Electro-thermal technology on pumped heat energy storage system

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Introduction

Current renewable energy technologies have progressed greatly in recent decades to address growing concerns over the harmful effects of fossil fuels and greenhouse gas emissions. Around the world, many nations have taken up the challenge of implementing green or renewable energy to replace their fossil fuel based energy grids and reduce their carbon emissions. The global push for such technologies is due in large part to concerns over global warming and the effects of climate change on human environments, such as rising sea levels, droughts and natural disasters. Examples of such green technologies include, solar farms to harness solar energy in parts of the world where the sun shines often, wind farms to produce electricity from ocean breezes or mountainous winds, or electric vehicles to reduce emissions from petroleum based engines.

A large and looming concern of renewable energy is the storage of energy as pertains to the inconsistent availability of energy throughout the day. Many forms of renewable energies are unavailable at certain times of day, such as solar or wind. Solar panels cannot provide energy at night and similarly, the wind doesn't always blow for wind turbines to produce energy, so it is crucial for energy grids to have a method to store this energy during low periods. However energy delivery systems also need to be wary of high periods and what to do with excess energy when consumers do not require as much energy.[1]

In addition to energy production periods, energy needs are varied throughout the day. For example, an average city requires more energy during the day and at night, when people are working and coming home from work. Energy consumption from computer systems and servers in workplaces and kitchen appliances and televisions at home cause energy consumption rates to be significantly higher during the mid afternoon and evening hours. This issue is a major concern for electrical plants and energy grids who must provide enough electricity to meet their consumer's needs.

The solution for the aforementioned problems is an energy storage system. While energy storage systems currently exist, the need for large scale energy storage has not been as heavy due to the convenience of fossil fuels, being able to produce energy whenever consumers need. However in the face of the global push for energy storage, many energy grids have realized the need for more efficient and larger scale energy storage systems that are also green and sustainable. The main technology of this paper, pumped heat energy storage belongs to this category of renewables research.

Overview of Technology

The pumped heat energy storage system proposed in this paper is not a novel idea, rather it is an engineering innovation instead of a scientific one. The main researcher behind this project is Robert Laughlin, a Stanford professor and Nobel Laureate working in collaboration with Malta, Inc. to develop new storage farms. The technology is all based on 19th century thermodynamics, but has been brought to light due to new innovations in molten salt and steel corrosion resistance.[1]

There are two key points of the pumped heat energy system that make it uniquely advantageous to meet many of the needs of a modern energy grid. They are as follows: the closed nature of the system and the four molten solar salt reservoirs.

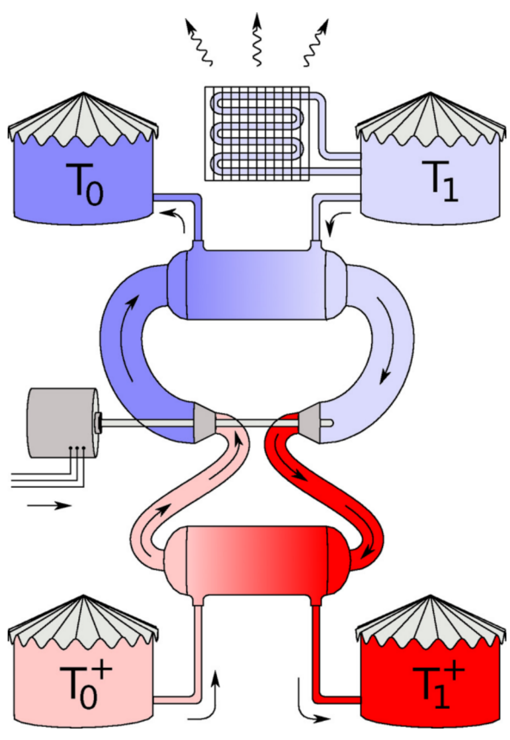

Figure 1. Conceptual Diagram of a Pumped Heat Storage System [1]

The pumped heat energy system shown in Figure 1 is a modified Brayton engine such that it can be used to convert and store energy within a closed system. This is why this system is also known as a Brayton battery. In taking a conventional Brayton engine, and closing the inlet and outlet from the atmosphere, the system's internal pressure can be increased. The current prototyped internal pressure is at about 77 atm, allowing for a higher number of moles of working fluid to pass through a single point, increasing the power for the system.[1] This increased power is part of the reason for the increased efficiency of the Brayton battery over other conventional energy storage systems.

The second unique innovation of the pumped heat energy system is the implementation of molten solar salt as the energy storage medium. The heat capacity of molten solar salt is approximately 3R, or three times the universal gas constant, which is about the same as any substance in this temperature range, however the benefit of this salt is it's low melting temperature.[1] This allows the salt to remain a liquid throughout its functional temperature range. The molten salt used for this system is usually 60% $NaNO_3$ and 40% KNO_3, which is remarkably cheap compared to running the system as a whole.[1] This composition of salts provide excellent properties such as a low vapor pressure compared to water, high compatibility with steel and being environmentally friendly, since it is simply basic salt.[1]

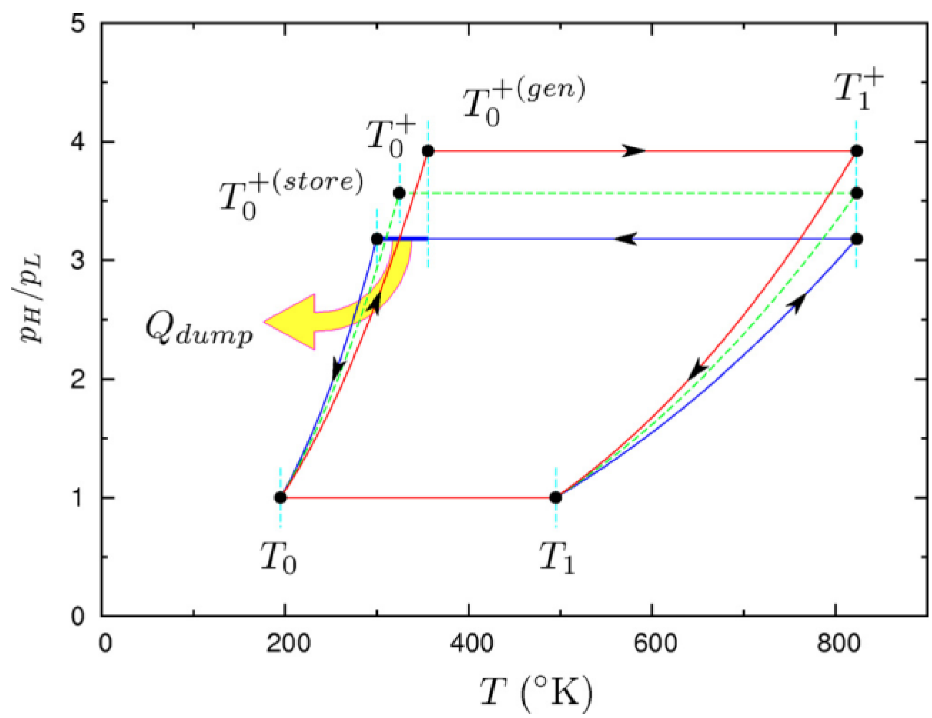

Figure 2. Pressure Temperature Diagram of a Fully Closed Brayton Cycle [1]

In the closed Brayton cycle, energy from plants is redirected into the system via a compressor that raises the pressure of the working fluid, Ar in this case. This compressed Ar transfers its energy via heat transfer fluids such as n-hexane or other hydrocarbons to the thermal reservoirs. [1] Now while it is impossible to maintain a high or low temperature reservoir for extended periods of time without inputting more energy into the system, the connected hot and cold reservoirs maintain their pressure for the duration of storage and so allow for the output of energy later. This high pressure working fluid is then pushed through a turbine and produces energy again. This loss of energy due to the drop in temperature due to storage is the waste energy that is sloughed off into the environment.

$$\eta_{store} < 1 - \frac{T_{dump}}{T_f} \quad \left(\frac{1}{T_f} = \frac{\Delta S}{E_{store}}\right).$$

Figure 3. Round trip efficiency of the storage system [1]

This sloughed off energy is measured as T_{dump} as seen in Figure 3. This is generally the temperature of the surrounding environment. T_f is known as the fictive temperature and is a function of the turbomachinery and sum of the heat transfers that occur inside the system.[1] As a result of this, the fictive temperature can also be defined as the change in entropy over the total energy stored in the system. Since change in entropy multiplied by temperature is equal to energy, the multiplication of T_{dump} and change in entropy is equal to the wasted energy in the system. [1] As a result, the efficiency of the system follows the inequality above, simply being one minus the wasted energy over the total energy stored. According to experimental data, the efficiency of the system generally reaches upwards of 90%. [2]

The advantages of the system as detailed by Malta, Inc. is that the system can effectively hold energy for long periods of time, is low cost and can be effectively scaled up for larger grids. The current scale of the system being developed by Malta is 100 MW, but could be effectively scaled up even more due to the simplicity of the Brayton battery. [2] In addition, the ability for the thermal reservoirs to hold heat, allows for energy to be stored anywhere from 8 to 24 or more hours. Whereas a standard Li battery could only hold energy effectively for 6 hours.[2] The most important advantage to this system, however, is the low cost of running the system. For a 100 MW storage facility, the cost would run at less than $100/KWh. [2]

There are relatively few disadvantages of the system, mainly cost of implementation compared to other renewable energy storage systems, and the research still required to meet the needs of this system, such as the limitations of steel.[1] There are still many challenges to overcome in regards to the implementation of this technology, as will be discussed in the following sections of this report.

	Malta PHES	Li-Ion Battery
Roundtrip Efficiency (e- to e-)	55-65%	85%+
Roundtrip Efficiency (including thermal)	90%+	85%+
Duration	8-24+ hours	0-6 hours
Projected Installed Cost ($/kWh at 10 hrs)	$100-150	$170-250
Economies of Scale	Significant	Limited
Expected Useful Life (Years)	30+ years	10-15 years
Annual Degradation	N✓e	✗
Ability to Decouple Charge-Discharge	✓	✗
OK to Operate at High Ambient Temps.	✓ ✓	✓ ✓
Frequency Response	✓	✓
Reactive Power	✓	✗
Voltage Management	✗	✓
Inertia	✓	✗
Blackstart Capability		
District Heat Applications		
Commodity Risk	None	Li/Co/Rh

Figure 4. Advantages and Disadvantages of PHES Compared to Li^+ batteries [2]

Heat Transfer Fluid

The development of heat transfer fluid started from the common material, water. Its high properties: latent thermal energy, thermal conductivity, specific heat, and density, makes it a very competitive candidate for heat transfer fluid. However, “the practical temperature range of water is much less than 100°C due to the high vapor pressure near the boiling point”. [3] The low range of temperature change cannot store enough thermal energy. Furthermore, the high pressure is needed to keep the water in liquid state, which leads to the high cost related to the pressure vessels and pipes. Therefore, if people want to develop renewable energy, water is not a suitable choice to start from.

Later on, they start to seek for other elements that can raise the temperature, which leads them to think of thermal oil, such as Santotherm 55. [3] Maintaining in a liquid state, thermal oil is able to afford the temperature up to 300°C that satisfies the requirements of the higher range of temperature for heat transfer fluid. Yet, those properties of thermal oil are so unsuitable that there are only limited applications, such as low decomposition temperature, low density, flammability, high vapor pressure, fuming tendency, and low chemical stability. That's how Malta and other prototypes tend to experiment with n-hexane because the cost is low and it is also used in the food industry. The following figure demonstrates the physical properties under different pressure, temperature, and weight.

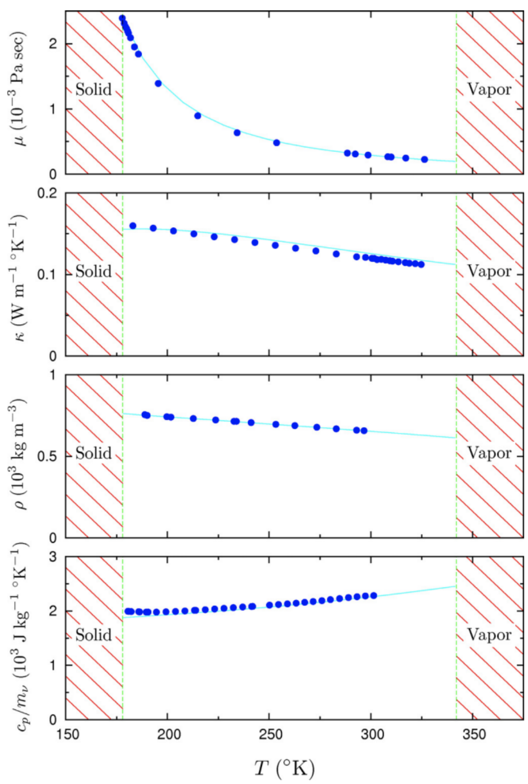

Figure 5. Thermophysical properties of n-hexane: The boiling point and the melting point is 350K and 179K respectively [1]

Molten Salt

From the perspective of a storage medium, molten salt is definitely one of the most commonly used materials. There are many different types of storage systems, but considering the cost, energy density, and the efficiency, molten salt performs remarkably. But what exactly is molten salt? Most people think about table salt - sodium chloride, but the corrosion problem will be severe since the chloride ion is strong. Many salts are being considered and there are even mixtures of those salts to balance the physical properties for storage medium, including chlorides, fluorides, bromides, nitrates and organic salts. The most common salt is the eutectic blend of 60% sodium nitrate ($NaNO_3$) and 40% potassium nitrate (KNO_3), which is also called solar salt. Sodium nitrate has a melting point of 307°C, and potassium nitrate has a melting point of 333°C. By mixing the two together, however, you can create a salt blend with a melting point of 222°C. This significantly expands the operational flexibility of the salt used in high temperature applications. With the large range of temperatures from 285 to 565°C, the storage of thermal energy will become more efficient. [4]

	Max Power Rating (MW)	Discharge time	*Max cycles* or lifetime	Energy density (watt-hour per liter)	Efficiency
Pumped hydro	3,000	4h – 16h	30 – 60 years	0.2 – 2	70 – 85%
Compressed air	1,000	2h – 30h	20 – 40 years	2 – 6	40 – 70%
Molten salt (thermal)	150	hours	30 years	70 – 210	80 – 90%
Li-ion battery	100	1 min – 8h	*1,000 – 10,000*	200 – 400	85 – 95%
Lead-acid battery	100	1 min – 8h	6 – 40 years	50 – 80	80 – 90%
Flow battery	100	hours	*12,000 – 14,000*	20 – 70	60 – 85%
Hydrogen	100	mins – week	5 – 30 years	600 (at 200bar)	25 – 45%
Flywheel	20	secs - mins	*20,000 – 100,000*	20 – 80	70 – 95%
Characteristics of selected energy storage systems (source: The World Energy Council)					

Figure 6. Characteristics of selected energy storage systems (source: The World Energy Council) [5]

Challenge & Improvements

Even though molten salts are efficient and cheap, there are still drawbacks. Firstly, molten salts have relatively high melting points, while this will freeze and block the pipeline during winter evenings. [4] The problem leads to auxiliary facilities needing to be installed, which could increase the investment and operational costs. Applications that use molten salts require heat tracing in all piping and equipment to prevent the salt from freezing. Moreover, salts expand when they re-melt. If the salt is not heated uniformly during the process, it can damage piping, valves and other equipment. As a result, when using a molten salt, it is essential to take care of freezing during operation. The physical properties, such as high viscosity and low thermal conductivity, are also the problem of molten salts that scientists can explore to prevent this issue.

The potential improvement of the specific molten salt is to develop novel eutectic mixtures since the combination of these salts can generate higher order eutectic systems, which lower melting points than that of the binary eutectic temperatures. [6]

	%Weight	Fusion Temperature (°C)	Decomposition Temperature (°C)
	Nitrate-based		
Solar Salt	60 $NaNO_3$–40 KNO_3	240	565
Hitec	7 $NaNO_3$–53 KNO_3–40 $NaNO_2$	142	450
Hitec XL	15 $NaNO_3$–43 KNO_3–42 $Ca(NO_3)_2$	130	450
LiNaKNO3	30 $LiNO_3$–18 $NaNO_3$–52 KNO_3	118	550
LiNaKCaNO3	15.5 $LiNO_3$–8.2 $NaNO_3$–54.3 KNO_3–22 $Ca(NO_3)_2$	93	450
LiNaKNO3NO2	9 $LiNO_3$–42.3 $NaNO_3$–33.6 KNO_3–15.1 KNO_2	97	450
	Chloride-based		
KMgCl	62.5 KCl–37.5 $MgCl_2$	430	>700
NaKMgCl	20.5 NaCl–30.9 KCl–48.6 $MgCl_2$	383	>700
NaMgCaCl	39.6 NaCl–39 $MgCl_2$–21.4 $CaCl_2$	407	650
NaKZnCl	7.5 NaCl–23.9 KCl–68.6 $ZnCl_2$	204	>700
KMgZnCl	49.4 KCl–15.5 $MgCl_2$–35.1 $ZnCl_2$	356	>700
	Fluoride-based		
LiNaKF	29.2 LiF–11.7 NaF–59.1 KF	454	>700
NaBF	3 NaF–97 $NaBF_4$	385	>700
KBF	13 KF–87 KBF_4	460	>700
KZrF	32.5 KF–67.5 ZrF_4	420	>700
	Carbonate-based		
LiNaKCO3	32.1 Li_2CO_3–33.4 Na_2CO_3–34.5 K_2CO_3	397	670

Figure 7. Composition, fusion, and decomposition temperatures for selected molten salt thermal energy storage (TES) materials. [6]

The criteria of being a suitable storage medium needs to possess those characteristics. Specific heat capacity is significant since it controls the capacity of temperature rise, which can be stored in the thermal system, improving the efficiency. Melting temperature is an aspect that when high melting temperature often encounters freezing facilities, while decomposition temperature refers to the maximum temperature to operate and the efficiency has direct relationship with the maximum temperature. Furthermore, thermal conductivity shows the rate of heat exchange, which also relates to efficiency. Viscosity and density are also valuable parameters to be measured. [6]

The most popular materials, nitrate-based salts, are utilized because of the low cost and safety advantage. The small number of corrosion rates on stainless steel is also its strength, but the degradation will often happen when reaching the crystallization temperature. The scientists have conducted experiments showing that If only sodium and potassium nitrates are present, the thermal stability limit is around 600°C, and adding lithium nitrates leads to thermal stability limits lower than 600°C. The degradation depends on many factors such as concentration of chemical elements, atmosphere, humidity, and CO_2 content. [6] For chloride-based materials, owing to the low cost, it has been the candidate of testing. They usually have higher melting points than nitrate salt, but lithium and zinc chlorides provide the lowest melting point with expensive cost. In addition, corrosion is significant since the chloride encourages corrosion of steel. Though using nickel-based helps solve the issue, the cost is not worth it. Thus, chloride-based materials are still being discovered for future applications. Fluoride-based salts are considered to be a potential eutectic system with carbonates that decrease from the original 500°C to about 397°C, but individually, they are not ideal because of the unstable thermodynamics and dissolve in layers.

As an electrolyte, molten salts tend to lead to severe oxidation in high temperatures. Just as discussed above, many of the potential candidates for storage medium have their own strength in specific environments. However, they all tend to have a common problem of corrosion. To retard the phenomenon of corrosion, graphite is a potential improvement. Even though graphite decomposes at a high temperature, the local decomposition will create a protective layer due to carbonate formation at the steel-molten salt interface. [7] Thus, having a small amount of graphite benefits the storage system in the perspective of protection.

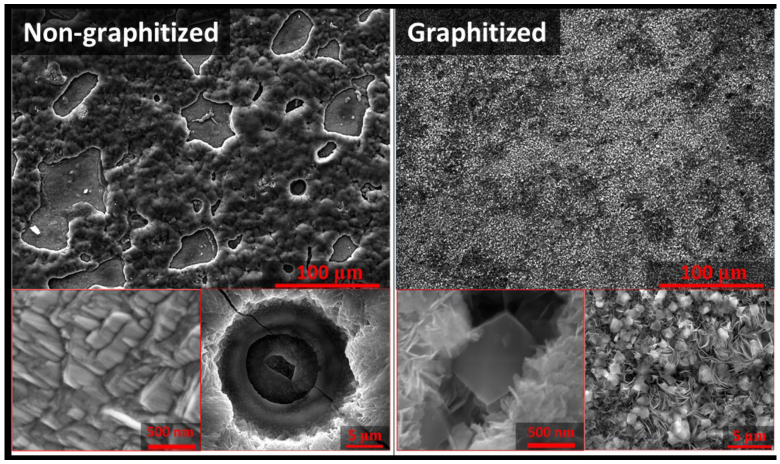

Figure 8. Comparison of graphitized and non-graphitized steel surface [7]

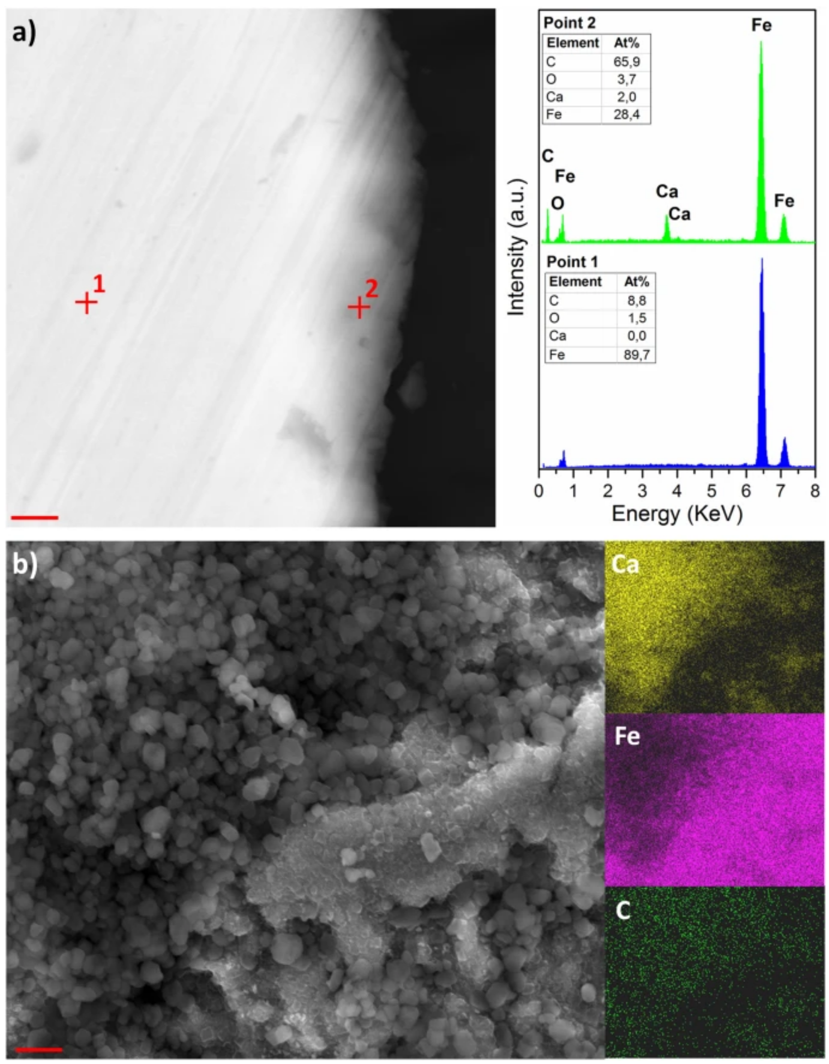

Figure 9. SEM images and EDX mapping of a cross-section (scale bar is 1 µm) and b surface of graphitized carbon steel after 1500 h corrosion test with HitecXL·H2O (scale bar is 2 µm) [8]

To provide new solutions, scientists also propose to use nanoparticles as corrosion solution. This enables diffusion and chemical reactions with construction materials and this results in the formation of a corrosion layer, enhancing stability and preventing diffusion of chromium into the molten salt, which also reduces corrosion rates and material loss. Making it nanoparticles also increases the specific heat capacity, which follows with the rise of efficiency. “Different types and sizes of NPs like alumina, silica, iron, titanium, and copper or zinc were reported to have an enhancement of 31.1% with 0.5%wt of silica NP.” [6] Overall, the discovery of eutectic mixtures is still a long way and still needs to be experimented.

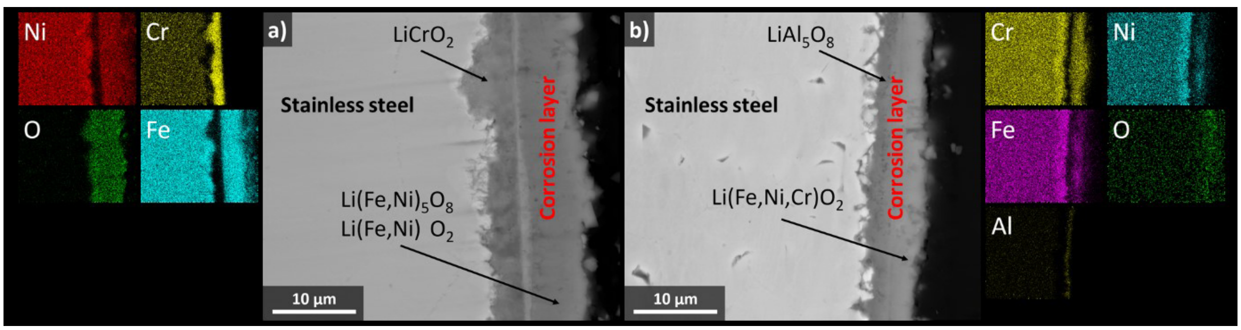

Figure 10. Nanoparticles into corrosion layer [7]

Upon the efficiency that those materials bring, the economic calculation is always the consideration as a lot of materials have the disadvantage of the high cost, while there are three main parameters to show the techno-economic analysis for storage medium: specific mass energy density (E^m), specific volumetric energy density (E^v) and energy storage cost (E^c). [6]

$$E^m = \int_{T_{fus}}^{T_{dec}} c_p dT$$

$$E^v = \int_{T_{fus}}^{T_{dec}} \rho c_p dT$$

$$E^c = \frac{C}{E^m}$$

where T_{fus} and T_{dec} are the fusion and decomposition temperatures (in °C), ρ is the density (in kg/m^3), c_p is the specific heat (in J/kg °C), and C is the cost (in \$/kg) of the molten

Figure 11. Functions for calculating economic parameters [6]

Specific mass energy density quantifies the energy stored within the operation temperature, while volumetric energy density is similar, but easy to solve for the flow rate. In the analysis, the range of the temperature will always be higher and narrower due to safety, including solidification and decomposition.

	Specific Cost $/kg	E^m MJ/kg	E^v MJ/m^3	E $/MJ
		Nitrate-based		
Solar Salt	1.3	0.491	901.1	2.65
Hitec	1.93	0.480	826.9	4.02
Hitec XL	1.66	0.464	928.1	3.58
LiNaKNO3	1.1	0.683	1285.7	1.61
LiNaKCaNO3	0.7	0.542	977.1	1.29
LiNaKNO3NO2	N/A	0.408	764.9	N/A
		Chloride-based		
KMgCl	0.35	0.271	431.3	1.29
NaKMgCl	0.22	0.325	541.6	0.68
NaMgCaCl	0.17	0.289	739.7	0.57
NaKZnCl	0.8	0.447	986.6	1.79
KMgZnCl	1	0.298	553.4	3.36
		Fluoride-based		
LiNaKF	2	0.391	824.1	5.11
NaBF	4.88	0.474	885.4	10.29
KBF	3.68	0.313	833.3	11.75
KZrF	4.85	0.280	750.3	17.32
		Carbonate-based		
LiNaKCO3	2.02	0.448	9912	4.15

Figure 12. Specific cost and energy of selected molten salt TES materials [6]

Compared to solar salt, nitrate-based materials are the most appealing one in terms of specific mass energy density. However, in the aspect of specific volume density, the fluoride-based materials had a slight better performance versus solar salt. Remarkably, the KPI of the chloride-based material does not seem to be a suitable choice, but the specific energy cost is more than solar salts with a reduction of 75%, which encourages it to be the most potential materials for high temperature applications.

Conclusion

Through the explanation of electro-thermal technology on pumped heat energy storage systems and the analysis of the thermal storage medium, we understand the properties that are valuable for being a storage medium. Even though solar salts are widely used nowadays, there are still a large number of eutectic mixtures for scientists to try out and discover the ones that are suitable with properties of high heat capacity, bigger range of temperatures, and high thermal conductivity materials. In general, the technology is still in an early stage of development and the future is full of possibilities, but the choice of materials and the satisfaction of KPIs are essential, so experimenting as many mixtures as possible is precious experience for developing new mediums of storage and establishing a solid basis for renewable energy. In certain circumstances of high temperature, chloride-based materials tend to be the most popular applications owing to the low cost in spite of the lower KPIs. On the other hand, nitrate-based materials tend to be an efficient choice with low melting points and the remarkable KPIs. However, the discovery of new eutectic mixtures always leads to another issue: corrosions. [6]

Bibliography

1. Laughlin, Robert B.“Pumped thermal grid storage with heat exchange”. J. Renewable Sustainable Energy 9, 044103 (2017) https://doi.org/10.1063/1.4994054
2. Bollinger, Benjamin R. ,Ph.D. “Malta Pumped Heat Energy Storage DOE Long Duration Energy Storage Workshop ‘BIG’ Energy Storage: Priorities and Pathways to Long-Duration Energy Storage” (2021) retrieved from https://www.sandia.gov/ess-ssl/wp-content/uploads/2021/LDES/Ben_Bollinger.pdf
3. Reddy, R.G. Molten Salts: Thermal Energy Storage and Heat Transfer Media. J. Phase Equilib. Diffus. 32, 269 (2011). https://doi.org/10.1007/s11669-011-9904-z
4. Patrik Mcmullen, Using Molten Salts as a Heat Transfer Fluid and Thermal-Storage Medium (2016). https://www.process-heating.com/articles/91918-using-molten-salts-as-a-heat-transfer-fluid-and-thermal-storage-medium
5. Amaury Laporte, Fact Sheet | Energy Storage (2019). retrieved from https://www.eesi.org/papers/view/energy-storage-2019
6. Caraballo,A.; Galán-Casado, S.; Caballero, Á.; Serena, S. Molten Salts for Sensible Thermal Energy Storage: A Review and an Energy Performance Analysis. Energies 2021, 14, 1197. https:// doi.org/10.3390/en14041197
7. Yaroslav Grosu, MITIGATING MOLTEN SALTS CORROSION FOR HIGH-TEMPERATURE THERMAL ENERGY STORAGE, retrieved from https://cicenergigune.com/en/blog/mitigating-molten-salts-corrosion-high-temperature-thermal-enerty-storage
8. Grosu, Y., Nithiyanantham, U., Zaki, A. et al. A simple method for the inhibition of the corrosion of carbon steel by molten nitrate salt for thermal storage in concentrating solar power applications. npj Mater Degrad 2, 34 (2018). https://doi.org/10.1038/s41529-018-0055-0