



REVIEW

A Review of Seasonal Hydrogen Storage Multi-Energy Systems Based on Temporal and Spatial Characteristics

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Received: 08 January 2021 Accepted: 16 March 2021

ABSTRACT

The temporal and spatial characteristics of seasonal hydrogen storage will play a very important role in the coupling of multi-energy systems. This essay believes that there are several key issues worth noting in the seasonal hydrogen storage coupled multi-energy system, namely, hydrogen storage methods, coupling models, and benefit evaluation. Through research, this article innovatively divides seasonal hydrogen storage into two types: space transfer hydrogen storage technology and time transfer physical property conversion hydrogen storage technology. Then sort out the two most typical seasonal hydrogen storage multi-energy system application scenarios and their hydrogen storage unit models. Finally, it is shown that hydrogen storage methods should be selected according to different periods of time and regions, and the benefits should be evaluated before they can be used in practice. This review study is applicable to the process of coupling seasonal hydrogen storage in multi-energy systems. Hydrogen energy is used as an intermediate energy link for the selection, evaluation and modeling of the optimal selection and rational utilization.

KEYWORDS

Temporal and spatial characteristics; multi-energy system; hydrogen storage technology; modeling

1 Introduction

The energy transition problem based on renewable energy and the realization of large-scale decarbonization and temperature control goals mentioned in the Paris Agreement are the two major challenges facing China's energy industry. Therefore, hydrogen energy storage, which has the advantages of clean, flexible, sustainable, and diverse storage methods, has emerged. People have made technological breakthroughs in hydrogen production, storage, transportation and other links, so that hydrogen energy has become an important form of supplementary energy. As an energy carrier or raw material, hydrogen energy not only has significant advantages in dealing with the problem of mismatch between wind/photovoltaic power generation and electricity load, but also has a wide range of uses, either directly entering the hydrogen industry chain, or entering hydrogen refueling stations through transportation to supply fuel cell vehicles, or converted into electricity and heat for users [1]. This article classifies hydrogen storage technologies based on temporal and spatial characteristics to complete the overview of seasonal hydrogen storage multi-energy systems. At present, there have been a large number of research results on hydrogen energy at home and abroad, but the hydrogen storage technology with temporal and



spatial characteristics has not been rationally sorted and classified. Through research in this article, it is found that the choice of hydrogen storage method should consider the principle of adapting measures to time and local conditions, that is, involving space and time dimensions. At the same time, in the research process, the hydrogen storage technology is coupled to other multi-energy systems in the form of modeling, in order to better realize the use of hydrogen as an intermediate storage unit for in-depth research. Finally, through benefits evaluation, the multi-energy system coupled with seasonal hydrogen storage can play an important role in the practice of production and life.

2 Multi-Energy System and Seasonal Hydrogen Storage

2.1 Concept of Seasonal Hydrogen Storage and Multi-Energy Systems

On the one hand, the energy storage methods involved in the current power system mainly solve short-term-scale problems, such as intra-day peak regulation, frequency modulation, and grade climbing, but it is difficult to overcome long-term power fluctuations and maximize the use of renewable energy. On the other hand, as the installed capacity of renewable energy increases, the imbalance between load and renewable energy output has become increasingly prominent. Fig. 1 shows the monthly curve of the annual electricity consumption and wind power output of a certain grid. It can be seen that the power load demand is at the peak in summer, while the peak wind power output is in the spring and winter. In order to achieve long-term energy translation, smooth monthly and even seasonal power fluctuations, and participate in the quarterly or even cross-yearly adjustment process, long-term, large-capacity energy storage technology is required [2]. This paper refers to this form of long-term hydrogen storage as seasonal hydrogen storage. Seasonal hydrogen storage can achieve long-term and large-scale energy transfer, providing new ideas for solving energy challenges.

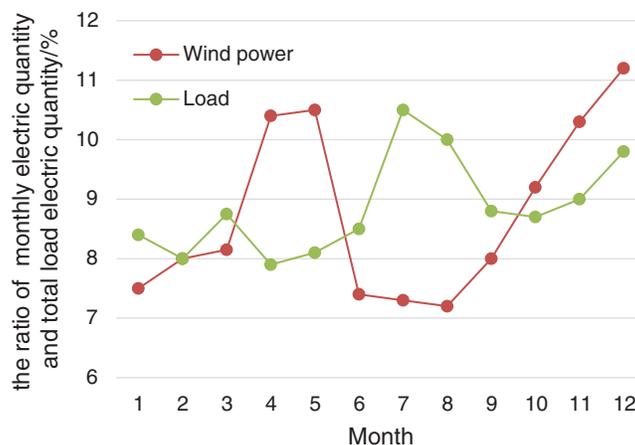


Figure 1: The Ratio curve of monthly electric quantity and total load electric quantity

Multi-energy System refers to a new energy system view formed by coupling multiple energy systems such as cold, heat, electricity, and gas in the links of energy production, transmission, and use. From the perspective of operational planning, the interaction between energy departments is currently becoming more frequent. For example, in most cases, electricity, cooling/heating, and natural gas networks interact through various distributed technologies. Similarly, the interaction between the electricity, fuel chain, and transportation sectors has also been carried out through the transportation of electric vehicles, biofuels, and hydrogen. Based on these, the key to the study of a multi-energy system for cross-season hydrogen storage is to start with hydrogen storage methods, coupling models, and benefit evaluation. Combine seasonal hydrogen storage with multi-energy systems to realize a regional-scale energy management

system, and create new value for improving the coupling and reliability of the energy system, reducing carbon emissions and improving economy.

2.2 The Research Status of Multi-Energy Systems Involving Hydrogen Storage

Regarding the hydrogen storage technology coupled in the multi-energy system, scholars at home and abroad have carried out relevant research, but the advantages of long-term storage of hydrogen energy have not been well utilized. For multi-energy systems containing hydrogen storage units, domestic scholars have made a lot of research results. In the technical field, Liu et al. [3] proposes P2G technology with intermediate buffer links to realize a “system-hydrogen-natural gas” hybrid energy storage system. In the field of models, Yang et al. [4] proposes a wind power and hydrogen storage cooperative power supply system, establishes a wind-hydrogen coupled system planning model considering the randomness of wind power generation, and evaluates its economic benefits. Cai et al. [5] proposes a wind power/photovoltaic/hydrogen/supercapacitor grid-connected system model and control strategy, and verifies the accuracy and effectiveness of the strategy through simulation. Gan et al. [6] consider the mutual coupling relationship of cold-heat-electricity and the corresponding energy storage form, which proves that the operating cost of microgrid under the coordinated optimization of multi-energy flow is significantly reduced, and the increase of energy storage capacity increases the utilization rate of renewable energy. Regarding system problems, foreign scholars have not paid much attention to domestic ones. Mancarella [7] proposes a multi-energy system modeling method that considers the characteristics of energy hubs, microgrids, and virtual power plants. This article describes simulation optimization tools that can be used for multi-energy system operation and planning, points out the latest models and evaluation techniques that can be used to analyze multi-energy systems, and then explains the main evaluation methods and performance evaluation standards from the perspectives of energy, environment, and technology and economy. Alarcon-Rodriguez et al. [8] proposed that distributed energy distribution network is a multi-objective planning problem, and discussed the latest trends in this field. Including the possibility that multi-objective distributed energy planning methods have not been applied to analyze controllable loads and demand-side management, and electric vehicles can be used as a large-scale distributed electric energy storage.

Research on hydrogen storage technology is more advanced in Japan, the United States and Europe, especially the research on seasonal time scale hydrogen storage systems, which have relatively mature research results abroad. In view of the differences in resource conditions and grid structures in different regions, seasonal hydrogen storage is generally based on specific regions for research. Vogt et al. [9] assesses the self-supplied energy supply of small off-grid renewable energy systems based on actual weather data and demand patterns in Zurich, Switzerland. Analysis shows that, on the seasonal time scale, hydrogen is the ideal choice for long-term large-capacity energy storage, while batteries are most suitable for short-term energy storage. Oloyede [10] research and put forward the high-level demand and design of the seasonal hydrogen storage peak power supply system. Researchers collected actual electricity demand data from grid operators in the northeastern and southwestern United States, determined daily, weekly, and seasonal demand. Oloyede also developed analysis and numerical models of nuclear, wind and solar power generation coupled with storage systems, and gave the functional structure and physical architecture of various design schemes. Reus et al. [11] proposes a supply chain model of electrolytic hydrogen unit with seasonal hydrogen storage, which can bridge the gap between the fluctuations in renewable energy generation caused by excess electricity and the demand for fuel supply stations. Researchers have also developed a set of models that can calculate the cost of hydrogen supply, energy consumption and greenhouse gas emissions of fuel cell vehicles, and analyzed the potential impact of Liquid Organic Hydrogen Carriers (LOHC) on the future hydrogen mobility. It provides an in-depth overview of related infrastructure technologies and combinations from the perspectives of ecology and economy. Ivalin et al. [12] analyze the uncertainty and sensitivity of

Multi-energy system with seasonal energy storage through an optimized framework. According to differences in regional conditions, study the possibility of electricity-to-hydrogen conversion as seasonal hydrogen storage in a multi-energy system, and evaluate the impact of technology and uncertainty on the implementation of electricity-to-hydrogen conversion. Petkov et al. [13] The literature uses a mixed-integer linear programming optimization framework to optimize the design of multi-energy systems. Through selection and adjustment of various technologies in the system, the factors affecting the power configuration of Power-to-H₂ are analyzed under the conditions of meeting the power and heat requirements. The results show that a low-emission multi-energy system with a large amount of renewable energy generation and high seasonal demand for thermal power can offset the long-term mismatch between renewable energy generation and energy demand through seasonal energy storage containing Power-to-H₂, So as to achieve zero CO₂ emissions.

For multi-energy systems, seasonal hydrogen storage will actually achieve good results. However, judging from a large amount of literature, people have not classified them according to the characteristics of hydrogen energy, so that they can be better coupled to the energy system and give play to the greatest advantages of hydrogen storage units. Therefore, this article innovatively believes that seasonal hydrogen storage should be classified according to two key characteristics of space transfer and time transfer, and then used in different regions and scenarios.

2.3 Key Factors for Seasonal Hydrogen Storage

Seasonal energy storage needs to solve the following problems: suppress the imbalance of power supply and demand on a long-term scale; when coordinated with short-term energy storage, it can make up for the limited scale of short-term energy storage capacity, peak shaving and energy transfer capabilities; and when renewable energy is coordinated with each other, it can cooperate to achieve efficient consumption of renewable energy and enhance system flexibility. Therefore, based on the two storage characteristics of hydrogen energy that are transferable in space and transferable in time, this paper proposes that seasonal hydrogen storage is more appropriate for long-term energy storage in a multi-energy system.

On the one hand, seasonal hydrogen storage is based on the phenomenon that the electricity and heat load in spring and autumn are less than that in winter and summer. It can achieve long-term energy translation, smooth power fluctuations, and solve the imbalance between renewable energy output and seasonal load. Therefore, the hydrogen storage technology has high requirements on the time scale, which not only requires low self-loss rate of energy storage equipment when it is not used for a long time, but also requires high energy round-trip efficiency. Compared with short-term energy storage, its efficiency characteristic curve is shown in Fig. 2.

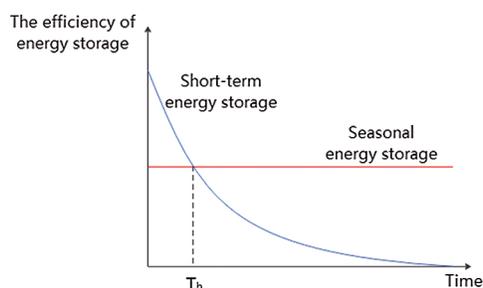


Figure 2: The relationship between short-term energy storage and seasonal energy storage efficiency

On the other hand, current technology cannot directly store the electricity converted from renewable energy for a long time, and usually needs to be converted into other forms of energy. Through the establishment of electricity-heat, electricity-gas or electricity-hydrogen conversion forms, the power

system can be coupled with other energy systems, and the supply and demand balance and energy translation of renewable energy can be realized in a wider range of energy systems. So in order to meet the above characteristics, it is necessary to select an appropriate hydrogen storage method, and to make reasonable planning and optimization in energy system planning.

3 Temporal and Spatial Characteristics of Cross-Season Hydrogen Storage

The hydrogen energy described in this article comes from the technology of water electrolysis. The surplus electricity from wind power, photovoltaic power or part of nuclear power is electrolyzed into hydrogen gas, and then the hydrogen is stored through advanced storage technology. When electricity is needed, the stored hydrogen is converted into electrical energy and sent to the Internet through different methods; or carbon dioxide is methanated for use in the gas system. The latter uses hydrogen as the medium to bridge the gap between the traditional power system and the natural gas system, making the bidirectional flow of power and natural gas energy a possibility, which is the energy complementation and interoperability advocated by the multi-energy system. It not only promotes the deep integration of gas and electricity networks, but also provides a good way to solve the volatility of renewable energy development. The following innovatively divide hydrogen storage technology into two types: space transfer and time transfer hydrogen storage technology. Then select suitable hydrogen storage methods based on the above-mentioned long-term, cross-energy form seasonal characteristics.

3.1 Hydrogen Storage Method for Space Transfer

The space transfer type hydrogen storage technology described in this article includes three types: underground salt cavern hydrogen storage, physical adsorption hydrogen storage, and glass microsphere hydrogen storage, mainly storing hydrogen through different physical spaces. Hydrogen storage in underground salt caverns is mostly suitable for on-site consumption due to its special geological conditions. Physical adsorption and hydrogen storage in glass microspheres can be used for spatial scheduling, but due to capacity limitations, they are temporarily not used in multi-energy systems. Therefore, only a brief introduction is given. Further development requires further breakthroughs in cost and technology.

3.1.1 Hydrogen Storage in Underground Salt Caverns

Underground hydrogen storage (UHS) technology was proposed by Gregory [14], Kippenhan et al. [15], Walters [16] in the 1970s. Later, Carden [17], Lindblom [18] expanded their work to the quantitative analysis of various reservoirs and caves in mining areas. Because salt caverns can reach the capacity and conditions required for seasonal hydrogen storage, hydrogen storage in salt caverns is considered one of the most realistic and promising solutions in large-scale seasonal hydrogen storage devices.

On the one hand, the development of underground hydrogen storage technology is related to the large-scale use of hydrogen energy and the volatility of hydrogen demand; on the other hand, it can convert excess renewable energy into hydrogen energy for storage. The salt cavern storage technology and operating conditions of hydrogen are similar to those of natural gas underground storage, and the volumetric energy density of hydrogen is almost one third of that of natural gas. So gaseous hydrogen storage is more expensive than natural gas storage [19]. Studies have shown that compressing hydrogen to 20 MPa and above for storage can improve storage efficiency [20]. Rock is almost impermeable to high-pressure gas, and the saline environment prevents the occurrence of biochemical reactions, thereby preventing the consumption of stored hydrogen. There are many researches on the feasibility and potential of hydrogen storage in salt caves, from the analysis of the thermo-mechanical properties of the cave [21] to the determination of the best regional location [22–27], as well as the evaluation of the economic and environmental benefits of underground hydrogen and natural gas storage [28]. In addition, when the salt caverns already exist, even with relatively high injection and extraction rates, limited construction costs

can be guaranteed [29]. Fig. 3 shows the structure of a pure hydrogen underground storage well constructed by ConocoPhillips in the United States. The maximum radius of the salt cave is about 75 m. The maximum injection rate is 153400 m³/h, and the maximum injection pressure is 15 MPa.

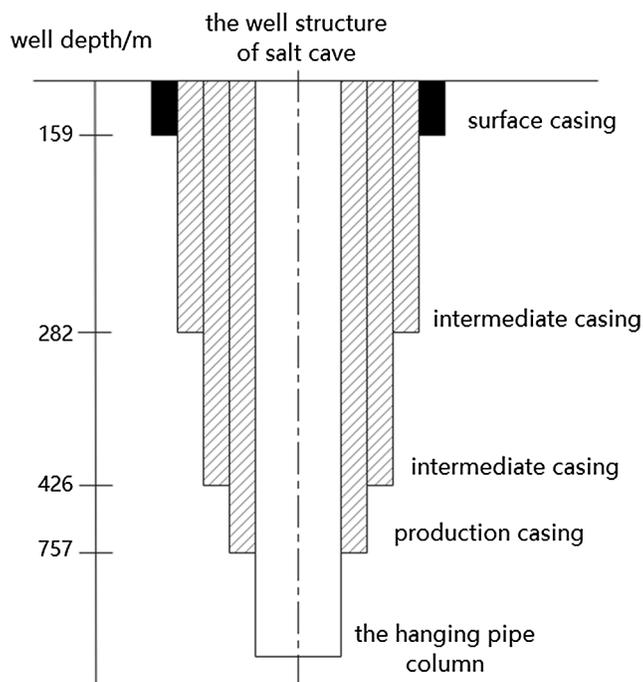


Figure 3: Schematic diagram of wellbore structure of salt cavern hydrogen storage tank

The characteristics of underground storage in different regions are different. In response to this situation, domestic and foreign researchers have made preliminary explorations on underground hydrogen storage technologies in different regions. Bai et al. [30] classified and introduced conventional underground hydrogen storage modes. By comparing the physicochemical properties of hydrogen and methane, the article deeply analyzes the feasibility and existing problems of underground hydrogen storage. Provide references for the development of underground hydrogen storage in my country from the perspectives of energy structure, policy and technological development. Ozarslan [24] studied a large number of gas storage methods and design issues for salt cavern underground gas storage. The article conducted a pre-evaluation of a salt cavern gas storage in Turkey, and believes that hydrogen and natural gas systems can be used to meet future large-scale energy storage needs. Hubner et al. [31] studied porous geological structures in Scotland and pointed out that porous geological structures have great potential in providing capacity and local positioning for hydrogen storage. The geological combination containing reservoirs and caps can provide the best hydrogen storage layer conditions, which will be an ideal choice for future experimental and commercial hydrogen storage research projects. Leighty [32] proposed an underground hydrogen storage route suitable for Germany, and pointed out that underground hydrogen storage should be geologically analyzed according to complete engineering standards. Any behavior that exceeds the limits of underground hydrogen storage equipment may cause hydrogen leakage, which can only be implemented after selection according to geological standards.

3.1.2 Physical Adsorption Hydrogen Storage

The principle of physical adsorption hydrogen storage is to use the van der Waals force of different materials to adsorb hydrogen on a porous structure with a high specific surface area. Its characteristics are simple storage method, fast hydrogen absorption and desorption speed, and low activation energy. The main materials are carbon-based materials, metal organic framework materials, mineral porous materials and microporous polymer materials.

Carbon-based hydrogen storage materials include activated carbon (AC), graphite nanofiber (GNF), carbon nanotube (CNT) and carbon nanofiber (CNF) [33], and their properties are shown in Tab. 1. Activated carbon, also known as carbon molecular sieve, has the advantages of large adsorption capacity, long cycle life, and high hydrogen storage density, and is easy to produce on a large scale. Xu et al. [34] pointed out that Max-sorb can store up to 0.67 wt% of hydrogen at 303 K and 10 MPa, and up to 5.7 wt% at 77 K and 3 MPa; under the conditions of 12 MPa and 25°C, the mass fraction of hydrogen storage of carbon nanofibers with herring bone shape can reach 67%; Single-walled carbon nanotubes with an average diameter of 1.85 nm can store up to 4.2 wt% hydrogen at room temperature, and 80% of hydrogen can be released at room temperature. The carbon nanofiber hydrogen storage material introduced by Ma et al. [35] can store up to 10% of hydrogen after its surface is treated at room temperature and 12 MPa.

Table 1: Characteristics of common carbon-based hydrogen storage materials

Name of the material	Fahrenheit/K	Pressure/MPa	Mass density	Economy
Activated carbon	77	2–4	5.3–7.4	Compared with compressed hydrogen storage, it saves hydrogen compression cost.
	93	6	9.8	
Graphite nanofiber	indoor temperature	7.04	3.8	Compared with liquid hydrogen, the cost of liquefaction is saved.
	25	12	67	
Carbon nanotube	indoor temperature	11	12	Activated carbon has a long life, and based on current technology, super activated carbon can be produced on a large scale.
	indoor temperature	10/12	10	
	298	10–12	4.2	
Carbon nanofiber	80	12	8.25	
	indoor temperature	0.05	6.5	

The metal-organic framework is a 3D framework structure formed by the coordination of metal ions through rigid organic ligands. The material has the advantages of strong structural design, low density, large specific surface area and pore volume, and high spatial regularity. Sagara et al. [36] conducted a study on metal organic framework compound-5 and showed that the hydrogen storage capacity can reach 5.1 wt% at 77 K. Combining theoretical calculations, simulation and density functional methods, it is concluded that in the metal-organic framework with saturated coordination, the main determination of the adsorption is the aromatic ligand, which is not necessarily related to the metal ion itself.

Inorganic porous materials refer to porous materials with nano-pores in the structure, and representative materials are zeolite, sepiolite, etc. The results of Jung et al. [37] showed that at 77°C and 0.11 MPa, reducing the ratio of Si/Al can significantly increase the amount of hydrogen adsorption.

3.1.3 Glass Microspheres Hydrogen Storage

Hollow glass microspheres are non-permeable under low temperature, but are porous under high temperature. Hydrogen can enter the glass body under certain temperature and pressure conditions. As the temperature drops to room temperature or below, the hydrogen stays in the glass sphere. Similarly, hydrogen can be released as the temperature rises. The outer diameter of the hollow glass microsphere (HGM) is generally on the order of millimeters or sub-millimeters, and the wall thickness is from a few microns to tens of microns. The main component of the spherical shell is SO_2 , which also contains elements such as K, Na and B, and its hydrogen storage capacity is above 15 wt%. The material has the special properties of hollow structure and pore wall structure, so it provides some possibilities for preparing materials with different functions. Rapp et al. [38] pointed out that under the conditions of high temperature and high pressure, hydrogen molecules can quickly enter the inside of glass microspheres through concentration diffusion and be stored, but the relatively low thermal conductivity of glass microspheres leads to hydrogen. The release rate is low. As a hydrogen storage material, hollow glass microspheres are currently a promising hydrogen storage technology. It is especially suitable for hydrogen-powered vehicle systems, but its industrial application is limited because it is difficult to produce high-strength hollow microspheres.

3.2 Time Transfer and Physical Property Conversion Hydrogen Storage Method

The focus of long-term physical property conversion hydrogen storage technology is to change the physical state or chemical properties of hydrogen through compression, liquefaction, or complex hydride, so that it can be stored for a long time for cross-season applications. This article focuses on hydrogen storage technologies such as high-pressure gaseous, low-temperature liquefaction, complex hydrides, and organic hydrides.

3.2.1 High-Pressure Gaseous Hydrogen Storage

The main advantages of high-pressure gaseous hydrogen storage are low storage energy consumption, low cost, fast hydrogen charging and discharging speed, and relatively mature technology; the disadvantages are low volumetric hydrogen storage density, small volumetric capacity, and potential leakage risks. The current technological breakthrough lies in the improvement of the material of the storage tank, and development in the direction of lighter weight, higher pressure, and further improvement of the mass density of hydrogen storage under the premise of ensuring safety performance. Of course, when considering economic issues, it's not that the higher the pressure, the better. For example, under the condition of 70 MPa, the hydrogen storage tank and the pressure are no longer in a linear relationship, and doubling the pressure can only increase the hydrogen storage capacity by 40%–50%. Furthermore, as the pressure increases, the requirements for the wall thickness and pressure-bearing capacity of the tank also increase, resulting in an increase in the weight of the container and a reduction in the efficiency of hydrogen storage. Through calculation, it is most in line with economic benefits when it is around 55–60 MPa [39]. In addition, Zhao et al. [40] also proposed a low-temperature and high-pressure hydrogen storage method above the critical pressure of hydrogen, which can realize the hydrogen storage and release process without the pressure being too high and the temperature being not too low. At the same time, recommended parameters are given according to the method of boost analysis.

At present, the materials for high-pressure gaseous hydrogen storage tanks are mainly aluminum liner fiber winding and plastic liner fiber winding. A typical domestic company is Sinoma Technology (Chengdu), which mainly produces three-type hydrogen storage tanks with aluminum inner tank and carbon fiber winding. The product has high safety performance, and the inner tank adopts the aluminum sheet stretching forming process. Compared with aluminum tube forming, the inner and outer surfaces of the sheet-formed inner liner are smoother, the inner liner fibers are tighter, the fatigue performance of the product is greatly improved, and the consistency is good, and it is expected to reach 70 MPa working

pressure. The 70 MPa high-pressure hydrogen storage tank of Toyota of Japan is used in commercial fuel cell models, as shown in Fig. 4. South Korea's ILJIN has developed an ultra-light composite hydrogen tank, The product uses carbon fiber composite material and reinforced nanocomposite material lining, its advantages include high hydrogen storage efficiency; the use of leak-free nozzles ensures that there will be no air leakage in any environment; the use of high-tech carbon fiber composite materials with excellent heat resistance and fatigue resistance has excellent safety and will not suffer performance degradation under any circumstances. The Hexagon company in Norwegian has developed a high-pressure hydrogen tank for fuel cell vehicles that uses hydrogen as fuel and does not produce harmful emissions. At the same time, Hexagon also provides solutions for the ground storage, transportation and backup power of hydrogen. Compared with other hydrogen storage tanks, the Type 4 hydrogen storage tank produced by the NPROXX company in Germany has obvious advantages, including: carbon fiber reinforced structure can produce excellent strength to weight ratio, reduce the weight of gas sealing system in buses and trucks by 450 kg, can significantly improve fuel economy, and emphasize the economic argument of hydrogen fuel; use CFRP (a composite material) can improve the durability of the container, and improve the chemical resistance, X-ray transmittance and no thermal expansion.



Figure 4: High-pressure hydrogen storage tanks for fuel cell vehicles from Toyota, Japan

3.2.2 Low Temperature Liquefaction Hydrogen Storage

The main advantages of liquefied hydrogen storage are high density, high purity, large volumetric capacity, simple storage and transportation, etc.; the disadvantages are high energy consumption, volatility, and high cost in the liquefaction process. The liquid hydrogen storage tank is generally divided into two layers inside and outside. The inner tank contains pure liquid hydrogen cooled to 20 K, and a support made of glass fiber tape is placed in the center of the outer shell. The support has good thermal insulation, and the multilayer aluminized polyester film in the middle of the sandwich is used to reduce heat radiation. The tank liner is generally made of aluminum alloy, stainless steel and other materials, and the outer shell is generally made of low-carbon steel, stainless steel and other materials, and aluminum alloy materials can also be used to reduce the weight of the container [41]. The current research on liquid hydrogen tanks seeks technological breakthroughs in many aspects, including: how to choose insulation material to improve insulation efficiency; reduce the loss caused by hydrogen gasification in the hydrogen storage process; and reduce the energy consumed in the cooling process. At present, liquefied hydrogen storage is mainly used in the aerospace field, and only a few high-power commercial vehicles use this technology. The economy of liquid hydrogen storage is closely related to the size of the storage: when the amount of hydrogen storage is large, the cost of liquid hydrogen storage is lower than that of high-pressure gaseous hydrogen storage.

Liquid hydrogen storage and transportation has always been a research hotspot in various countries. In recent years, Japan, the United States, Germany and other countries have reduced the transportation cost of liquid hydrogen to about one-eighth of high-pressure hydrogen. At present, the world's largest cryogenic liquefied hydrogen storage tank is located at the Kennedy Space Center in the United States, with a volume of 112×10^4 L. However, in order to ensure low temperature and high-pressure conditions, liquid hydrogen storage not only has requirements on the tank material, but also needs to have a strict insulation scheme and cooling equipment. Therefore, the volume of storage tank for cryogenic liquefied hydrogen storage is generally small, and the mass density of hydrogen is about 10% [42]. Automobile companies such as General Motors, Ford and BMW in Germany have all launched concept cars that use on-board liquid hydrogen storage tanks to supply hydrogen. The "Hydrogen 3" sedan launched by GM in the United States in recent years has increased its maximum power to 94 kW, motor power of 60 kW, top speed of 150 km per hour, and mileage of 400 km, but the liquid hydrogen is reduced to 68 L, 4.6 kg. The liquid hydrogen storage tank used in this vehicle is 1000 mm long, 400 mm in diameter, 90 kg in weight, with a weight hydrogen storage density of 5.1% and a volumetric hydrogen storage density of 36.6 kg/m^3 . Considering only the weight and volume of hydrogen storage density, liquid hydrogen technology is close to the practical requirements. Japanese companies have invested a lot of research and development efforts in the liquid hydrogen supply chain system, and have solved a number of key technical problems in liquid hydrogen storage and transportation. Most of the products launched have entered the actual inspection stage. For example, the large-scale liquid hydrogen storage and transportation tanks developed by Japanese companies ensure the high strength of the storage and transportation tanks while achieving high heat resistance through the vacuum exhaust design; the Tanegashima Space Center's liquid hydrogen storage tank with a volume of 540 m^3 uses perlite vacuum insulation method makes the daily evaporation rate less than 0.18%. The Russian JSC company has produced two specifications of spherical tanks. The total height of the 1400 m^3 spherical tank is 20 m. The method of vacuum multi-layer insulation and high-altitude venting is adopted to make the daily evaporation rate less than 0.26%.

3.2.3 Other Hydrogen Storage Methods of Physical Conversion

With the development of chemical and physical technology, people not only use the transformation between gas, liquid and solid, but also use complexes and organic hydrides to store hydrogen energy. The hydrogen storage of complex hydrides originated from the high hydrogen content of boron hydride complexes. Japanese researchers first developed complex hydrogen storage materials such as sodium borohydride and potassium borohydride, which can produce hydrogen storage materials that are higher than their own through hydrolysis reactions. Hydrogen with a lot of hydrogen. Lin et al. [43] conducted a preliminary study on the hydrogen absorption and desorption properties of ball-milled composite materials such as $\text{MgC}_{12}(\text{NH}_3)_6-18\text{LiH}$; Bogdanovic et al. [44] found that doped NaAlH_4 exhibits the advantages of fast decomposition rate, low temperature, and good cycle stability; Shevlin et al. [45] simulated the reaction mechanism of complex hydrides based on density functional theory (DFT).

Liquid organic hydride hydrogen storage technology is realized by a pair of reversible reactions between some alkenes, alkynes or aromatic hydrocarbons and hydrogen. At present, there are more hydrogen storage media reported in the literature: C_6H_{12} [46,47], C_7H_{14} [48], $\text{C}_{10}\text{H}_{18}$ [49], $\text{C}_{10}\text{H}_{12}$ [50], etc. The reason is that the melting and boiling point range of these substances is appropriate, the raw materials are easily available, and the dehydrogenation conversion rate is high. The current research bottleneck of organic liquefaction hydrogen storage is how to develop dehydrogenation catalysts with high conversion rate, high selectivity and stability. At the same time, because the reaction is a heterogeneous reaction with strong endothermicity and is limited by equilibrium, it is necessary to select an appropriate reaction mode and optimize the reaction conditions to solve the heat and mass transfer problems. In addition, the economic problems of the overall process of hydrogen storage technology cannot be ignored, such as whether the

amount of precious metals in the catalyst can be reduced, and how to improve the energy conversion efficiency of on-board dehydrogenation. Tab. 2 compares the above typical hydrogen storage technologies in terms of technical cost, safety and application scope.

Table 2: Comparison of various hydrogen storage technologies

Hydrogen storage technology	Volumetric capacity	Cost	Security	Transportation convenience	Technical maturity	Application
Low temperature liquid hydrogen storage	Large	high	poor	convenient	immature	Aerospace, electronics, transportation, etc.
High pressure gaseous hydrogen storage	small	low	poor	more convenient	mature	Most hydrogen industries, such as automotive, chemical, transportation
Metal hydride	large	low	safety	most convenient	mature	Military (submarine, ship, etc.)
Organic liquid hydrogen storage	large	high	safety	most convenient	immature	Automotive sector, transportation, etc.

Cost is one of the key factors in choosing hydrogen storage technology. The research report “Hydrogen: The Economics of Storage” released by Bloomberg New Energy Finance gives the storage costs of various hydrogen storage technologies in different cycles, the specific comparison results are shown in Fig. 5. Studies have shown that the future hydrogen energy economy needs abundant hydrogen storage scale to ensure a balance between supply and demand. If hydrogen is produced from stable sources such as natural gas or coal, the scale of hydrogen storage is at least 10% of the annual demand. However, if hydrogen is produced from different types of renewable energy, the scale of hydrogen storage needs to reach 20% of the annual demand.

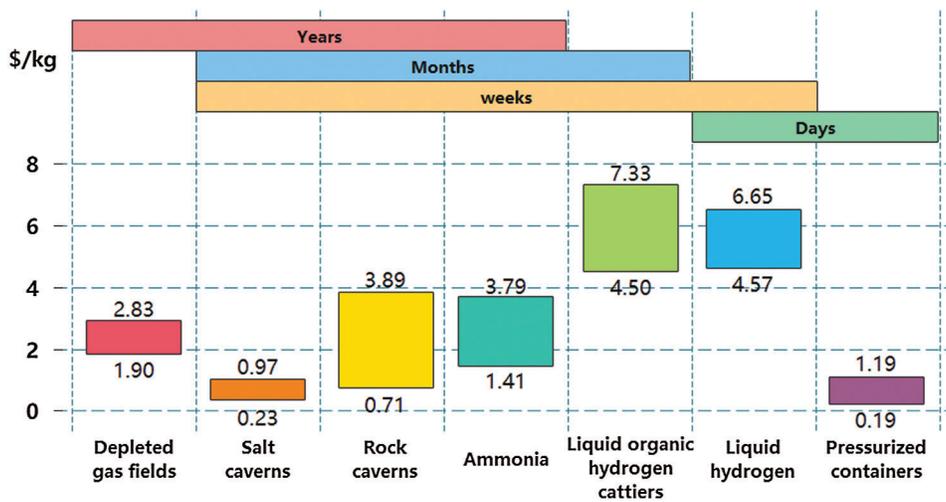


Figure 5: Comparison of hydrogen storage technology costs at different time scales

4 Research Status of Seasonal Hydrogen Storage Model

4.1 Application of Seasonal Hydrogen Storage in Multi-Energy Systems

Combining the above hydrogen storage technologies and screening the key factors of seasonal hydrogen storage, this paper sorts out two typical scenarios of seasonal hydrogen storage multi-energy systems. The first is to use salt cavern hydrogen storage as a seasonal hydrogen storage method for multi-energy systems when geological conditions permit. The schematic diagram of the structure is shown in Fig. 6. The second is a multi-energy system with Power-to-H₂ (P2H). P2H is composed of electrolyzer and hydrogen storage unit. The schematic diagram of the structure is shown in Fig. 7. The system uses surplus renewable energy to generate electricity, then electrolyze water to generate hydrogen and oxygen, which are stored in the hydrogen storage unit.

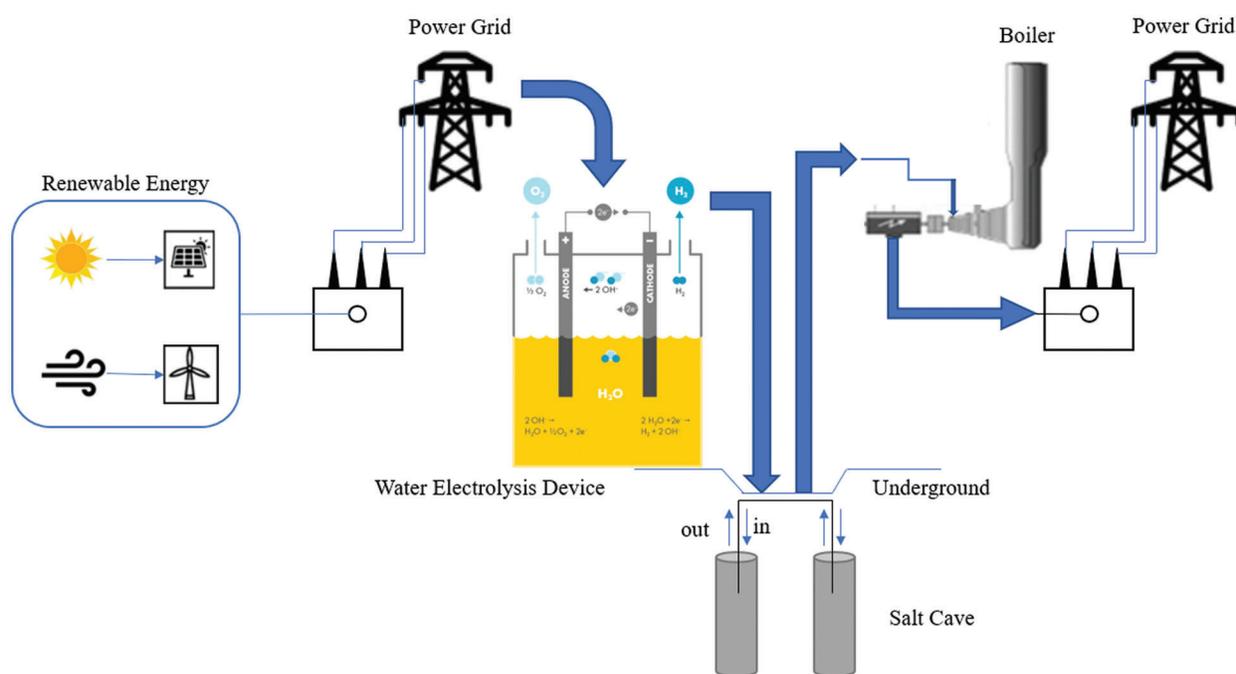


Figure 6: Seasonal hydrogen storage multi-energy system in underground salt caverns

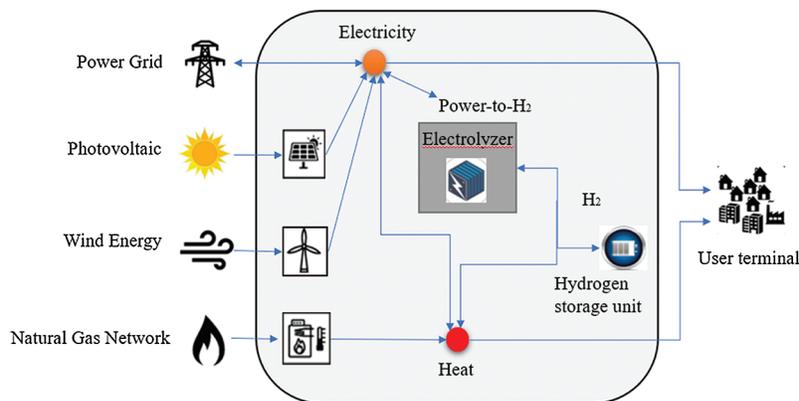


Figure 7: P2H seasonal hydrogen storage multi-energy system

4.2 Hydrogen Storage Models for Two Typical Scenarios

4.2.1 Underground Hydrogen Storage Model

In recent years, salt caverns have been researched and applied as natural gas storage. When the cave is storing natural gas, the state of the surrounding salt rock has also been analyzed in detail by many researchers [51–53]. Gabrielli et al. [54] established a seasonal underground hydrogen storage model suitable for multi-energy systems based on the existing knowledge of the salt rock state of natural gas reservoirs [51,55]. It can be seen that the space of the model consists of two connected subdomains, namely the cave and the damaged salt rock around it. Many mathematical models of underground gas storage do not consider the gas flow inside and outside the wall [54–59]. Therefore, the equilibrium equation of the model built by Peach et al. [55] takes into account the interaction between the gas in the cave and the salt rock gas, which is more in line with the realistic behavior of hydrogen storage. The model simulates the interaction between caverns and salt rock when H₂ is injected/extracted. The purpose is to describe the dynamic behavior of hydrogen storage, so as to reproduce with reasonable accuracy the behavior of the cave during the cycle of charging and discharging hydrogen, and to understand salt cave storage. The engineering quantity of hydrogen determines the minimum and maximum possible values of hydrogen pressure in the cave. When simulating the hydrogen storage process in a salt cave, it is assumed that the cave is a cylindrical uniform space domain with a constant temperature of 40°C, ignoring the gravitational effect of hydrogen, and flowing in one dimension along the radial direction. At this time, the hydrogen pressure is only a function of time. Based on these assumptions, taking r and t as the space-time coordinates, the model consists of the following balance equations:

1) The mass balance in the cave describes the dynamics of hydrogen in the cave:

$$V \frac{d\rho_c}{dt} - m_{in} + m_{out} + m_w = 0 \quad (1)$$

where ρ indicates the hydrogen density and V the cavern volume, m indicates the mass flow rate; the subscript “c” refers to the conditions inside the cavern, while the subscripts “in”, “out” and “w” refer to the mass injected, withdrawn and exchanged through the wall, respectively. All variables, but V , are time dependent.

2) The mass balance of the salt rock, described as a porous medium:

$$\varphi \frac{\partial \rho_r}{\partial t} + \frac{1}{r} \frac{\partial (r \rho_r v)}{\partial r} = 0, \quad R_i \leq r \leq R_o \quad (2)$$

where φ is the porosity of the damaged zone. The first term on the left-hand side represents the rate of hydrogen accumulation within the salt rock, while the second term represents the hydrogen advection.

3) Momentum balance of salt rock:

$$v = -\frac{k}{\mu} \frac{\partial p_r}{\partial r}, \quad R_i \leq r \leq R_o \quad (3)$$

where k is the hydrogen permeability, μ the hydrogen viscosity and p the hydrogen pressure.

In order to simplify the numerical solution and lay the foundation for the optimization model, after using the continuous equation, the dimensionless parameters are introduced. According to different constant parameters, three different types of hydrogen storage areas are obtained. The salt cave (Zone 1) is characterized by a linear distribution of pressure in the cave, and similar pressure changes are found throughout the rock area, similar to a sealed tank; On the contrary, the reservoir (Zone 2) is affected by the obvious penetration of H₂ through the rock formation, forming a nonlinear profile at all stages of the entire cycle. In addition, due to the relatively large porosity and permeability, the pressure change in

the reservoir area with time is limited, and the maximum change is less than 1 bar, which has no effect at the end of the area. Zone 3 ignores the rocky area and treats the cave as an impermeable storage tank.

4.2.2 Power-to-H₂ (P2H) Model

Different from underground hydrogen storage modeling, the P2H model needs to consider the mutual conversion of multiple energy forms while meeting long-term storage. The P2H model established by Gabrielli et al. [60] includes an electrolytic cell and a hydrogen storage unit. For these two devices, the first-principles model's piecewise affine approximation is used to describe the conversion efficiency. For all line segments $i = \{1, \dots, m\}$:

When $\delta Sx_t \leq F_t \leq Sx_t$:

$$P_t \leq \alpha_i F_t + \beta_i Sx_t \quad (4)$$

In the formula, the parameters α_i and β_i are the coefficients of the i -th approximate line segment. Due to the modularity of the system, the parameter size will not significantly affect the performance, so $\gamma = \zeta = \nu = 0$. Similar to a micro gas turbine, a fuel cell produces electrical power P_t and thermal power Q_t at the same time, and the two are related by $Q_t = P_t(\rho - 1)$, ρ is the average ratio of first-principle efficiency to electrical efficiency.

Ivalin et al. [12] compared three storage systems, including hot water sensible heat storage, lithium batteries and hydrogen storage tanks. In order to meet the long-term characteristics of seasonal hydrogen storage, this paper only describes the hydrogen storage tank by linear equation:

$$E_t = E_{t-1}(1 - \Lambda \Delta t) - (\Pi Sg(\Theta_t) + \eta P_t) \Delta t \quad (5)$$

where P_t represents the positive or negative value of charging and discharging power; Λ and Π indicate self-discharge parameters; $g(\Theta_t)$ indicates the impact of ambient temperature on the loss of storage equipment; η indicates charge and discharge efficiency; Δt is the duration of the time interval t .

4.3 Time-Domain Modeling Based on Cross-Season

The existing analysis methods of seasonal hydrogen storage are mostly based on traditional short-term energy storage mathematical models. For example, extend the time scale of energy storage to monthly or quarterly, and then establish a coupling relationship between adjacent periods to reflect long-term energy storage behavior. Jiang et al. [2] compiled a generalized model for the analysis of seasonal energy storage characteristics in the current power system. According to the time scale of the equipment participating in the optimization analysis, the time coordinates can be further divided into weeks, months, quarters, etc., and the time coupling relationship of the equipment scenes can be established [61]. However, the operating performance and characteristic parameters of different energy storage types are generally different. When establishing a hydrogen storage dynamic process model, the dissipation and dissolution characteristics of hydrogen must also be considered [60].

In order to combine other key components and equipment for hydrogen production and hydrogen storage, the mathematical linear models described in the previous section need to be combined with the schematic diagrams of the multi-energy system shown in Figs. 1 and 2, respectively. The main goal of seasonal hydrogen storage technology is to achieve long-term energy translation and solve the imbalance between renewable energy output and seasonal load. In the process of design and operation, multi-energy systems can maximize the penetration and energy efficiency of renewable energy by using the coupling of different energy carriers (such as electricity, hydrogen, etc.) [7]. When energy storage technology is integrated into the optimal design of multi-energy systems, Elsidio et al. [62] proposed some nonlinear methods to optimize the design of the system. However, mixed integer linear programming (MILP) can

not only fully reflect the characteristics of MES, but also become the best algorithm for system design and optimized operation with reasonable computational complexity.

As of the previous section, the system has been described as considering an hourly resolution optimization problem with a one-year time interval, namely $T = 8760$ h. However, the traditional MILP mentioned above cannot include seasonal storage, and when choosing different technical equipment, a large number of variables and constraints will be generated, making comprehensive optimization almost impossible. Pfenninger [63] conducted a systematic analysis of different techniques for reducing the time resolution of the energy model, including time slices and multiple typical design days or design weeks.

Based on this, Gabrielli et al. [60] proposed a method that allows for hourly optimization of energy storage levels while still describing the annual rate of change of a typical design day. Here we need to introduce the order σ of the number of days in time, allowing consecutive days in the year. That is, the energy stored in the last hour of a certain day of the year is selected to be associated with the energy stored in the first hour of the second day, where the day of the year is described by a given design day. In this case, the storage dynamics of the system of equations are as follows:

$$E_{y,k} = E_{y,k-1}(1 - \Lambda\Delta k) - \Pi Sg(\Theta_{y,k})\Delta k + \eta P_{\sigma(y),k}\Delta k, \quad \forall y, \forall k \in 2, \dots, K \quad (6)$$

$$E_{y,1} = E_{y-1,K}(1 - \Lambda\Delta k) - \Pi Sg(\Theta_{y,1})\Delta k + \eta P_{\sigma(y),1}\Delta k, \quad \forall y \quad (7)$$

$$E_0 = E_{Y,K} \quad (8)$$

where $y \in 1, \dots, Y$ indicates the y -th day of the year, with $Y = 365$; $P_{\sigma(y),k}$ is the charging/discharging power at day y , described by the typical day $\sigma(y)$. The above equation shows that although the two days of the year described by the same design day must have the same energy storage change characteristics, they can have different energy storage values at the beginning of each day. The storage flexibility in this method comes at the cost of a large number of variables and constraints. Actually, $E \in \mathbb{R}^{Y \times K}$, can assume different values at each hour of the year, and the corresponding number of constraints are imposed by formulas (6) and (7). For overall optimization, the periodic constraint of formula (8) is for the entire year, not for each design day.

5 Benefit Evaluation of Seasonal Hydrogen Storage Multi-Energy

Due to the difference in seasonal load demand of multi-energy systems, as well as the randomness and indirectness of renewable energy, the demand for seasonal hydrogen storage capacity is very large. The investment and planning of seasonal hydrogen storage requires detailed demand analysis and benefit evaluation to balance the sufficiency of system capacity and investment economy, and to achieve a reasonable allocation of seasonal hydrogen storage. According to different resource conditions, installed capacity, and load requirements in different regions, the size of energy storage capacity is also different. Therefore, scholars usually conduct seasonal hydrogen storage research on multi-energy systems for specific regions or design parameters. Gabrielli et al. [60] designed a seasonal hydrogen storage operation model based on a multi-energy system near Zurich, Switzerland. The system is optimized in terms of total annual cost and carbon dioxide emissions, and is sensitive to different characteristics of the energy system. Analyze and view the topology of the energy hub to reveal the behavioral pattern of the energy system. Petkov et al. [13] studied a residential area composed of five multistory buildings in Palermo, Italy. The residential area used renewable energy to produce and use hydrogen as an energy carrier, and was developed by NREL and the Midwest Research Institute in the United States. The power and renewable energy hybrid optimization model (HOMER) software developed to study the energy balance of the system and its components. In addition, the hourly operation of each system was simulated to calculate technical, economic and environmental performance parameters. Oloyede et al. [10] obtained actual power demand data from grid operators in the northeastern and southwestern United States, and

proposed high-level demand and design for seasonal hydrogen storage peak power supply systems. In order to analyze the daily, weekly and seasonal demand in detail, this article establishes all the numerical analysis models of nuclear, wind and solar power generation coupled with the storage system. The results show that compared with the existing power infrastructure, the base load demand capacity will increase by 50%, and 93% of the power will be directly delivered to customers. About 7% of the annual power generation will be stored when power demand is low and used when power demand is high. Vogt et al. [9] described a self-sufficient seasonal energy storage project. The project compared three renewable energy supply models based on actual weather data and demand patterns in Zurich, Switzerland. The results show that the production and storage of hydrogen is conducive to achieving complete energy independence and the smallest energy volume ratio. Seasonal fluctuations in photovoltaic production will generate excessive demand for additional battery capacity. Hydrogen is very suitable for seasonal energy storage due to its high energy density.

6 Conclusion

The key driving force of hydrogen storage is the excess of renewable energy generation. Therefore, in the context of the rapid development of renewable energy, the conversion of excess energy into hydrogen has been recognized by many countries in the world. On the one hand, the seasonal hydrogen storage multi-energy system can coordinate multiple energy forms and utilize the complex coupling relationship between various links to make electricity, heat, natural gas and other systems interconnected and develop into an organic whole, thereby making the energy system more flexible; On the other hand, it can also promote the stable operation of multiple energy systems and achieve large-scale decarbonization and temperature control goals.

This article analyzes the characteristics of multi-energy systems and hydrogen storage through literature reading, and proposes two seasonal hydrogen storage modes suitable for multi-energy systems: One is underground hydrogen storage. Its advantage is not only the convenience of large-scale long-term storage, but also the potential for zero carbon emissions when renewable energy power generation and energy demand have the same seasonal dynamics; The other is the P2H system, which has the advantage of a wide range of applications, especially suitable for smooth wind power generation [13]. On the basis of the two hydrogen storage modes, a mathematical model suitable for multi-energy systems is established, combined with long-term time-scale modeling, to obtain the required model research foundation.

Seasonal hydrogen storage provides a viable option for solving the intermittent problem of renewable energy, and the wider the scope of implementation, the more significant the effect of reducing carbon emissions and balancing energy supply and demand throughout the year. At present, more and more large-scale hydrogen-based energy storage demonstration projects are planned, promoted and implemented globally, including Germany, Denmark, and Japan. As the proportion of renewable energy sources increases, hydrogen energy as a long-term energy storage method is expected to accelerate its development and implementation. It is speculated that the cost of hydrogen storage in salt caverns is expected to drop to 140 Euro/MWh in 2030, which is even lower than the predicted cost of pumped storage. This article is suitable for the study of seasonal hydrogen storage multi-energy systems, and provides references for optimal selection and rational utilization of hydrogen energy as an intermediate energy link in the selection, evaluation and modeling.

Acknowledgement: All authors contributed equally to this work.

Funding Statement: This research was funded by two projects of Science and Technology Commission of Shanghai Municipality, Grant Nos. 20DZ1206300, 18DZ1203304 and 18DZ1203403.

Conflicts of Interest: The authors declare that they have no conflicts of interest to report regarding the present study.

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