ion battery has been in development more than 40 years. Li-ion battery has a much higher energy density (130~200 Wh/kg) [25,26] and power density than lead-acid battery. Li-ion battery also shows a brilliant performance in response time for load fluctuation. Adachi et al. [27] set up a Li-ion battery pack and tested its performance. Experiments showed that its response time is lower than 200 ms under different load fluctuations. After the development in Li-ion battery, response time was shortened considerably. Furthermore, Nanophosphate^{TM} Li-ion battery unit of A123's Smart Grid Stabilization System (SGSS) only needs 20 ms for the response of power output changes [28].

Li-ion batteries are designed to be modular so that they could be integrated easily and formed a large-scale BESS. Li-ion BESS is a popular and relatively mature ESS, and this system is put into practical applications widely. Tesla won the bidding of the project which was a construction of large-scale 100 MW/129 MWh BESS in South Australia in 2017. Before the project, they had just installed a 20 MW/80 MWh BESS for a transformer substation owned by Southern California Edison Company (SCE) in Miraroma. The battery of both projects used was Tesla's featured product, Powerpack. Single Powerpack is connected by 16 units whose capacity is 13.5 kWh in parallel [29].

However, expensive cost, serious safety issues, and limited lifetime are the barriers for the utilization of large-scale stationary Li-ion BESS. Although the energy efficiency of Li-ion battery ranges from 85%~98% with the lifetime of 5~15 years, the performance reduces substantially within a ten-year operation life [30]. Otherwise, safety issue is one of the most concerned aspects. There were about 30 accidents reported within 2017-2019 in South Korea caused by Li-ion battery. Research institutions investigated those accidents and classified them into four aspects which are inherent defect of battery, external shocks, adverse operating environment, and unreliable management system. The most serious threat to system safety is the battery itself. Overcharge exists in the full state of charge (SOC) and makes thermal runaway be triggered more easily [31]. With the development of Li-ion battery technology, capital cost will be reduced. The focuses are transfer to prolongation of cycle lifetime and improvement of safety [32].

3.3 Molten Na battery

Molten Na battery includes sodium sulfur (Na-S) battery and sodium-metal chloride battery (ZEBRA battery).

Na-S battery is mainly demonstrated and developed in Japan. This battery has both high energy and power density which are 4 times more than those of lead-acid battery. Also, this battery has a high efficiency (75%~86%) with a long cycle lifetime and is fabricated by cheap and plentiful materials [20]. A Japanese company, NGK Insulators, manufactured Na-S battery which can charge at a rate of 50 kW for 7 h. The energy density and the energy efficiency of this battery are 151 kW h/m^3 and 85%, respectively [19]. In addition, American Electric Power (AEP) has installed a 1.0 MW Na-S BESS which consists of 20 individual 50-kW Na-S battery modules. This BESS could store more than 6 MWh of electric energy with a short interval about one second or less. Volume energy density is one of the most crucial indices for scalable application in a limited space. The length, width and height of this Na-S BESS are 10.3 m, 2.3 m and 5.3 m, respectively. So, Na-S BESS may take up overlarge space for large-scale energy storage [33].

Meanwhile, Na-S battery is different with both batteries mentioned earlier. The materials of positive and negative electrodes are molten liquid Na and S respectively. To keep the electrodes in liquid form and achieve a good ionic conductivity in electrolyte which is a solid ceramic material, the battery should work at high temperature between 300 and 350 °C [34]. However, higher operating temperature makes accidents happening more likely. For instance, a fire accident was happened in the Mitsubishi and Tsukuba materials corporation in Japan in 2011 due to the thermal runaway and corrosion of Na-S battery [21]. So, equipping with a thermal management and insulation facility are the stringent demand for Na-S battery at the present stage, which will make systems quite expensive [34].

During recent decades, researchers' interest is shifting to room temperature Na-S battery and research results have demonstrated the practical utility by significant discharge capacity and cycle lifetime [35]. Modification of new structures and materials would reduce the whole temperature of battery system to minimize above-mentioned damage.

ZEBRA (Zero Emission Battery Research Activities) battery was developed in the 1980s. It's usually combined by a liquid Na negative electrode and a metal chloride positive electrode [36]. As one of the potential stationary BESSs, safer failure mode, higher voltage, and zero self-discharge are ZEBRA BESS's distinct advantages over Na-S battery [37,38].

ZEBRA battery based on Na-NiCl$_2$ was first invented by Coetzer in 1978 [38]. Na-NiCl$_2$ battery has been tested and utilized successfully in Stingray developed by the Santa Barbara Electric Transportation Institute. Similarly, buses powered by ZEBRA battery showed equally well performance with diesel buses in another test in 2004 [39]. Also, there are other chlorides in ZEBRA batteries researched by many groups for cheaper application and results showed satisfying performance. Li et al. [37] proposed an advanced Na-FeCl$_2$ battery for stationary ESSs. Intermediate operating temperature (<200 °C), high energy density (135 Wh/kg), and good overall energy efficiency (>92%) were the outstanding improvement of their works. Kim et al. [40] demonstrated a high-performance Na-CuCl$_2$ battery toward room temperature. Test results showed that a superior capacity retention over 1,000 cycles and round-trip efficiency of 97% at room temperature were the most outstanding advantages.

Although excellent performance is acquired from laboratory, reduction of cost and improvement of cycle lifetime at room temperature are still the keys requiring development efforts for practical stationary energy storage [37].

3.4 Ni-Cd battery

Ni-Cd battery has an excellent charge/discharge performance so that they could be fully charged within a very short time. The battery could be chargeable more than 3500 cycles at normal without any loss and 50,000 cycles at 10% depth of discharge (DoD) [35]. Unfortunately, this technology has not been commercial due to its cost which is 10 times more than that of lead-acid battery technology. Ni and Cd which are toxic heavy metals would cause health risk in humans. So, Ni-Cd battery is not suitable for large-scale stationary BESS.

3.5 Flow battery

Flow battery is quite different with the conventional batteries. There are two reservoirs stored two different aqueous electrolytes and a reactor in the whole battery system. Electrolytes are pumped from tanks to reactor and charge/discharge reactions occur here. Because of this special operational mode, the energy and power capacity are easily scalable by enlarging the volume of reservoirs and the size of electrodes respectively. Meanwhile, flow battery has the advantages of high energy and power capacity, low self-discharge, high efficiency (75%~85%), and long cycle lifetime (>15 years or >10,000 cycles). The flow battery is suitable for large-scale stationary BESS with a relatively high energy density. Vanadium redox flow battery's (VRB) energy density is 40 Wh/kg, and Zinc-bromine (Zn-Br) flow battery's (ZBB) energy density is 80 Wh/kg.

MW-scale energy storage and peak-regulating power station supported by VRB has connected to the grid and the total construction scale was 200 MW/800 MWh. Primus Power has also designed and constructed a 25 MW/100 MWh ZBB BESS in 2017 in Astana, Kazakhstan [41]. But the operating costs which include energy and money consumed by pump are not negligible. The average cost of a flow battery system with a 4-hours design storage duration is about 2,000~3,000 $/kWh. So, the actual energy density, energy transfer ratio and production cost should be recounted. The points which need to be improved in the future research are the reduction in the cost, the improvement in energy density and the avoidance in harmful gas leakage.

3.6 Novel metal-ion battery

The lack of lithium with the increasing cost forces people to search new materials for equal even better electrochemical performance for large energy storage. Researchers try to find other alternative metal-ion batteries like aluminum-ion battery, sodium-ion battery, magnesium-ion battery, and so on. To find the possibility of novel metal-ion batteries in future EES, the characteristics, advantages, and challenges are summarized as bellows:

Aluminum-ion (Al-ion) battery technology was first revealed in 2015 by Dai group [42]. According to their reports, this type of battery could be fully charged within one minute and the cycle lifetime could be up to 7500 cycles with a little capacity decay. Likewise, this battery has excellent performance in the power density (3000 W/kg), but it is not ideal in the energy density (80 Wh/kg). Meanwhile, ultrafast charging times and long-lasting durability make Al-ion battery have potential and advantages to be a candidate of large-scale stationary BESS for renewable energy [21,43].

Sodium-ion (Na-ion) battery is demonstrated to be a promising technology for stationary energy storage system because of the abundance of sodium resources (low cost) [44]. The availability of Na-ion battery was investigated in parallel with Li-ion battery in 1970s [45]. But the slow progress made Na-ion battery be largely discontinued and caught up by Li-ion battery [46]. Low specific energy, poor cyclic stability, low initial coulombic efficiency, large volume expansion and high safety risk are key issues which have to be settled before practical application [44]. These performances are mainly related to the materials of anode, cathode, and electrolyte. Until now, materials with outstanding performance have not been found yet. In 2015, a 120-Wh/kg Na-ion battery was built by Faradion (UK) and assembled into electric bicycles in a test successfully. A cylindrical Na-ion battery with an energy density of 90 Wh/kg and a cycle lifetime of more than 2,000 cycles was developed by TIAMAT (France) [44]. Energy density is far from the requirement for energy storage. So, this technology is still immature and far from commercialization [47]. Development of nanotechnology and accumulated experience in Li-ion battery promoted its revival [48]. In recent years, the number of research publications in SIBs has arisen and more than 10,000 papers have been published [49,50]. So, this emerging energy storage technology would be to come available soon [51].

Magnesium-ion (Mg-ion) battery attracts people's attention by abundance of magnesium resources and low cost, and it is thought to be a considerable candidate for energy storage [52,53]. Its high theoretical specific capacity (2205 mAh/g) and volumetric capacity (3833 mAh/cm^3) are comparable with Li [52-54]. However, similar with Na-ion battery, progress of Mg-ion battery is restricted by all components. The actual performance shown in experiments is far below theoretical capacity because of low discharge voltage and capacity [53]. So, this battery still can't meet the demand of practical applications [52]. The absence of high-performance of electrolytes and anode/cathode material is the challenges for practical application [52-55]. Unsatisfying performance like passivation on the anode side [53,55,56], sluggish cathode dynamics [54], poor reversibility, low energy density, short cycle lifetime, and unsafety [53] determines that magnesium-ion battery is still in the research stage and far from realizing commercialization.

Calcium-ion (Ca-ion) battery is also a research direction in metal-ion batteries region. The low redox potential (3.04 versus standard hydrogen electrode), high volumetric capacity (2073 mAh/cm^3), fast ion diffusion kinetics in solid electrode materials, and high power density are the superiorities compared with other batteries [58,59]. The passivating layers on calcium anode, the sluggish kinetics, and the electrolyte decomposition are the facing problems due to the lack of electrode and electrolyte materials, and many researchers have specialized in the attempt of various materials, structures, and methods [60].

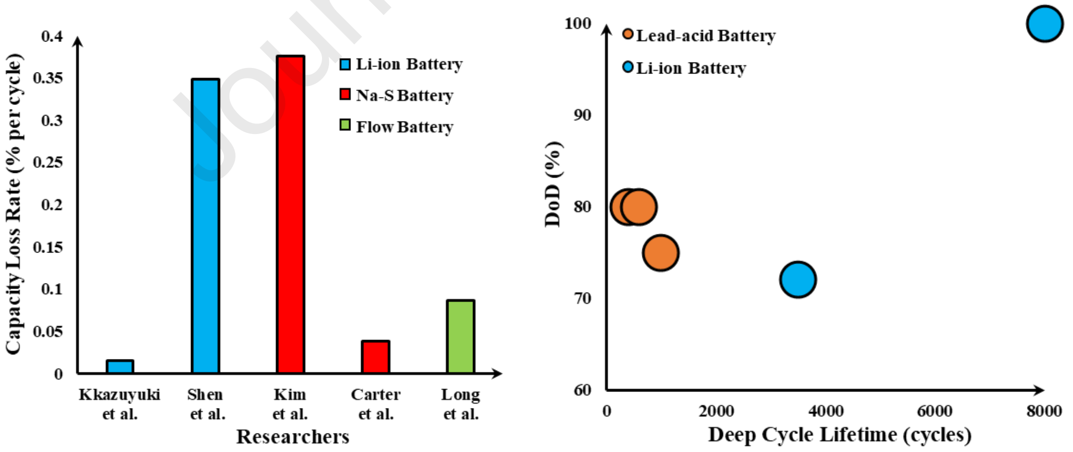
Aqueous zinc-ion (Zn-ion) battery is another novel energy storage component. The advantage of high theoretical capacity (820 mAh/g, 5855 mAh/cm^3), low redox potential (-0.76 V versus standard hydrogen electrode), high abundance, low toxicity, and intrinsic incombustibility shows its potential to be the candidate of ESS [61,62,63]. However, there are two main issues affecting its electrochemical performance. One is the stability issue of the MnO_2 cathode. Due to the much stronger electrostatic interaction between Zn^{2+} and O^{2-}, the cathode stability is worse significantly [62]. Another is that the nonuniform stripping and plating Zn-ions over the anode surface. The dendrite growth of Zn during charging and discharging cycles could cause the short circuit risk leading to the battery failure. Low practical capacity, high initial irreversible loss, poor cycle stability and life, and low coulombic efficiency are the facing issues [63]. Therefore, the applicable anode electrode, cathode anode, and electrolyte materials [63,64,65] are still the research points, and many researchers focus on them from several directions.

Dual-ion battery is quite different from other metal-ion batteries. The positive and negative ions in the electrolyte transfer to the cathode and anode electrode in the discharge process, respectively. The simultaneous movement of two ions shortens the transfer path and makes the charge/discharge process quicker [66,67]. That meets the demand of power fluctuation for renewable energy storage. Therefore, one of the most attractive advantages is the fast intercalation kinetics, and others are high operating voltage, low cost, high energy density, and so on [68,69]. Like other novel batteries, the materials of anode electrode, cathode electrode, and electrolyte are the research directions for more stability, more capacity, longer lifetime, and so on [70,71,72].

Above all, those novel metal-ion batteries are in the preliminary research stage. The most research directions are on the performance improvement of applicable materials, and the mature battery product is developed little. To meet the energy storage demand, there are still a lot of challenges to overcome.

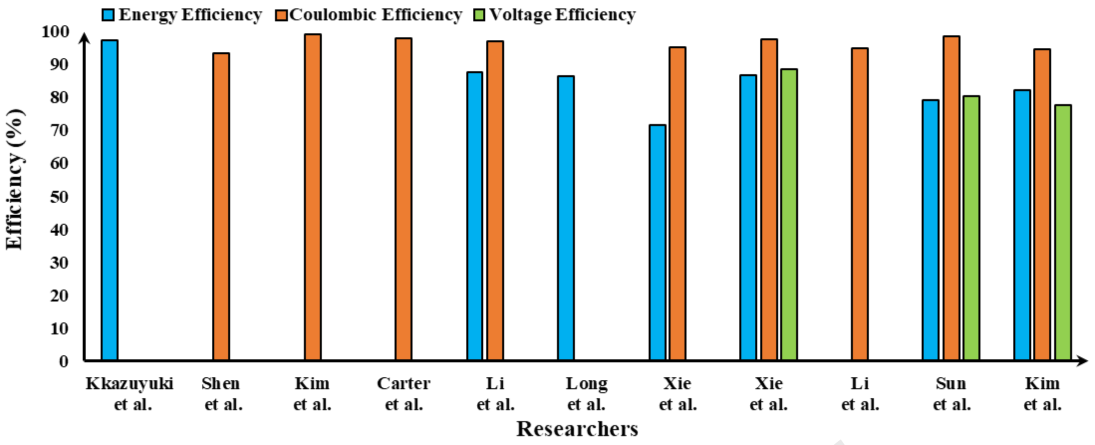
3.7 Comparison and advanced research of batteries

Each battery possesses its outstanding aspects and flawed aspects in energy storage performance. Table 2 summarized the advantages/disadvantages of these batteries. To achieve high-performance and extensive-applied BESS, researchers have focused on the development of advanced batteries. Table 3 shows some advancement done by researchers improving battery performance and contributing to energy storage. And there is a comparison of among these advanced batteries summarized by Figure 6. Performance improvements are in one or several aspects which are evaluated by indices Section 2 mentioned. Most of them focused on new materials and new methods. Researchers have made great efforts to developed advanced batteries for a better performance and a wider range of applications. Although battery has been studied decades and been mature in practical application, it is still not the most suitable large-scale energy storage.

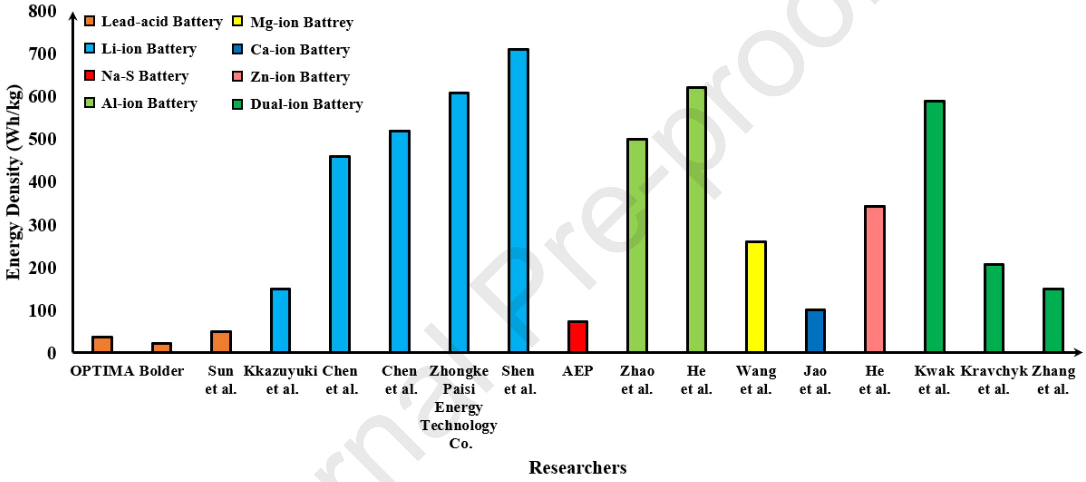


(a)

(b)



(c)



(d)

Fig. 6. Comparison of (a) capacity loss rate, (b) deep cycle lifetime, (c) efficiency and (d) energy density among several types of batteries.

Table 2

Advantages/disadvantages of batteries

Category	Advantages	Disadvantages
Lead-acid battery	Maturest; Low cost.	Low charge/discharge rate; Low energy/power density; Short cycle lifetime; High self-discharge rate; Toxic.
Li-ion battery	High energy/power density; Modular; High energy conversion.	High cost; Security issues; Limited life time.
Na-S battery	High energy/power density; High energy conversion; Long cycle lifetime; Low cost.	High operating temperature; Security issues; Extra thermal management.
ZEBRA battery	Relatively safe; High voltage; Zero self-discharge.	Relatively high operating temperature; Low cycle lifetime.

Table 2 (*continued*)

Category	**Advantages**	**Disadvantages**
ZEBRA battery	Relatively safe; High voltage; Zero self-discharge.	Relatively high operating temperature; Low cycle lifetime.
Ni-Cd battery	High charge/discharge rate; Long cycle lifetime; Low capacity loss.	High cost; Low commercialization; Toxic heavy metal.
Flow battery	Extend easily; Low self-discharge; High energy conversion; Long cycle lifetime.	High cost; Low energy density; Leakage risk of toxic gas.
Al-ion battery	High charge/discharge rate; Long cycle lifetime; Low capacity loss; High power density.	Low energy density; Immature.
Na-ion battery	Low cost; Abundant resource; High theoretical specific energy/power.	Immature.
Mg-ion battery	Low cost; Abundant resource; High theoretical specific energy/power.	Immature.

Lead-acid battery is the most mature. But it's mostly replaced by Li-ion battery due to the more excellent performance in energy density, safety, and so on. Other batteries like Na-S battery, Ni-Cd battery, and flow battery are developed rapidly and have been commercialization of a certain scale. Some advanced batteries like Al-ion battery, Na-ion battery, and Mg-ion battery also are researched by many groups and have the potential of energy storage candidate. But restricted to energy density and capacity loss, BESSs don't have the advantages on price, capacity, and service life aspects in terms of large-scale LDES.

Table 3

Recent progress on improvement of BESSs

Capacity	Usual properties	Researchers	Product/ Direction	Highlights	Developed Properties							Ref.
					Capacity Density	Power Density	Capacity Loss	Deep Cycle Lifetime	Cost	Efficiency Coulombic (CE) Voltage (VE) Energy (EE)	Response	
Lead-acid Battery	Density: 35~40 Wh/kg	CSIRO	Ultrabattery	\	\	\	0.79 %/d	\	Little higher	\	\	[73,24]
	Efficiency: 75%-80% Life time: 5-15 years/ 1200-1800 cycles	OPTIMA	Spirally wound battery	High charge current (300A); Charge rapidly (<1 h); Low leak (50% after 250 days)	36 Wh/kg	\	\	400 cycles in 80% DoD	\	\	\	[74]
		Bolder	Thin Metal Film	High discharge current (>1000A); Charge rapidly	22 Wh/kg	5329 W/kg	\	\	\	\	\	[74]
		Exide	Orbital valve regulated	Low-temperature startup	\	550 W/kg	\	1000 cycles in 75% DoD	\	\	\	[74]
		Sun et al.	Spirally wound battery	High energy dnesity; Long deep cycle lifetime	>50 Wh/kg	\	\	>600 cycles in 80% DoD	\	\	\	[74]
Li-ion Battery	Density: 130~200 Wh/kg	Kkazuyuki et al.	270-Wh cell	\	150 Wh/kg; 290 Wh/L	\	\	3500 cycles in 70% DoD	\	EE 97.3% (cell); EE 78% (system)	200 ms	[28]

Table 3 (*continued*)

Capacity	Usual properties	Researchers	Product/ Direction	Highlights	Developed Properties							Ref.
					Capacity Density	**Power Density**	**Capacity Loss**	**Deep Cycle Lifetime**	**Cost**	**Efficiency Coulombic (CE) Voltage (VE) Energy (EE)**	**Response**	
		A123's	Nanophosphate	\	\	460 W/kg	0.015 %/cycle	8000 cycles in 100% DoD 10+ years	\	\	20 ms	[29]
		Chen et al.	Soft-package Li-S Batery	High energy density;	460 Wh/kg	\	\	\	\	\	\	[75]
		Chen et al.	Li-S Batery	High energy density;	520 Wh/kg	\	\	\	\	\	\	[75]
		Zhongke Paisi Energy Technology Co.	Soft-package Li-S battery	High energy density; Ultralow-temperature operation allowance; High discharge rate;	609 Wh/kg	\	\	\	\	\	\	[75]
		Shen et al.	Sillicon/sulfur Li-ion battery	High energy density; Stability	710 Wh/kg (cell); 420 Wh/kg (system)	\	82.6% after 50 cycles	\	\	CE 93.5%(cell)	\	[76]
Na-S Battery	Density: 130~200 Wh/kg	AEP	NAS battery system	\	72.64 Wh/kg 50.3 kWh/m^3 (system)	12.06 W/kg 8 kW/m^3 (system)	\	\	\	\	<1 s	[77]

Table 3 (*continued*)

Capacity	Usual properties	Researchers	Product/ Direction	Highlights	Developed Properties							Ref.
					Capacity Density	Power Density	Capacity Loss	Deep Cycle Lifetime	Cost	Efficiency Coulombic (CE) Voltage (VE) Energy (EE)	Response	
		Kim et al	Room temperature Na-S.	Low operational temperature.	855mAh/g	\	521 mAh/g after 104cycles	\	\	CE 99%(cell)	\	[36]
		Yu et al.			450 Wh/kg	\	\	\	\$10 per kWh	\	\	[36]
		Carter et al.			700 mAh/g	\	300mAh/g after 1500 cycles	\	\	CE 98%(cell)	\	[36]
		Xin et al.			1610 mAh/g	\	stable for 200 cycles	\	\	\	\	[36]
ZEBRA		Li et al.	Advanced Na-$FeCl_2$	Intermediate-temperature (190 °C) Low cost	135 Wh/kg	\	\	No degradation in a 100-cycles test (60% DoD)	\	EE >92%(cell)	\	[38]
		Chang et al.	Core-shell microarchitecture Ni-coated graphite	Low Ni (40% less) Low cost	133 Wh/kg	\	\	\	\	EE 92%(cell)	\	[78]

Table 3 (*continued*)

Capacity	**Usual properties**	**Researchers**	**Product/ Direction**	**Highlights**	**Developed Properties**							**Ref.**
					Capacity Density	**Power Density**	**Capacity Loss**	**Deep Cycle Lifetime**	**Cost**	**Efficiency Coulombic (CE) Voltage (VE) Energy (EE)**	**Response**	
Flow Battery	Density: 40Wh/kg - VRB; 80Wh/kg-ZBB Efficiency: 75%~85% Cost: 2000~3000 $/kWh Life time: 15 years /10000 cycles	Li et al.	VRB	High energy density; Wide working temperature range	36.2 Wh/L	\	Stable in a 20-days test	\	\	CE 97%(cell); EE 87.5%(cell)	\	[79]
		Long et al.	VRB	High efficiency; stability	\	\	55% after 200 cycles 47.6% after 600 cycles	\	\	EE 86.37%(cell)	\	[80]
		Xie et al.	New Solution ZRB	Low cost; Alow corrosive strenth	\	\	\	202 cycles	\	CE 95.2%(cell); EE 71.7%(cell)	\	[81]
		Xie et al.	Neutralzinc-iron FB	Low cost; High energy dnesity	56.3 Wh/L	\	Stable in a 100-cycles test	\	$50 per kWh	CE 97.75%(cell); VE 88.65%(cell); EE 86.66%(cell)	\	[82]
		Li et al.	Polysulfide /iodide redox FB	High energy density; Low cost	43.1 Wh/L	\	\	\	$85.4 per kWh	CE 93%~95%(cell)	\	[83]
		Sun et al.	Sulfonated poly (ether ether ketone) (SPEEK) membrane	High efficiency	\	\	\	>10 years	$124 per kWh	CE 98.53%(cell); VE 80.31%(cell); EE 79.13%(cell)	\	[84]
		Kim et al.	Ultrathine nafion filled	High efficiency; Low cost	\	\	Stable in a 166-cycles	\	\	CE 94.7%(cell); VE 77.7%(cell);	\	[85]

Table 3 (*continued*)

Capacity	Usual properties	Researchers	Product/ Direction	Highlights	Developed Properties							Ref.
					Capacity Density	**Power Density**	**Capacity Loss**	**Deep Cycle Lifetime**	**Cost**	**Efficiency Coulombic (CE) Voltage (VE) Energy (EE)**	**Response**	
			porous membrane				test			EE 82.1%(cell)		
Al-ion Battery	Density: 3kW/kg; 80Wh/kg Life time: 7500 cycles	Zhao et al.	MnO2|Al(OTF)3|TAI cell	High energy density	500 Wh/kg	\	\	\	\	\	\	[86]
		He et al.	MnO2|Al(OTF)3 +MnSO4|TAI cell	High energy density	620 Wh/kg	\	Stable in a 65-cycles	\\	\	\	\	[86]
Na-ion battery	\	Yang et al.	New cothode material	\	\	6400 W/kg	92% after 6000 cycles	\	\	\	\	[87]
Mg-ion battery	\	Wang et al.	High-voltage aqueous magnesium ion batteries	\	260 Wh/kg	\	75% after 50 cycles	\	\	Initional CE 87%(cell)	\	[56]
Ca-ion battery	\	Jao et al.	PTCDI//AM-CPCA cells	\	100 Wh.kg	2000 W/kg	Ultra-stable in a 4000-cycles test	\	\	\	\	[60]
Zn-ion battery	\	He et al.	Zn//LVO H_2O battrey	\	341.8 Wh/kg	3220 W/kg	No decay after 2000 cycles	\	\	CE 98.2%(cell);	\	[64]

Table 3 (*continued*)

					Developed Properties							
Capacity	**Usual properties**	**Researchers**	**Product/ Direction**	**Highlights**	**Capacity Density**	**Power Density**	**Capacity Loss**	**Deep Cycle Lifetime**	**Cost**	**Efficiency Coulombic (CE) Voltage (VE) Energy (EE)**	**Response**	**Ref.**
Dual-ion battery	\	Kwak et al.	Mesoporous Cu_2O cathode	\	590 Wh/kg	\	Stable in a 300-cycles test	\	\	CE 94%(cell)	\	[69]
		Kravchyk et al.	Concentrated potassium fluorosulfonyl imide	\	207 Wh/kg	\	\	\	\	EE 89%(cell)	\	[70]
		Zhang Et al.	Aluminum-graphite	\	150 Wh/kg	1200 W/kg	88% after 200 cycles	\	\	\	\	[71]

4 Hydrogen storage system

As one of the most potential energy forms, hydrogen has attracted extensive attention worldwide. Because of its high energy density and utilization without any pollution, hydrogen would be the substitute of traditional fossil fuel as energy carrier. Most of the hydrogen on the market is industrial by-product hydrogen. Due to the technical barriers, low productivity and high unit cost are the apparent shortcomings for electrolysis of water. Combination of renewable energy and hydrogen production of water electrolysis would be a possible and economic way. HSS also realizes the LDES of fluctuant renewable energy to solve the problem of unevenly seasonal energy. So, developing hydrogen energy and HSS is the future trend.

According to hydrogen storage state, there are several hydrogen storage ways like high-pressure gaseous hydrogen storage, low-temperature liquid hydrogen storage, metal hydride, and so on. The concerned aspects are not only the hydrogen storage capacity, but also the storage conditions which influence safety, operational cost, and so on. So, HSSs supported by different hydrogen storage technologies could be divided into several types based on operational conditions. According to the storage environment and conditions, HSSs are preliminary classified into extra vessel and natural vessel. More detailed classification in extra vessel is made based on hydrogen storage methods as shown in Fig. 7.

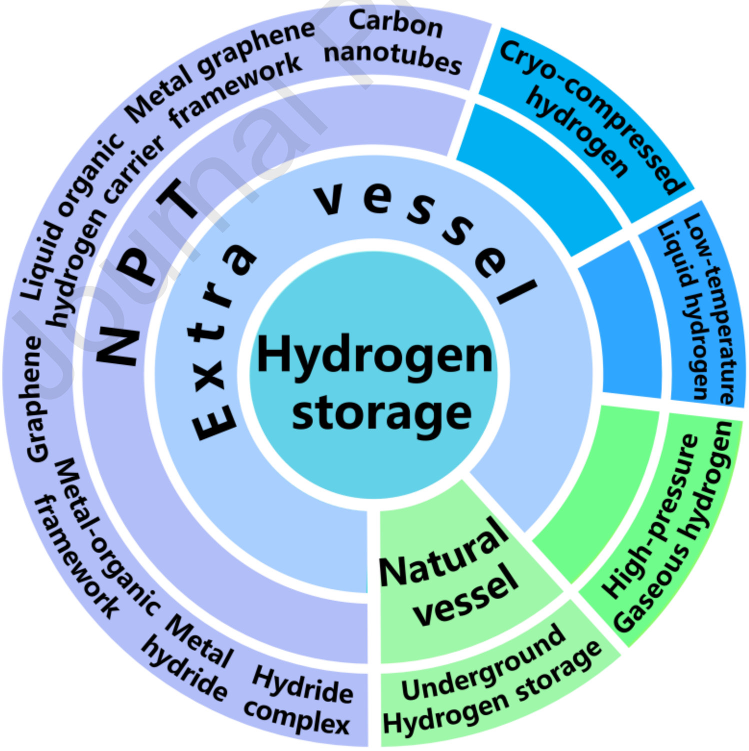


Fig. 7. Categories of hydrogen storage methods applied in HSSs

4.1 Extra vessel

Normally, hydrogen storage needs to maintain high pressure or low temperature. In addition, the process of hydrogen storage and release are only reacted under the influence of catalysts at a certain high temperature and pressure conditions in some systems. In this category, a pressure and temperature resistant artificial extra vessel is essential for hydrogen storage.

Those HSSs would be divided into four types according to the operating conditions: normal pressure and temperature (NPT), normal pressure and low temperature (NPLT), high pressure and normal temperature (HPNT), high pressure and low temperature (HPLT). There are some specific hydrogen storage technologies of each type and practical HSS applications are summarized.

4.1.1 Normal pressure and temperature

There are many technologies storing hydrogen at NPT, like metal hydride (MH), metal-organic framework (MOF), hydride complex, graphene, carbon nanotubes, metal graphene framework (MGF), and liquid organic hydrogen carrier (LOHC). As two of the most attractive materials in large-scale HSSs, MH and LOHC are analyzed by many researchers.

A MH is formed via a chemical reaction between hydrogen and metal under properly pressure and temperature. Researchers have focused on hydrogen storage materials with outstanding hydrogen absorption and desorption properties for a long time. Meanwhile, to achieve the practical applications of MH HSS, research of the system performance test and improvement method has been carried out by many groups.

Some teams have set up demonstration projects of hydrogen storage. Rizzi et al. [88] set up a system which was a combination of commercial proton exchange membrane (PEM) fuel cell (FC) and hydrogen storage tanks filled with 29 kg of $LaNi_{4.8}Al_{0.2}$. Research suggested that this system could produce 4.8 kWh of electricity at an average power of 0.76 kW for over 6 h. Results revealed the feasibility of long duration hydrogen storage and energy production preliminarily. Parra et al. [89] presented an advanced and large-scale HSS for the collection and storage of solar energy. The HSS was composed of PV panels for solar energy collection, a PEM electrolyser, a PEMFC, and a hydrogen storage tank filled with MgH_2 which could store up to 4 kg of H_2. Through various tests of efficiency for a LDES, results showed that the H_2-storage implementation was potential. However, technical barriers of unfriendly reaction conditions (1.2 MPa H_2 and 390 °C) and efficiency loss restricted further development. For large-scale HSS, a demonstration building, The Sir Samuel Griffith Centre (Fig. 8), was reported [90]. The building has a MH reservoir which can store 120 kg of H_2 (equal to 2 MWh of electricity) and generated hydrogen by more than 1000 PV panels which are installed on the roof with a peak effective output of 320 kW. Although there are probably zero sunshine, the HSS can power the building for several days based on average consumption rates through two 30-kW PEMFCs. This building is a successful application in multifunctional large-scale HSS.

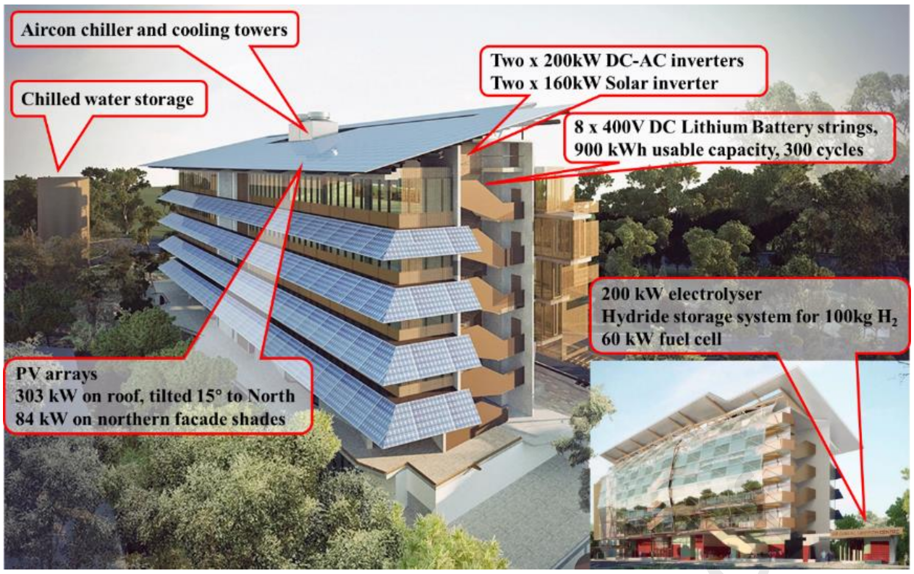


Fig. 8. Sir Samuel Griffith Building (Adapted with permission [90], Copyright 2020, HyResource).

Through these research and practical applications, choosing MH HSS as the ESS of renewable energy generation system is feasible. In conclusion, the most influenced obstacle of MH is material's intrinsic property. Improvement of MH hydrogen absorption/desorption capacity and development of new catalysts with excellent performance are the two most important objects. The design of reactors and auxiliary facilities is secondary.

In addition to MH, there is another form for hydrogen storage at ambient temperature which is LOHC. The hydrogen storage principle of LOHC is typically based on reversible hydrogenation and dehydrogenation of carbon double bounds [91]. Fig. 9 shows detailed LOHC's reaction process of hydrogenation and dehydrogenation. For hydrogenation process, unload LOHC (H_0LOHC) combine with H_2 through exothermic reaction at high temperature and pressure under the effect of catalyst. Vice versa hydrogen can be released from loaded LOHC (H_nLOHC) at a higher temperature. Until now, various LOHC systems are extensively researched by scientists and Table 4 shows the characteristics of 5 main commercialized LOHC systems.

Table 4

Characteristics of 5 main LOHC systems

System		**TOL$^{(1)}$-MCH$^{(2)}$**	**H0/H12-NEC$^{(3)}$**	**H0/H18-DBT$^{(4)}$**	**Benzene-CHE$^{(5)}$**	**NAP$^{(6)}$-Decalin**
Restricted Melting Point, K		178	341	234	279.5	353
Restricted Boiling Point, K		374	543	627	354	458
Reaction Enthalpy, kJ/mol-H_2		-68.3	-50	-65.4	-66.8	-63.9
Hydrogen Density	Volume, kg/m^3	47.3	54.5	56.4	56	64.8
	Weight wt.%	6.16	5.8	6.21	7.19	7.3
Toxicity		Low	Medium	Low	High	High
Price		Very low	High	Low	High	Very low

(1) TOL: toluene; (2) MCH: methylcyclohexane; (3)NEC: ethylcarbazole; (4) DBT: Dibenzyltoluene; (5) CHE: cyclohexane; (6) NAP: naphthalene.

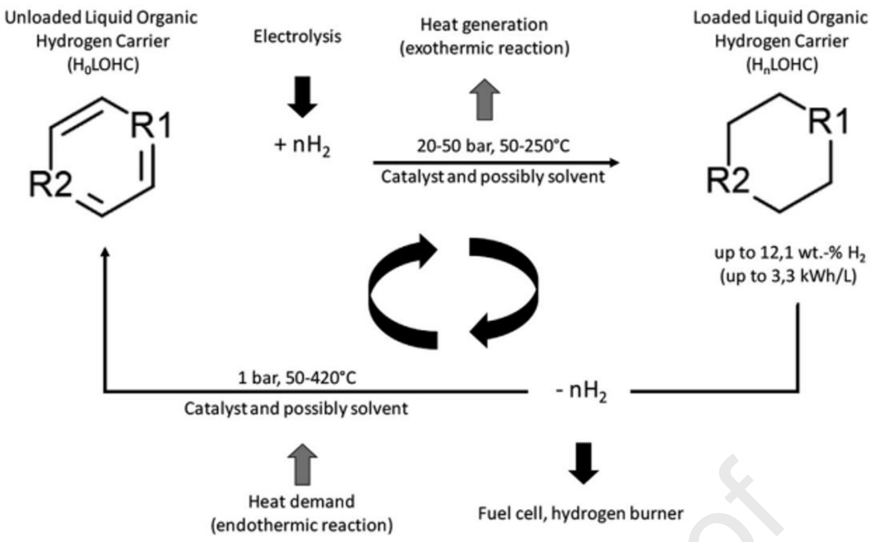


Fig. 9. The schematic of LOHC hydrogenation/dehydrogenation process (Adapted with permission [91], Copyright 2019, Elsevier).

As one of the potential hydrogen carriers, LOHC is researched in the field of hydrogen transport and storage. Many companies have set a series of projects of LOHC and formed a systematic industry chain. Chiyoda Corporation, together with Mitsubishi Corporation, Mitsui & Co. Ltd. and NYK Line, the other members of the Advanced Hydrogen Energy chain Association for technology Development (AHEAD), successfully completed the world's first global hydrogen supply chain system in 2020 [92]. This system adopted Chiyoda's SPERA Hydrogen^{TM} technology storing and transporting hydrogen by MCH which is produced from toluene and hydrogen (Fig. 10). SPERA Hydrogen, a stable liquid at ambient temperature and pressure, is as easy to handle as petroleum. So, it's feasible to utilize existing petroleum storage, transportation, and distribution infrastructures so that capital investment could be lowered [93]. Hydrogenious LOHC Technologies built a demonstration worked as electric vehicle charging station called Fraunhofer IAO Micro Smart Grid at Stuttgart [94,95] (Fig. 11). This system runs on H18-DBT transported from Erlangen to Stuttgart via road transport and has a 1000-L storage capacity (equal to 2.05 MWh). Hydrogen which is generated by PEM electrolysers provided by Siemens is the source of LOHC hydrogenation unit which developed by Hydrogenious. For hydrogen utilization, a 30-kW FC is set in the system to consume hydrogen which produced by a 100-kW dehydrogenation unit.

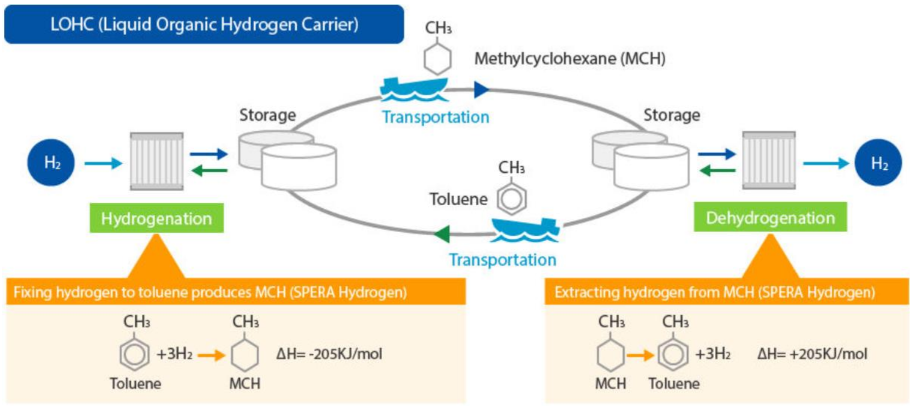


Fig. 10. SPERA Hydrogen^{TM} - Chiyoda's Hydrogen Supply Chain Business (Adpated with permission [92], Copyright 2020, Chiyoda Corp.).

Fig. 11. A LOHC demonstration project with Fraunhofer IAO Micro Smart Grid at Stuttgrat (Adapted with permission [94,95], Copyright 2020, Hydrogenious).

Similarly, the key barrier of LOHC is also material's property. Some expected characteristics are concluded shown in the Table 5, and these could be the standards to evaluate the performance of LOHC systems.

Table5

Desirable properties of ideal LOHC system

Characteristics	Melting Temperature	Boiling Point	Storage Capacity	Reaction Enthalpy	Reaction Conditions	Cycle Lifetime	Conversion & Selectivity	Safety	Technical Availability	Cost
Recommended Value	Low <30 °C	High >300 °C	High >56 kg/m^3 or >6 wt%	Low 42-54 kJ/mol-H_2	Mild, <200 °C at 1 bar	Long	High >90 %	High toxicological or eco-toxicological	Mature	Low

4.1.2 Normal pressure and low temperature

Normally, low-temperature liquid hydrogen storage is the main method at NPLT. Density of liquid hydrogen, 70.78 kg/m^3, is constant so that the mass and volume energy density is much larger than other hydrogen methods. For low-temperature liquid hydrogen storage, more important storage condition is temperature. In 0.1 MPa, hydrogen temperature should be lowered to 20.37 K for the formation of liquid hydrogen. Meanwhile, good insulation and extra temperature management are important for the avoidance of hydrogen evaporation which causes serious safety issues. So, the cost is correspondingly high.

To store and transport with low loss of liquid hydrogen, the design of vessel and performance of auxiliary equipment are important. Liquid hydrogen storage tank for stationary storage is designed to be multiple shapes, among which the cylindrical and spherical structures are used commonly. The spherical storage tank is more desirable for stationary liquid hydrogen storage, which has advantages on low evaporation loss caused by heat leakage, high mechanical strength, and uniform stress distribution. National Aeronautics and Space Administration (NASA) adopted a large spherical liquid hydrogen storage tank with the diameter of 25 m and the volume of 3800 m^3 commonly, and the daily evaporation rate of 0.03% [96]. With the development of liquid hydrogen storage technology, Kawasaki Heavy Industries and McDermott have completed the design of 10000 m^3 and 40000 m^3 spherical liquid hydrogen storage tank separately. Both tanks adopted vacuum double-layer insulation structure and Kawasaki's boil-off rate is less than 0.1% per day [97].

Other researchers adopted hollow glass microspheres (HGMs) as thermal insulation material. Xu et al. [98] designed a composite thermal insulation system including HGMs, multilayer insulation (MLI), and self-evaporating vapor cold shield (VCS). The reduction of heat leakage is 64.9% through the structure optimization. Zheng et al. [99] established a thermodynamic model to analyze the thermal insulation characteristic of the combination of multilayer HGMs and VCS. The results showed that it's effective to lower heat leakage in a number of layers obviously.

High energy and money expenditure make liquid hydrogen make liquid hydrogen be not suitable for LDES. Liquid hydrogen is commonly used as industrial raw material for high-end manufacturing, metallurgy, electronics, and aerospace.

4.1.3 High pressure and normal temperature

High-pressure gaseous hydrogen storage is the earliest and maturest technology in hydrogen storage development. Hydrogen is compressed to a certain pressure by multi-stage hydrogen compressor and stored in pressure vessels fabricated by different materials and structures. Although hydrogen is compressed to a high pressure like 80 MPa, volume and mass energy density are still far below other hydrogen storage forms restricted by its inherent properties.

Without the transformation of energy forms in process, high-pressure gaseous hydrogen storage is more suitable for some applications requiring moderate hydrogen reserves but rapid charge speed. High-pressure gaseous hydrogen has been widely used in stationary hydrogen fueling station apart from traditional industry hydrogen storage. There are four types of vessels which are designed for multi-stage hydrogen pressure shown in Table 6 [100]. The material for large-scale high-pressure gaseous hydrogen storage tank is steel mostly based on consideration of property, manufacturing difficulty, and economy. The most widely used stationary storage vessel is single layer spinning seamless pressure vessel [101]. This kind of vessel is made of tubing skelp by the spinning process and it has the advantages of low cost in manufacturing or operating and convenience in regular checking. In the world, stationary hydrogen fueling station is roughly divided into two types in pressure grade aspect: 35 MPa and 70 MPa [102]. Limited by the bottleneck of hydrogen compressor and processing technologies of high-pressure vessel, 35 MPa is in general use in China [103]. For the sake of matching between upstream supply and downstream demand, hydrogen pressure degree has better to reach 40 MPa now and 80 MPa in the future for larger amount within similar limited space.

Table 6

Properties of 4 generations hydrogen storage pressure vessel

Generation	Material	Pressure MPa	Hydrogen storage density		Price	Lifetime year
			wt.%	g/L		
I	Steel	17.5~20	1	14.28~17.23	Low	15
II	Liner: steel Outer: fiberglass	26.3~30	1.5	14.28~17.23	Medium	15
III	Liner: steel/aluminum Outer: carbon fiber reinforced composites	30~70	2.4~4.1	35~40	Highest	15~20
IV	Liner: plastic Outer: carbon fiber reinforced composites	>70	2.5~5.7	38~40	High	15~20

As the possible future applied energy, facilities responsible for transportation and LDES are essential. In brief, superior materials and exquisite craft are still needed for higher-pressure gaseous hydrogen storage in the future.

4.1.4 High pressure and low temperature

Combining the property of high-pressure gaseous hydrogen storage and low-temperature liquid hydrogen storage, a hybrid technology, cryo-compressed hydrogen (CcH_2) storage, is worked out. The hydrogen is compressed to high-pressure like 35 MPa and stored at -233 °C in special vessels. In the vessel, hydrogen may be in different states which include liquid hydrogen, cold compressed hydrogen, and hydrogen in a two-phase region. Meanwhile, this way overcomes many shortcomings of high-pressure gaseous hydrogen storage and low-temperature liquid hydrogen storage. Firstly, shown in Fig. 12 [104], the hydrogen storage density, 80 g/L, is higher than low-temperature liquid hydrogen and much higher than high-pressure gaseous hydrogen. This system has the largest storage density in terms of both volumetric and gravimetric. Secondly, due to the high pressure, the boiling point of liquid hydrogen is increased, which means the vessel has a higher heat receptivity. Compared to low-temperature H_2 tanks, the dormancy is greatly extended as the allowable pressure inside the vessel increases. CcH_2 storage technology is still being developed and tested, which means that the applications are rarely. Lawrence Livermore National Laboratory (LLNL) developed a novel CcH_2 vessel for onboard storage and designed a supply system for FC stacks shown in Fig. 13 [105,106]. Its actual operating effect is much better than the Type III 35 MPa H_2 system. BMW AG released its prototype cryo-compressed cars for testing and schematic of CcH_2 storage vessel shown in Fig. 14 [104]. The testing results showed that there was no degradation of vessel after more than 1000 cycles at 30 MPa so that it could be a potential hydrogen storage technology in the future. Like liquid hydrogen storage system, the CcH_2 storage system should also focus on the reduction of generation and maintaining cost and the decrease of hydrogen loss.

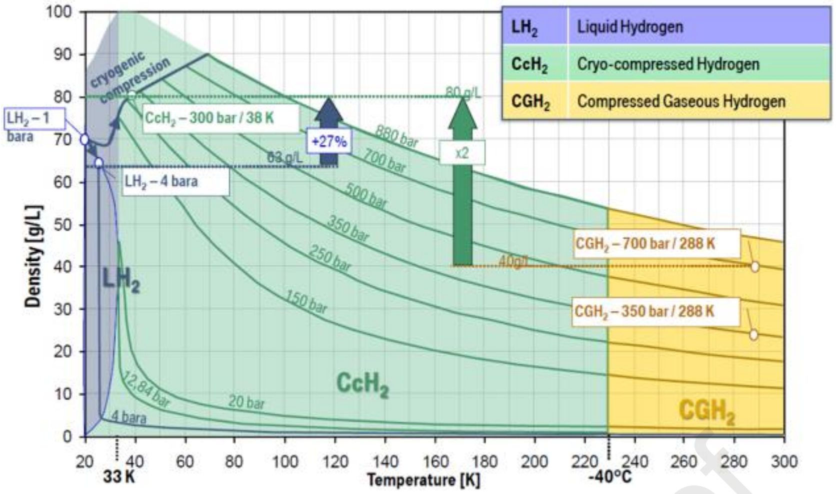


Fig. 12. Hydrogen density versus pressure and temperature from BMW (Adapted with permission [104], Copyright 2022, MDPI).

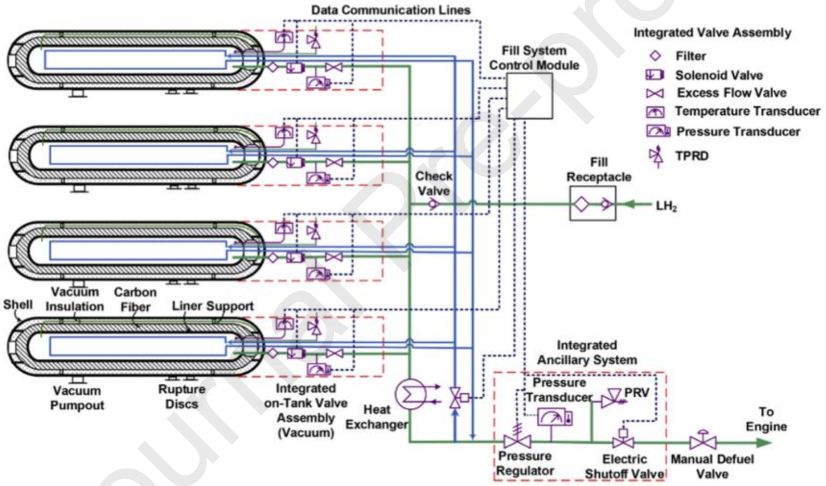


Fig. 13. Schematic of a supercritical cryo-compressed hydrogen storage system for FC electric buses (Adapted with permission [106], Copyright2018, Elsevier).

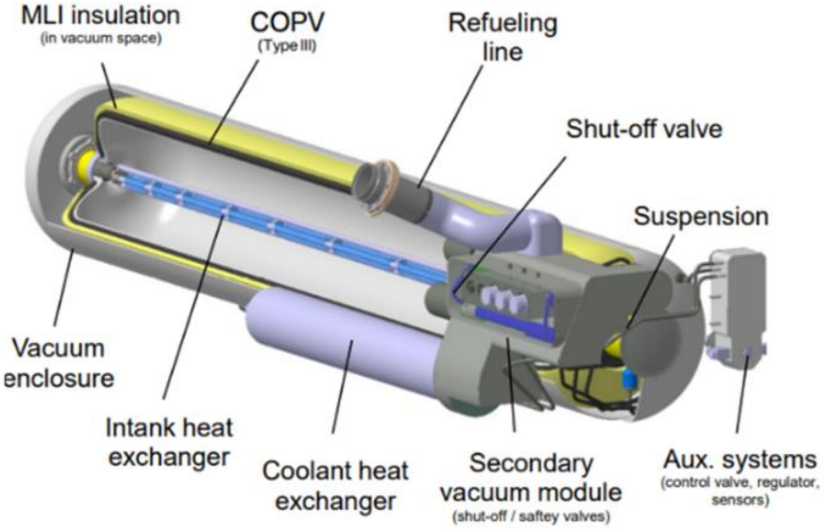


Fig. 14. Schematic of CcH$_2$ storage vessel from BMW (Adapted with permission [104], Copyright 2022, MDPI).

4.2 Natural vessel

Natural vessel, just as its name implies, is the vessel which is a natural structure and exists in environment all along. Usage of natural vessel will save space and reduce the cost of extra vessel manufacturing. There are a lot of natural vessels in the world and many of them qualify for hydrogen storage. In principle, salt caverns, salt domes, oil and gas reservoirs, and aquifers are concerned environments. In the 1970s, scholars researched the possibility of hydrogen storage underground and then proved the feasibility in technical and economic. However, underground hydrogen storage (UHS) was not paid much attention until the demand of large-scale energy storage. Due to its short development process, there are a few UHS projects in different countries. The greatest project of United Kingdom is on Teesside. The vessel is a salt cavern with a hydrogen storage capacity of 2.1×10^5 m^3 (equal to 25 GWh) whose depth is between 350~400 m. Texas launched three projects for pure hydrogen storage in salt caverns called Clemens Dome, Spindletop and Moss Bluf respectively. Their average depth is about 800 m calculated from cavern roof to ground. The total capacity of Clements Dome and Moss Bluf is 5.8×10^5 m^3, equals to 70 GWh [107]. Geographical conditions are concerned primarily which impose restrictions on widespread usage. Many researchers have focused on and studied the different rock-fluid interaction mechanisms of various rock characters so that they supported the theoretical basis for the construction of UHS in different landforms [108-110]. Other scholars tried to find more barriers and issues of actual applications through visual approaches like experiment and model simulation [111-114]. With the governments' attention, more efforts on the exploration of properly sites and the perfection of construction methods are paid. UHS would become one of the most potential large-scale ESSs.

4.3 Comparison of advanced hydrogen storage technologies

Hydrogen stored in various states is suitable for different applications with apparent characteristics. Summary and comparison of these hydrogen storage systems in advantages/disadvantages are shown in Table 7. Various key issues demanding prompt solution exist in every HSS and these systems are restricted by capacity, energy density, and cost in different degrees. Many methods have been tried to break performance restrictions for hydrogen storage at these conditions. Table 8 introduces portion contribution done by scholars for development of hydrogen storage. Although there are apparent improvements under researchers’ efforts in hydrogen storage, no one HSS could be used as a multifunctional ESS with excellent comprehensive storage performance. ESSs using hydrogen as the single energy storage medium are still not suitable for commercial applications.

Table 7

Advantages/disadvantages of HSSs

Category	Condition	Method	Advantages	Disadvantages
Extra Vessel	NPT	MH	High volume storage density; Safe; Simple operation; Pure; Low cost for storage.	Immature; Harsh reaction conditions; Low mass storage density; High cost for transformation.
		LOHC	Safe; Pure; Low cost for storage.	Immature Harsh reaction conditions;

Table 7 (*continued*)

Category	**Condition**	**Method**	**Advantages**	**Disadvantages**
				High cost for transformation.
	NPLT	Low temperature liquid	High storage density Safe; Pure.	High cost; High equipment requirements.
	HPNT	High-pressure gaseous (70MPa)	Mature; Low cost; Simple structure; Rapid rate.	Low storage density; Poor safety; Hard to enhancement.
	HPLT	CcH_2	High storage density; No evaporation loss.	Lower cost than liquid Hydrogen; Poor safety.
Natural Vessel		UHS	Huge natural space; No extra containers; Save space.	Immature Impure; Low storage density.

Table 8

Recent progress on improvement of HSSs

Category	**Usual Properties**	**Researchers**	**Directions**	**Highlights**	**Ref.**
High-pressure Gaseous Hydrogen Storage at Room Temperature	Pressure: 20~70 MPa; Density: 14.28~40 g/L; 1~5.7 wt.%.	Quantum Fuel System.	Trishield10-70 MPa hydrogen cylinder.	Aluminum; Pressure: 70 MPa; Density: 6.03 wt.%, 39.83 g/L; Life: 15 years; Light weight.	[100,115]
		Toyota.	Mirai.	Pressure: 70 MPa; Density: 5.7 wt.%; Volume: 122.4 L; Capacity: 5 kg.	[84]
			Ti-Cr-Mn + 35 MPa composite hydrogen cylinder.	Density: 3.7 wt.%, 37 g/L; Capacity loss: 94% after 1000 cycles.	[116]
		Hexagon	Tuffshell; Polyethylene plastic + carbon fiber reinforced plastic wrapping;	Pressure: 70 MPa; Light weight; Fatigue and corrosion resistance.	[117]
		Cao et al.	$(Zr_{0.85}Ti_{0.3})_{1.04}Fe_{1.8}V_{0.2}$ + 35 MPa composite hydrogen cylinder.	74% improvement of hydrogen volume storage	[118]

Table 8 (*continued*)

Category	Usual Properties	Researchers	Directions	Highlights	Ref.
				density; Density: 40 kg/m^3, 2.72 wt.%.	
		Zhevago et al.	Quartz glass capillary array.	Pressure >70 MPa; Density: >7.5wt.%; e.g. 40 g/L at 94 MPa.	[119]
		C.En	Hollow glass fiber.	Pressure:>150 MPa; No H2 loss for years; Easy extension; Fast refueling.	[120]
Low-temperature liquid hydrogen storage	Spherical steel tank; Vacuum insulation; High cost for liquefaction.	XU et al.	HGMs + MLI + self-evaporating VCS.	29.7% reduction of heat leakage.	[98]
		Zheng et al.	HGMs with more than one VCS.	68.21% reduction of heat flux into tank.	[99]
MH hydrogen storage (e.g. MgH_2)	High enthalpy: 76 kJ/mol; High entropy: 130 kJ/mol; high activation energy: 104.85 kJ/mol; release hydrogen above 573 K at 1 bar H_2.	Pei et al.	Alloying.	$LaMg_{3.93}Ni_{0.21}$ alloy; derive enthalpy and entropy.	[121]
		Lu et al.	Doping catalyst.	MgH_2 doped with TiFe and carbon tubes; Reduction of reaction temperature and activation energy.	[122]
		Lin et al.	Nanocrystallization.	Nano-Mg_2NiH_4/$CeH_{2.73}$ Reduce activation energy.	[123]
LOHC hydrogen storage		Modisha et al.	Catalyst.	H0-DBT H18-DBT Improvement of reaction rate, conversion, selectivity, and	[124]

Table 8 (*continued*)

Category	Usual Properties	Researchers	Directions	Highlights	Ref.
				deactivation.	[124]
		Yang et al.		MCH; Improvement of conversion, selectivity, and turnover frequency.	[125]
CcH_2 storage	Density: 80 g/L at 33 MPa, 38 K; High heat receptivity; Thick wall.	Zhevago et al.	Quartz glass capillary array.	90 g/L, 26 wt.% at 77 K, 220 MPa.	[119]
Underground hydrogen storage	Large capacity; High pressure; Geography restriction.	Pan et al.	Influential multi-scale parameters.	Review of key criteria.	[126]
		Bai and Tahmasebi	3D model.	Geochemical coupled with hydro-mechanical analysis.	[127]

5 Battery & Hydrogen hybrid energy storage system

Increasing serious energy crisis requires more large-scale energy storage systems for renewable energy. But at present stage, energy storage projects are in the preliminary stage. More systems are served as off-grid power station for a small area like remote mountain village to replace traditional fossil fuel diesel generator, and others are demonstration projects for performance research.

Meanwhile, these ESSs usually adopt single energy storage medium. Their performance and cost are totally restricted by technical maturity. However, the huge technical breakthrough is hard to be achieved in a short time. So, it seems like that the speed of technical development is relatively slow compared with the increasing rate of energy storage needs. Contradiction of urgent demand and slow development is a still existed problems.

HESS is a possible solution. HESS is composed by two or more ESSs to improve the system capacity and implement specific functions. Outstanding short duration, rapid charge/discharge energy storage performance of BESS make it attract much attention in several years. Hydrogen technology is always the research hot pot and HSS is thought to be the potential long duration large-scale ESS for renewable energy to achieve the transformation of zero-emission energy structure. Due to technical obstacles, neither BESS nor HSS can satisfy the requirement of multifunctional large-scale ESS with rapid energy storage rate and enough energy storage capacity simultaneously.

So, the combination of BESS and HSS is what we concern.

In the B&H HESS, BESS is the part of short duration ESS because of its excellent performance in quick response time, and flexible power. The power and energy capacity of battery are always connected so that large-scale BESS would cause the waste of power capacity and lead to a huge facility which covers vast area. Similarly, for HSS, hydrogen storage rate and amount are decoupled by the change of storage condition like temperature and pressure. Green hydrogen which is stored in various forms usually produced by electrolysis of water. However, the energy consumption of hydrogen production and transformation is pretty high which is about half of the produced hydrogen energy. That means HSS is more suitable for long duration large-scale rather than short duration frequent energy storage. So, B&H HESS is an appropriate transition system from mid-scale BESS to large-scale HSS under technical restrictions.

5.1 Application-oriented B&H HESS

BESS possesses proven technique and has been constructed in vast area for several years. However, the key technology of HSS is grasped by a few countries only. Moreover, the HSS could not work systematically in both economic and technological terms. In addition, capital investment of HSS is much higher than BESS. So, the payback period is longer due to lower energy storage efficiency. Hydrogen safety issues should be controlled within an acceptable range and solved gradually soon, and hydrogen promotion is needed to be pushed ahead by society to make hydrogen be accepted by people. These are some of the reasons why long duration large-scale HSS is restricted by the degree of development. The smart control system and efficient control strategy are necessary and important for B&H HESS. Large-scale HESS involves many assembly units like energy collector, SDES system, energy transformer, LDES system and so on. To achieve the interwork of these units, intelligence control system is essential. More complicated HESS needs more accurate and stable control system which also means more complex. That's another reason why HESS is rare and hard to design. But intelligence algorithm is powerful now and artificial intelligence (AI) is a hotpot in many fields including electricity distribution and process control. So, developing HESS is a good choice to realize flexible energy storage.

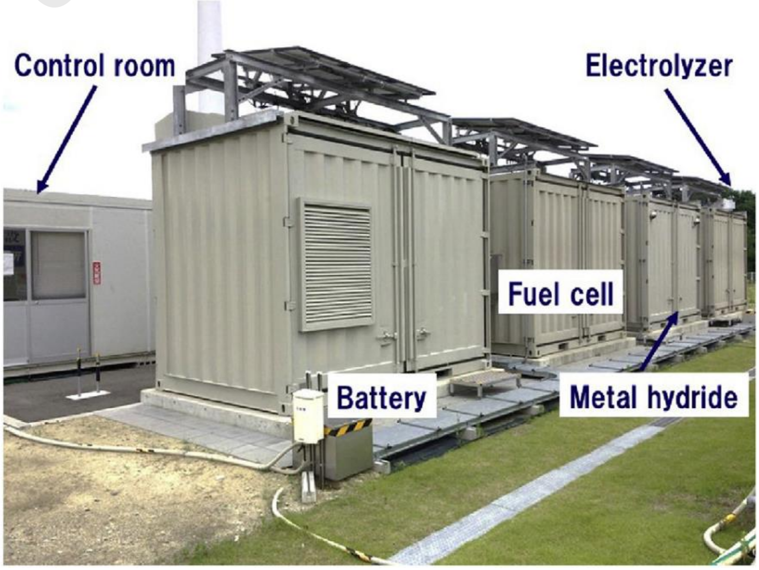


Fig. 15. An integrated solar energy utilization system combined by PV panels, BESS, and HSS (Adapted with permission [128], Copyright 2019, Elsevier).

Many researchers have studied on techno-economic feasibility and designed practical demonstration projects of HESS. Endo et al. [128] constructed a bench-scale HESS (Fig 15) based on 20-kW PV panels, Li-ion battery (20 kW/20 kWh), a PEM electrolyser producing hydrogen at a rate of 5 Nm^3/h, 3.5-kW PEMFCs, and MH tanks storing 80 Nm^3 hydrogen (equal to 520 kg AB-type TiFe-based alloy). A smart building energy management system (BEMS) was adopted to control this HESS. The direct-use PV power has the highest priority and excess PV power is stored in batteries for small-scale SDES firstly. Power-to-hydrogen was selected for large-scale LDES to maximally reduce grid power consumption. As mentioned earlier, the Sir Samuel Griffith Centre is also a HESS demonstration building. Solar energy is collected to produce electricity by more than 1,000 PV panels for the energy consumption of whole building, and extra solar energy is stored in over 1,000 Li-ion batteries. When batteries are fully charged, excess electricity powers a 160-kW alkaline electrolyser which can produce hydrogen at a rate of 2.7 kg/h. Besides, the hydrogen is stored in a stable form (MH) for LDES and could power the building for several days without any sunshine [90]. This energy control strategy is similar with Naruki's project, and results showed people unanimously agree the rationality and effects of HESS and its strategy. Other researchers mainly focus on the optimization of HESS and efficient control strategy. Table 9 concludes some recent studies of optimization in efficiency, cost, and reliability through simulations or experiments. Different research groups have made great efforts to improve performance from various aspects. Some projects have already been validated for practical application. But it's hard to be promoted extensively in consideration of economy. So, development of B&H HESS is still in the early stage and there are many barriers that need to be overcome. To promote standardization development of HESS and achievement of energy storage transition, a series goals and demands of performance should be set in different fields.

Table 9

Recent progress on performance improvement of HESS

Researchers	Project	Methods	Highlights	Ref.
Kharel and Shabani	Design of HESS for renewable energy.	Techno-economical feasibility analysis; Model design using HOMER.	Reduction of battery pack size; Low cost: $0.626 per kWh; Excess hydrogen generate; Extra electricity: $0.494 per kWh;	[129]
Zhang et al.	Optimization of HESS.	Hybrid Heuristic methods;	More reliable and cost effective.	[130]
Zhang et al.	Optimization of structure and control strategy.	Multi-energy experiments.	Design an AC/DC bus structure; Reduce system power loss; Propose a control method; Based on expert strategy.	[131]
Scamman et al.	Solution for off-grid power.	Hybrid system model.	Reduction of 55%-79% renewable energy waste; Reduction of 54%-77% battery capacity;	[132]
Vosen and Keller	Optimization of performance and cost for HESS.	Time-dependent model; Two hybrid energy-storage algorithms.	Low cost: 48% of the cost of a hydrogen system. 9% of the cost of a battery system;	[133]

Table 9 (*continued*)

Researchers	**Project**	**Methods**	**Highlights**	**Ref.**
Zhu et al.	Optimal Allocation of capacity of island multi-energy system.	island multi-system system model; Capacity optimization model.	Low total net present value cost; and averaged energy cost; Reduce energy waste; Extend battery service life.	[134]

5.2 Development directions

To promote standardization development of B&H HESS and achievement of energy storage transition, a series goals of performance should be set in different fields. The followings are some of the demands outlined and summarized in this article:

5.2.1 Hundreds of MW-scale HESS

Most ESSs are hundreds of kW scale for off-grid energy usage. A few MW-scale ESSs are constructed for renewable energy storage. Facing the growing serious issue of energy depletion, construction of large-scale ESS is essential. Recently, several hundreds of MW-scale ESSs were reported [30,42,107]. So, the power and energy capacity of B&H HESS should be hundreds of MW-scale even larger for growing requirements of energy storage.

In the B&H HESS, the responsibility of large-scale energy storage is mainly taken charge by HSS. The capacity of power density and energy density is decoupled for HSS, which means realization of large-scale HSS is easy to come true through reasonable connection of numbers of systems. However, one of the most serious technical barriers in the application of large-scale HSS is the large floor space and capital investment due to low volume storage density. It's not economical in energy production, storage, or utilization. So, improvement of storage density is the primary consideration.

Researchers have come up with many approaches in accordance with different HSSs. For instance, the energy density of high-pressure gaseous hydrogen would be increasing with the rising of the storage pressure theoretically. Higher-pressure hydrogen could be generated by advanced hydrogen compressor. Accordingly, the advances materials and optimized design of storage vessels' structure are required to withstand higher pressure. Both aspects have been researched. Gkanas et al. [135,136] studied the comparison of different candidate materials and modeled the operation of a complete compression cycle for multi-stage MH hydrogen compression by numerical simulations. They achieved a maximum compression ratio of 22:1 at a temperature range between 20 °C and 130 °C, and the delivery pressure of final dehydrogenation process reached 32 MPa. Zhou et al. [137] designed a liquid piston hydrogen compressor. This compressor could pressurize hydrogen to 27 MPa stably and continuously. Meanwhile, Badida and Hurajt [138] designed a composite gas hydrogen storage vessel for very high pressure of approximately 100 MPa. They adopted high-strength aluminum alloy (AW-7075) to make liner, and epoxy-carbon fibers were taken as shell to enhance its stiffness and strength. The vessel could store hydrogen of 6.6 kg in a volume 138 L. The corresponding hydrogen volume density is about 47.82 kg/m^3, which is higher than 39.26 kg/m^3 of 70 MPa storage.

In addition, improving the performance of hydrogen storage materials is an effective way for increasing storage density regarding some hydrogen storage methods like MH hydrogen storage. In this field, scholars modified the existing materials, and discovered new materials for high volume hydrogen density [91,139,140].

Promoting the development of UHS is another direction to scale up the amount of hydrogen storage. Utilizing abandoned large natural space for hydrogen storage is an economic and effective method to realize hundreds of MW-scale hydrogen storage without the consideration of density barrier. China's first hydrogen station using UHS has been constructed and put into operation in Chongqing [141]. It could supply more than 1000 kg hydrogen per day.

Building hundreds of MW-scale HESS is an inevitable development tendency. Renewable energy generation station with large-scale ESS is expected to replace traditional power stations completely in the future and contributes to sustainable development.

5.2.2 **High energy storage efficiency**

Energy storage efficiency is a crucial index to judge the practical application value of ESSs. For SDES, BESS's energy storage efficiency has reached 85% without the consideration of self-discharge loss. The main factor causing a large loss of energy is HSS. Extra energy is consumed through the process of energy storage. Hydrogen production by electrolysis is the first energy loss progress. Current development level of electrolytic hydrogen production technology could reach the energy efficiency of 62%~87% [142]. In addition, hydrogen compression, heating of reaction, maintenance of storage environment, and transport consume partial energy in the process of energy storage. In conjunction with other processes, the overall energy storage efficiency is only 40%~50%. Technical barriers of low energy storage efficiency are what researchers have been trying to figure out.

To decrease energy consumption and increase utilization, lots of attempts have been carried out for specific HSSs. For hydrogen storage materials, modification is a basic and effective way to improve hydrogen storage efficiency. Theoretically, materials with better performance could be manufactured through various methods like chemical combination, doping, milling, nano-crystallization, and so on [143-147]. The research and development of more effective catalysts is also a general manner [125,148-150]. Generally, these methods focus on materials' characteristics to lower activation energy and reaction enthalpy so that energy consumption through hydrogen transformation process will be reduced.

Meanwhile, innovative design of facilities and development of new technologies are reasonable solutions for high efficiency. Working process of B&H HESS is divided into three parts which are energy transformation, energy storage, and energy transportation. Focusing on different parts, the researchers have put forward a variety of improvement methods.

For energy transformation part, new electrolytic technologies with high production efficiency and hydrogen purity have been developed step by step and these would be commercialized in the future [151,152]. The analysis and comparison of mature technologies have been studied to find some optimization methods and realize large-scale use in hydrogen production and storage gradually [153-157]. Accordingly, performance of hydrogen utilization technologies is developed, too.

For energy storage part, B&H HESS stores electric energy and hydrogen simultaneously. So, the improvement of equipment is divided into battery part and hydrogen storage vessel part. Main energy loss occurs in the hydrogen storing and releasing process. Optimization of reactor structure could save portion energy in storage process. Wu's team has focused on the thermal energy management of metal hydride reactor for a long time, and they have presented several reactor structures based on bionic thoughts and proven the feasibility of heat self-equilibrium reactor coupled with phase change materials [158-161]. Similarly, some scholars presented new type reactors for LOHC systems and worked on the key parameters influencing hydrogenation/dehydrogenation reaction energy consumption [162-165].

Due to the complexity of B&H HESS, connection methods and controlled strategies are important for the stability and efficiency of actual energy storage operation. Normally, series and parallel are two connection modes to achieve various control functions. Series mode requires the match of power between upstream and downstream, and parallel mode is usually to meet the demand for energy capacity. Therefore, the distribution of power and capacity for BESSs and HSSs is one of the top concerns. Meanwhile, adoption of complex optimal controlled strategy could reduce extra equipment requirements and take full advantage of existing utility. Some researchers have studied HESS operational performance in simulation and experiment. Kharel and Shabani [127] have built large-scale BESS, HSS, and HESS optimization simulation models respectively. They studied the three ESSs' performance for the electricity generation based on the data of South Australia using a commercial software, HOMER (ie. the Hybrid Optimization Model for Electric Renewables). Simulation results showed that HESS has the lowest unit cost which proved that HESS has great potential in energy storage. Other researchers, like Scamman et al. [132], Dawood et al. [166], Sharma et al. [167], Barzola-Monteses and Espinoza-Andaluz [168], also designed HESS model and made optimum simulation for various application scenarios through HOMER. Huawei Digital Power provided intelligent string type inverters for 1.6 GW PV park project in Qinghai. This system controls each module accurately through intelligent and digital methods so that work efficiency and yield have been increased by 50% and 2%, respectively [169].

The improvement in efficiency could also be acquired in energy transportation part. For energy transportation part, fluctuant energy input, properly distribution, and moderate conversion require control system for precise energy transportation. Energy transportation is divided into electric power transmission and hydrogen transportation. China has built ultra-high voltage grid supported by ultra-high voltage alternating current and direct current (UHVAC/DC) transmission technology which transmits about 1000 kV and 800 kV level electricity. With the help of advanced technology, electricity can be transmitted to any further place with less unit cost and line loss [170].

The technology of hydrogen transportation is lacking. Hydrogen is usually stored in the form of high-pressure gas or liquid and transported by tanker with small capacity and low efficiency. There are few hydrogen pipelines in the world because of technical barriers and expensive costs. The length of the longest hydrogen pipeline is about 400 km and the whole length of hydrogen transmission network system is about 16000 km in the world which is much shorter than natural gas pipeline network [171]. So, many scholars consider the utilization of the existing natural gas pipelines for the transportation of hydrogen and several relative research and experiments have been done [172]. United Kingdom initiated HyDeploy project in 2017 and has finished the first stage experiment and came into service in 2020, which confirms the feasibility of transporting mixed gas (20% hydrogen and 80% natural gas) through the existing pipelines [173]. Wei [174] analyzed the leakage of mixed gas in pipelines and pointed out that the mass flow rate of hydrogen leakage would increase with the hydrogen ration. The design and modification of pipelines are necessary. Wang et al. [175] put forward some suggestions in the design of hydrogen pipelines, which helps to reduce transportation loss through a technical comparison.

Extreme environment conditions like low temperature may cause the performance reduction in power and capacity for BESS. Maintaining BESS temperature for normal work status is important. Therefore, waste heat produced by cell, electrolyser, fuel cell, even hydrogen absorption/desorption reaction of metal hydride deserves to be collected through heat transferring medium for heating BESS itself. Meanwhile, the energy efficiency is improved with utilization of waste heat and without other cost.

Through the improvement of efficiency, the ultimate realization of reducing hydrogen costs would come true. With the innovation of hydrogen technologies, the price of hydrogen will be lower than the price of current electricity in some day.

5.2.3 Regional customization

Before the construction of renewable energy generation and storage systems, assessment and performance analysis should be done first. The main purpose of B&H HESS is storing extra or unused renewable energy to reduce or even replace the utilization of traditional fossil energy. Fossil-fuel power station will eventually be replaced by the renewable energy power station which is equipped with high-efficient and enough capacity ESS. To ensure production and living organized, transformation of energy structure is required to be smooth. So, the principle of power station transition is important.

Normally, production capacity and service time are the two main factors for the judgement of demolishment. Efficiency and pollution are the two main factors during electricity production process. Without the advantage of scale, investment in low-capacity power stations is small. That means these stations lag in the technique and equipment, and the production process is characterized by low efficiency and high pollution. Meanwhile, there will be a small influence during energy transition process because of these stations' narrow scope of service. In addition, based on the harmonious consideration of profitability and sustainability, stations serving enough time have better to be transformed from fossil fuel power stations to clean energy power stations as soon as possible. As the service time increases, equipment is falling behind gradually and must be obsoleted. On the premise of guaranteed returns, close these stations gradually and promote the construction of clean-energy power stations. So, stations with low capacity and long service time would be eliminated first.

Next, the concerns are capacity design and site selection for B&H HESS. Usually, the actual energy storage demand can be acquired from the comparison between renewable energy generation and normal consumption. However, inhomogeneity of renewable energy distribution in a country with vast territory need to be considered during design process.

Usually, there is a minimum energy demand for each region. To ensure the normal operation in some unexpected situations, practical capacity is always slightly greater than demand. Oversize design consumes extra resources for standby facilities. Cost of idle equipment is larger than its income from production. So, the global optimization target is that acquiring enough energy production in a properly scale of capacity. Make sure that every facility is in operation actively for about a certain high ratio of working time in one storage period. Take it as the design criterion to optimize whole system.

Generally, there is a contradiction between energy consumption and generation. An area that consumes a large amount of energy doesn't have enough land for the construction of renewable energy generating installations and ESSs, and vice versa. For example, some first-tier cities like Shanghai owning small area of land consume far more electricity than its own generation. So, the building site of ESS with huge renewable energy generating installations is usually chosen in the remote regions like China's western region. Generated and stored energy could be transmitted to the east of China in the form of electricity through the power-grid of West-East power transmission project. The feasibility of this thought has been proved and some demonstration projects have been constructed. Large-scale wind and PV power project which consisted of 5.6 GW for local consumption and 5.3 GW for outward transportation was constructed in Qinghai [176]. Equipment of large-scale HESS could enlarge production capacity and supply for more districts. Hydrogen would be transported to other places after the development of hydrogen economy in the future through existing pipelines like pipelines built for West-East natural gas transmission project. In the east, reservoir, cultivated land, and building proof are utilized for renewable energy collection widely and regional centralized ESSs built in these places are needed gradually with larger production and distribution density.

Meanwhile, exploiting the UHS potentiality of natural structures and realizing the reuse of abandoned pits are quite effective approaches in large-scale storage. Although it is studied latterly in China, more and more theoretical analysis, analogue simulations, field tests and application prospect have been done for the development of large-scale HSS by various teams [177-181].

Classification of ESS is conducive to local conditions. First is the self-sufficient type. For this type, energy capacity is designed based on local demands and the selection is nearly. ESSs satisfy the energy demand of daily lives and only a small portion of energy may be sold for industrial production. Another is the supply type. The energy generated by and stored in this kind of system is not only consumed by local demands but also supplied to other places primarily. The energy capacity of this kind of ESS may be extended to a certain large scale after considering the market demands, transportation cost, and so on. Usually, this kind of ESS is built in remote areas for the large energy demands of other places. Construction of supply-type ESS boosts local economic development and ensures the energy consumption in other places.

5.2.4 High safety

One of the most concerned problems for people is safety issues. It is the critical factor which determines whether multifunctional large-scale B&H HESS could be implemented for practical application or not. There have been many fire and explosion accidents of BESS in the world due to battery defects, internal short, thermal runaway, and faulty integrated management system [182]. Hydrogen explosion accidents were happened frequently in the last few years with the rapid development of hydrogen economy. Application of B&H HESS needs effective prevention and control technology. Deng [183] summarized relative technologies of Li-ion BESS in several aspects and national mandatory standard for the safety of Li-ion battery for energy storage was started to write in 2022 [184]. High risk is one of the barriers for hydrogen application. For example, gaseous hydrogen is very easy to leak and diffuse which may cause burn and explosion even without the fire. Selection of materials used for hydrogen storage is also restricted because of its strong degradation. Zheng et al. [185] have summarized extensive basic research about hydrogen safety, and Zhang et al. [186] introduced safety status of infrastructure and analyzed the faced challenges. Some cases are hard to be explained reasonably. Simple improvement of precautionary measure is not a permanent solution, and targeted reinforcement for specific risk reasons is the effective method. The mechanism of hydrogen still requires to be explored and validated through multiple ways. Accordingly, applicable special equipment for hydrogen should be developed continuously. Apart from focusing on directly related equipment like reactor, container, and pipelines, contributing to the development of auxiliary equipment is also important. Precise control system, reliable early warning system, and effective accident handling system ensure the safety of B&H HESS.

The risk of safety issues will be restricted to an acceptable degree with technical progress. So, hydrogen will be accepted by people and B&H HESS will be constructed widely.

5.2.5 **Low carbon emission**

As mentioned earlier, efficiency of HESS is low restricted by imperfect technology. Fossil energy is still needed as assisted energy in the whole industrial chain. Although more renewable energy is acquired with less fossil energy consumption, there is still a quite number of carbon emission through process. Many researchers have done studies on the combination of different energy systems for more energy utilization which means less carbon production. For the B&H HESS, some possible combinations could be designed. For example, waste heat produced by photoelectric cell, energy storage battery, compressor, and fuel cell could help hydrogen production by preheating water and hydrogen release by heating medium. Combination of hydrogen storage in the form of MH and high-pressure gas is also a potential way to reduce extra energy consumption. The pressure degree of hydrogen in the MH's absorption and desorption process is quite different, and practical hydrogen pressure is related to reaction temperature. According to this property of MH, hydrogen at any pressure is easy to be produced. So, the workload of hydrogen compressor will be reduced and the carbon emissions from pressurization will be reduced, too. Wang et al. [187] designed a double-stage hydride compressor and the experimental results showed that it needs only hot water to produce high-pressure hydrogen. Many institutes and companies have been involved in the development of MH hydrogen compressors, and this technology has been used in many applications like the EU-funded ATLAS-H2, ATLAS-MHC, COSMHYC and COSMHYC XL [188].

Reduce extra energy requirement in B&H HESS through more approaches and realize zero carbon emission in the future.

5.3 Section summary

B&H HESS as the candidate of future ESS for renewable energy has been proven to be feasible through lots of analyses, simulations, and tests. Meanwhile, with the support of policies, immature hydrogen technology will be developed rapidly along the trend of energy structure transformation. BESS built and operated already can be utilized as the foundation of HESS, and HSS parts which are responsible for large-scale LDES is integrated into them forming B&H HESS. In the future, each performance barrier above mentioned will be overcome, and the application of B&H HESS will be widely. As the transition between BESS and HSS, B&H HESS is an excellent solution for the complicated energy storage tasks of large storage capacity in limited space, frequent storage with rapid response, and continuous storage without much loss. Ultimately, B&H HESS will pave the way for the prosperity of HSS and commit to the transformation to the zero-carbon energy structure.

6 Prospects

Reduction of greenhouse gas emission and rapid growth of renewable energy put forward higher level requirements for ESS. Development of technologies, construction of ESSs, and operation of energy market are strongly supported in policy worldwide [189,190]. In United Kingdom, feasibility of BESS is proved through several 'proof of concept' projects, and the benefit of BESS far outweighs the harm [191]. The Smart Network Storage project is one of the policies related to ESS. With the support of this policy, a test site combined by renewable energy and Li-ion manganese battery for power grid regulation has been put into operation [192]. 'A Clean Planet for all' published by European Commission in 2018 pointed out that deployment of energy storage system is an essential action for the transition of power system towards a distributed system relying on renewable energies [193]. In this publication, the potential of renewable hydrogen as an energy storage technology was highlighted [194]. In Germany, the electricity market was fully gradual regulatory reform [195]. The Energy Industry Act (EnWG) provided explicit benefits to energy storage technologies. Some eligible new storage facilities are exempted from grid access charges for 20 years. In addition, power-to-gas installations which produce hydrogen or biogas are exempted from gas injection fees [195,196]. In United States, each state is responsible for its own procurement of energy storage facilities. California became the first state to mandate utilities to procure 1.3 GW of storage capacity by 2020 [197]. One of the complements, Senate Bill (SB) 1369, added green electrolytic hydrogen as one of the eligible technologies [198]. In China, government responds to the call of carbon peaking and carbon neutrality goals actively. National Development and Reform Commission, National Energy Administration have enacted several guidance and implementation plans about energy storage. In recent years, China pays more attention to the development of renewable energy and energy storage. Guidance on 'integration of wind, solar, water, fire and storage' and 'integration of source, grid, load and storage' [199], guidance on accelerating the development of new energy storage [200], and implementation plan for the development of new energy storage in the 14th five-year plan [201] are enacted successively. With the strong support of governments around the world, the development of ESS is an inevitable tendency.

In the future, to fit more constructions of renewable energy production, the development of B&H HESS should be toward to several directions:

- More large-scale level: hundreds of MW-scale B&H HESS is favored for many renewable energy production projects recently.
- High energy storage conversion: weaken strict storage conditions and reduce storage energy consumption.
- Zero carbon emission in storage process: no additional energy is required as assistant causing extra carbon emission in energy storage process.
- Low accident probability and low safety risk: improve device safety performance, standardize the working behavior of operator, and configure the on-set safety precautions.
- Achieving a breakthrough in HSS: focus on improving volume density of hydrogen storage, hydrogen storage rate, and energy conversion rate, and realize the transition from BESS to HESS and eventually to HSS.
- Adjusting measures to local conditions: design and construct B&H HESS based on the data of energy generation and consumption within a certain region.

7 Conclusions

The application of large-scale ESS faces technical challenges such as extended discharge-charge cycle lifetime, high energy consumption, low volume storage density, costly capital investment, and safety concerns. This article reviews advanced research findings and commercial applications of BESS, HSS, and their combination in HESS. The following key points are summarized:

- Single-technology ESSs struggle to meet the rapidly increasing demand for energy storage. HESS, acting as a transitional and effective method, proves to be a suitable choice for complex energy storage tasks.
- The combination of BESS and HSS, known as B&H HESS, emerges as a potential multifunctional large-scale ESS. BESS, with high power and rapid response, handles short and frequent storage, while HSS, offering large capacity and stability, manages long-duration large-scale storage.
- Various battery-supported BESSs have found wide applications. However, major defects such as self-discharge rate (>1%) and capacity loss (~20%) limit their performance in large-scale LDES. Most BESSs remain small-scale for peak-load regulation, facing challenges of limited space, low volume energy density, and high costs (e.g. Li-ion battery, 168 $/kWh).
- HSSs, characterized by stable energy forms and long cycle lifetimes, are divided into diverse types based on storage conditions. Despite their advantages for LDES, hydrogen storage faces technical barriers, including low efficiency (~50%), harsh conditions, slow response, and high costs. Comprehensive development of HSS remains a long-term goal.
- BESS and HSS complement each other, forming the B&H HESS. Some projects have adopted the combination of renewable energy and B&H HESS. Serving as a transition between mature BESS and developing HSS, B&H HESS addresses rapid response, SDES, LDES, and large-scale storage simultaneously within limited space. Its overall cost is significantly lower (9% and 52%) than equivalent BESS and HSS. With enhanced comprehensive performance, B&H HESS functions in frequent regulation, peak load regulation, stand-by power, and renewable energy time shift. This contributes to the gradual increase in renewable energy capacity, replacing traditional fossil energy.

In conclusion, multifunctional large-scale stationary B&H HESS emerges as an effective solution to meet the growing demand for renewable energy storage. It serves as a reasonable transitional system during the undeveloped stage of hydrogen technology, ultimately contributing to the establishment of a low-carbon energy system.

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Declaration of interests

☒ The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

☐The authors declare the following financial interests/personal relationships which may be considered as potential competing interests: