Supporting information

Gigawatt-hour to terawatt-hour salt cavern supercapacitor and supercapattery

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1. Fluids storage in salt caverns for energy purposes

Salt caverns, distinguished by their unique properties such as self-repairing capability, exceptional tightness, and ultra-low permeability, hold critical importance in large-scale fluid-based energy storage systems—particularly for gaseous and liquid energy carriers like hydrogen, natural gas, and compressed air. Their vast volumetric capacity enables salt caverns to act as pivotal regulators for grid stability and renewable energy integration, effectively balancing supply-demand mismatches caused by intermittent sources like wind and solar. Commercially, these geological reservoirs have been successfully deployed to store diverse gaseous and liquid energy media, including oil, natural gas, hydrogen, compressed air, and even CO_2 for carbon sequestration, positioning them as versatile infrastructure in the global transition toward carbon neutrality.

1.1. Compressed air storage in salt caverns

Compressed air storage represents the most prevalent and pervasive methodology for energy storage utilising salt caverns.[1-4] The consumption and utilisation of electricity exhibit a typical wave-like pattern, comprising day peaks and night troughs, which is not conducive to the efficient and stable operation of the power grid. A compressed air is capable of storing energy by functioning as a medium for storing and utilising energy. The operational principle of compressed air storage is similar to that of hydro pumping energy storage. In periods of low electricity consumption (e.g. night troughs), the compressor is driven by electric or mechanical energy to draw air from the surrounding environment, compress it to a high-pressure state (up to 16-18 MPa, against the typical pressure of 24-31 MPa in a steel gas cylinder)[2] and store it in the salt cavern. In this process, the electric or mechanical energy is converted into the internal energy and potential energy of the compressed air. At the peak of electricity consumption, the stored compressed air can be expanded to release the internal and potential energy for generation of electrical or mechanical power by reconverting the contained energy in the compressed air into electrical power and/or mechanical work. Note that a minimum pressure of 10-12 MPa is retained in the salt cavern to, for example, prevent creep in the salt rock, and enable minimum operation and management. This technology can enhance the reliability and stability of the power grid and, at the same time, can operate in conjunction with renewable energy power plants, as shown in Figure 1b.

Compressed air energy storage (CAES) in salt cavern has been a globally acknowledged and validated approach to large-scale clean energy storage. This technology facilitates the optimisation of spatial and temporal structures in power generation and consumption. The distinctive structural and operational characteristics of salt caverns can offer a number of advantages upon compressed air energy storage. Firstly, it offers energy storage at such large scales that are capable of meeting the peak demand of the power grid. Secondly, it is truly clean because the processes of energy storage and power generation are entirely carbon zero, making it an environmentally friendly technology. Furthermore, the continuous maturation of the construction and operation process of compressed air storage in salt caverns has resulted in a cost-effective and efficient approach. CAES in salt cavern was initially deployed in Germany and the United States. In recent decades, many countries, including several provinces in China, have constructed salt cavern compressed air power plant to support the generation of clean energy from renewables.[3, 5]

Nevertheless, the efficiency of CAES (40 – 70%) is relatively low in comparison with other energy storage methods such as pumped hydro (70 – 85%) and batteries (63 – 97%). It is well known that compression and expansion of a gas involve heat generation and absorption, and the heat to work conversion is thermodynamically inefficient. In other words, for electric power generation, the energy efficiency (η) of CAES can be expressed by equation (1) below.

$$\eta = \frac{\Delta G}{\Delta H} = 1 - \frac{T\Delta S}{\Delta H} \quad (1)$$

where T is temperature, ΔH the enthalpy change which is the total energy input for air compression, ΔG the Gibbs energy change, representing the maximum work (mostly electric energy) that may result from CAES, and ΔS the entropy change between compression and expansion, reflecting the heat loss from the overall CAES process.

As shown in Figure 1b, in current designs of CAES in salt cavern, heat storage is combined with the air compressor before the compressed air enters the salt cavern, but reheating the compressed air using the stored heat for discharging via an expander.[4] By feeding the electric energy from wind turbines and solar panels through an inverter, the system responds quickly to grid demand. This makes it suitable for peak-valley smoothing of the output of renewable energy sources. This and similar strategies can obviously recover some of the heat resulting for air compression and hence help improve the overall energy efficiency of CAES, but the effectiveness is limited in terms of, for example, the working temperature and capacity and length of storage for electricity generation.[6]

Another issue is, similar to pumped hydro, CAES offers very low energy density (0.5 – 10 Wh L^{-1}) which compares poorly to, for example, the storage of hydrogen (214 - 458 Wh L^{-1}) and natural gas or methane (up to 1400 Wh L^{-1}). However, on weighing the pros and cons, CAES in salt cavern becomes industrially favourable largely because it is, like pumped hydro, a physical or mechanical storage method and uses mainly machineries to manipulate naturally abundant air (or water in pumped hydro), which translates into low cost.

1.2. Natural Gas

As a significant cleaner source of energy in comparison with other fossil fuels, such as coal and oil, natural gas represents an intermediate between fossil and non-fossil energy sources. It offers a number of advantages, including lower carbon emission, a high calorific value, and existing safety regulations and effective transport network for generation of either electricity or heat. However, the geographical distance between the production and consumption of natural gas is typically considerable, necessitating additional gas storage to stabilise the transport network. Furthermore, the consumption of natural is subject not only to seasonal fluctuations but also to temporal variations. The consumption of natural gas is significantly higher during the winter and at nighttime than it is during the summer or daytime. It can be reasonably deduced that the storage of natural gas in the salt caverns would help resolve these issues.[7]

The construction and operation of salt caverns for natural gas storage has existed for over 60 years since the Soviet Union and USA built salt cavern gas storage facilities in 1960s.[8] There are now over 100 storage salt caverns worldwide, capable of storing vast quantities of natural gas.[9] For example, in the USA, the highest demonstrated peak capacity for underground storage of natural gas is 4.362 trillion cubic feet (1.24×10^{11} m^3) in the USA.[10] (Note: Energy content of nature gas = 37 MJ m^{-3} = 10.28 kWh m^{-3}.) Apparently, the wide use of salt caverns for high-pressure and safe storage of nature gas is largely due to their favourable mechanical properties, gas impermeability, physicochemical stability and self-healing capability. Besides, it represents a more economical and efficient approach than other energy storage methods, and is capable of not only peak regulation and safe operation in energy supply, but also strategic provision when regional and national emergencies occur.

It is worth point out that current commercially supplied natural gas is one of the relatively cleaner forms of fossil fuels, and widely regarded as an effective and affordable intermediate step towards future non-fossil energy. This does mean these natural gas storage salt caverns will become either redundant when natural gas is no longer a major source of energy. Apparently, upon necessary modification, these natural gas salt caverns may be used for storage of other non-fossil gases (and oils) such as hydrogen. In principle, these natural gas salt caverns are particularly ideal for storage the anticipated commercial production of biomethane from various natural, grown or waste biomasses,[11, 12] although the amount of biomethane is not expected to match that of the currently produced commercial natural gas.

1.3. Hydrogen

The future energy technologies and market will be significantly influenced by hydrogen, due to its numerous advantages as an energy carrier, including high abundance, greatest specific energy and realistically clean production and consumption. As the lightest and most abundant element in the universe, hydrogen can be produced from sustainable resources or as industrial by-products (e.g. from the chlor-alkali industry), and can be used a fuel for the generation of electricity and in internal combustion engines. In order to enhance the proportion of hydrogen for global energy consumption, it is essential to optimise the production, storage, and transport of hydrogen. Especially, the storage of hydrogen has been a topic of considerable debate for decades.[13-15] The use of underground space has been demonstrated to offer a cost-effective and efficient solution for large-scale hydrogen storage.[16-18] Similar to CAES, salt caverns are the optimal choice for underground hydrogen storage. This strategy offers the potential for large-scale storage, low cost and high safety. A number of countries, including the United States, China and some in Europe, are actively encouraging and supporting hydrogen production from water electrolysis driven by renewable energy, part of which is pursuing the implementation of hydrogen storage in salt caverns.[16-20] The practical utilisation of salt cavern hydrogen storage commenced in the 1970s.[21] In contrast to CAES in salt caverns, additional considerations must be taken into account with regard to hydrogen storage. These include the necessity of aligning the storage of hydrogen with the production and transportation of hydrogen. Furthermore, in the case of storing a hydrogen mixture or pure hydrogen, contamination and the subsequent purification after extraction from salt caverns must be conducted.

It has to be acknowledged that hydrogen as a commodity finds a wide spectrum of applications, such as making fertilizers and polymers, and also fuel. It is therefore imperative to continue research and commercial efforts to improve hydrogen technologies at all stages from production via storage and transport to decommission. However, for energy storage and power generation, hydrogen has fallen behind in competition with rechargeable batteries, particularly those based on lithium. The question continues: is hydrogen the best choice for energy purposes.

1.4. Carbon dioxide

Carbon capture, utilisation, and storage represents a crucial approach to achieving carbon neutrality and reducing carbon emissions.[22] Among the various carbon storage methods, geological storage, i.e. the injection of CO_2 into deep underground impermeable salt caverns for disposal, is particularly preferred. By compressing the CO_2 gas into a supercritical state, a density of over 700 kg m^{-3} can be achieved, allowing for injection into underground salt caverns that are highly sealed.[23] That is to say, carbon dioxide is stored as a resource rather than being sealed as waste. It can be released again and transported for further applications, such as alkali plants, oil and gas production sites, if required by the industry. For example, it can be reacted with hydrogen to produce methane gas. The storage of CO_2 on a large scale can be achieved in salt caverns for the purpose of short-, medium- and long-term storage. The feasibility of storing CO_2 in salt caverns has already been studied and analysed based on the experience of compressed air storage in salt caverns.[24] This will become an indispensable part in the regulation of carbon emission peaks and carbon neutrality targets in the future.

1.5. Other fluids

In addition, salt caverns are anticipated to be utilised for the storage of some strategic gases, such as helium. Helium is, after hydrogen, the second lightest and second most abundant element in the universe. However, on the earth, it is a relatively scarce (5.2 ppm in atmosphere) but valuable strategic resource with a diverse range of applications in the aerospace, semiconductor manufacturing, and magnetic resonance imaging. It is well known as the technically best lifting gas in balloons and airships. More specifically, with the lowest boiling point (−268.928 °C) and high thermal conductivity, helium is an excellent "cold" carrier or cold transfer medium. Like heat (or thermal energy), cold (or cryogenic energy) is also an important form of energy that plays a crucial role in some unique energy areas, such as cryogenic cooling for superconductors and nuclear reactor coolant. However, the supply of helium is relatively limited. It is therefore of great significance to ensure the secure storage of helium in order to guarantee national energy security and to facilitate the development of related industries. Due to their unique physical and chemical characteristics, salt caverns represent a promising avenue for helium storage.[25, 26] Obviously, because the amount of helium, even at commercial scales, is far smaller than that of natural gas and CAES, the salt cavern for helium can be much smaller.

Due to their zero or low permeability and inertness to hydrocarbons, salt caverns are also suitable for storage of oils, particularly for strategic purposes, with economic and safety benefits, as large quantities of construction materials are saved in the construction of salt caverns by water solution mining compared to surface oil storage technologies. In addition, the environmental hazards associated with the evaporation of above-ground tanks can be avoided to a greater extent, which also helps reduction of carbon emission.[27]

Compared to natural gas storage in salt caverns, the sealing requirements for oil storage are lower, although the possibility of underground leakage must be taken into consideration. Due to incompressibility, the depth of salt caverns will be preferable for oil storage, and two-well cavern formation technology could enable rapid construction and operation. Oil storage in salt caverns is already in practices in many countries, including both the USA and China.[28] In the USA alone, the reported total oil storage capacity reached beyond 1.1×10^8 m^3 before 1980.[29] The success in oil storage means the potential of using salt caverns as organic or nonaqueous electrolyte containers, which will be discussed in the paper.

2. AME electrolysis for hydrogen production

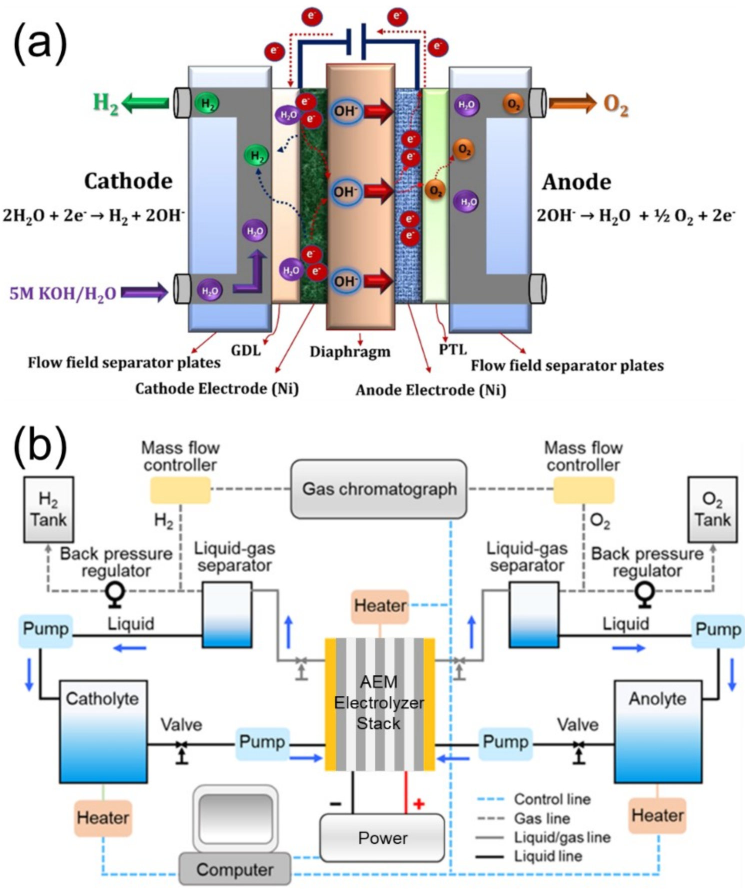

Figure S1. (a) Schematic illustration of the working principle of a single cell AEM electrolyser. Reproduced from ref. [30] with permission from Elsevier, copyright 2022. (b) The workflow diagram of an AEM electrolyser with bipolarly stacked multiple cells. (Redrawn according to Ref.[31] with permission from Elsevier, copyright 2022.)

3. Examples of Commercial Production of Zinc Ion Battery

3.1. http://www.yjgx.gov.cn/zsyz/zsxx/content/post_773767.html (accessed on 29 April 2025, in Chinese). Yangjiang city, Guangdong, China. Government press release on the launch of a 3 billion RMB project for the construction of a zinc ion battery production line with an annual capacity of 5 GWh.

3.2. https://www.enerpoly.com/technology (accessed on 29 April 2025). Enerpoly AB, Sweden. Manufacturer of zinc ion battery.

3.3. https://salientenergyinc.com/ (accessed on 29 April 2025). Salient Energy, Canada. Manufacturer of zinc ion battery.

4. Notes to the Graphic of Table of Contents

Top-left: Two 100 kWh primary stacks with each consisting of 1000 individual 100 Wh cells in serial (upper) or parallel (lower) connections.

Bottom-left: 1000 primary stacks in parallel connection to a 100 MWh secondary stack.

Bottom-right: 5000 secondary stacks in a suitable combination of serial and parallel connections to 500 GWh salt cavern supercapattery for desirable power outputs.

Hand-drawn part on the right: A vision of EES in salt cavern. Adopting the hand-drawn style allows future technological variations from the early-stage vision, while enhancing accessibility to the general public, particularly children who, with suitable adult assistance, may grow such an idea of clean energy innovation in mind, and nurture it to a future reality with their continuous learning and advancement of science and engineering.

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