Weekly to Seasonal Energy Storage Technologies

By John Benson

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1. Introduction

Various electrochemical battery energy storage technologies will work to mitigate renewable variability, up to a point. Where that point is depends on the climate when the mitigation is needed and the amount of mitigation (MWh) required in a given event. A large majority of large BESS procured by investor owned utilities in California are lithium-ion batteries with a 4-hour run-time at their rated output. Where I live (California), these battery energy storage systems (BESS) work well to mitigate most of the daily variability that comes with photovoltaic (PV) arrays. However wind-power has variability that is has low-output durations of several days to over a week. Currently there is still enough gas-fired generation to offset the wind-variability, but as this is retired in the future years, it would be good to have more long-term storage options.

Although hydro generation is not normally considered variable, it really is, albeit at longer time-scales than wind. In California we get all of our rain from mid-autumn to late-spring, and virtually no rain in mid-June through mid-October. Late in our dry season small hydro (most is run-of-the-stream) will mostly disappear, and even large-hydro will need to be sharply curtailed in the same period, especially in our frequent drought years.

The flip side of the above hydroelectric variability is that these energy sources have required releases for recreation, wildlife support, to maintain a safe reservoir-level and to fill downstream reservoirs. In wet years, this means releasing water through spillways rather than the hydro generators. As renewable energy generation takes over from fossil-fuel sources, there will be times when over-generation by the former precludes hydro generation, making the need for seasonal storage greater.

There is at least one option for seasonal storage that will be viable by 2030 (covered briefly in section 2 below). It would good to have a few more. There is also a greater need for forms of storage that last days to weeks. This would not only allow wind-intermittency to be backed up, but also provide a source of emergency capacity.

The flip-side of not having enough capacity in an emergency is excess renewable capacity requiring curtailment. Although this happens occasionally currently, these events are increasing in California and Texas: see the chart below (next page).[1]

Note that, although the photovoltaic curtailments are relatively minor now, they appear to be accelerating over time. These are an ideal source of very low-cost energy to be stored over long periods.

I was researching long-term storage recently and identified two existing technologies that might work in the near-term for the above requirements. These are: hydrogen energy storage, converting the green hydrogen to ammonia for longer-term (seasonal) storage. These are reviewed starting on the next page. Two emerging advanced energy storage technologies are reviewed in section 4 and section 5 further below.

[1] Mark Bolinger (LBNL), et al, "Plant-level performance and degradation of 31 GWDC of utility-scale PV in the United States," March 2022, https://eta-publications.lbl.gov/sites/default/files/plant-level_performance_and_degradation_of_31_gw-dc_of_utility-scale_pv_in_the_united_states.pdf

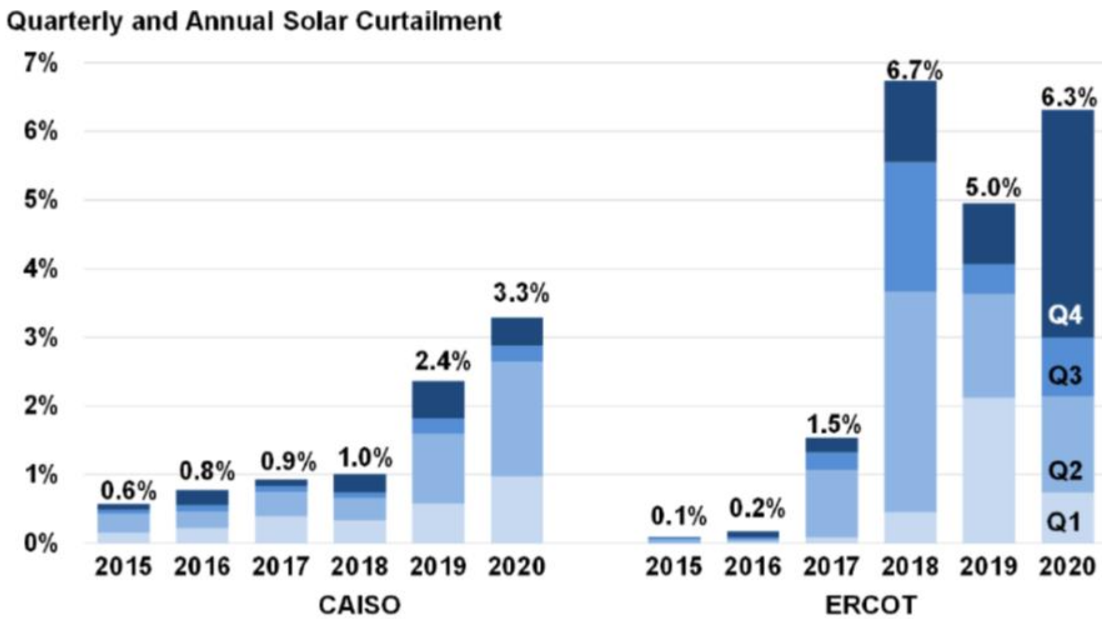


Figure 2. Solar curtailment history in CAISO and ERCOT

2. Hydrogen Energy Storage

I've touched on this in the past, so I will not spend much time on it here. The good news is that we already have most of the infrastructure required for it.

California has about 30 natural gas-fired combined-cycle power plants. Some of these are fast-starting / fast ramping, which is ideal for mitigating both renewable long-term intermittency and providing emergency capacity. But they also emit large amounts of greenhouse gases (GHG). Converting them to burn hydrogen would reduce their emissions of GHG to very near zero. For at least some of them this should be possible by 2030. See sections 2 and 3 of the post linked below:

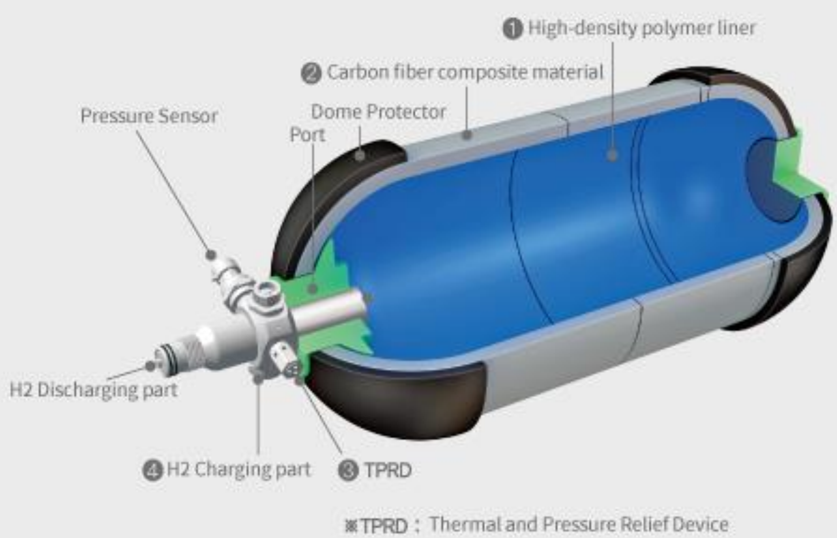
https://energycentral.com/c/gn/reasonable-transition

By using renewable electricity that would otherwise be curtailed to generate green hydrogen using electrolyzers, the price of this fuel should be reasonable. This would, of course require a storage facility. The simplest storage facility is currently a cluster of high-pressure storage tubes, see figures below (next page).[2]

I have seen hydrogen storage tubes rated up to 1,000 bar (14,500 psi).[3] Converting an existing combined-cycle power plant to 100% hydrogen fuel, adding an electrolyzer and hydrogen storage will create a hydrogen energy storage system. The cost of producing green hydrogen is coming down over time – see the post linked below.

https://energycentral.com/c/cp/economics-green-hydrogen

[2] Figure above from https://news.microsoft.com/innovation-stories/hydrogen-datacenters/ ,
[3] See https://www.tenaris.com/en/products-and-services/low-carbon-energy/hydrogen-storage-systems/?msclkid=796e3b9bc25911ecb4a4e5d22048c844



TPRD = Thermally Activated Pressure Relief Device

Credit : Process Modeling Group, Nnclear Engineering Division.
Argomme National Laboratory (ANL)

3. Ammonia Energy Storage

The text immediately below is from an earlier post.

Ammonia (NH_3) is a potential future hydrogen carrier. However producing ammonia does have a down-side. The most popular industrial process, the Haber-Bosch process, is extremely energy-intensive. This process is shown below:[4]

$N_2 + 3\ H_2 \rightarrow 2\ NH_3$ *ΔH° (change in enthalpy) is -91.8 kJ/mol*

The Haber–Bosch process is a reaction between hydrogen and nitrogen at an elevated temperature (840 °F) and high pressure (1,500 psi). The reaction, which happens in a special pressure vessel, disrupts the conditions required for the reaction, so it must be continually cycled, making it more expensive.[5]

Reasons that ammonia is being considered as a hydrogen carrier include: (1) it has a higher volumetric efficiency than other carriers (even liquid hydrogen), (2) cracking it to liberate the hydrogen does not produce undesirable byproducts (like GHG), (3) the cost of renewable energy has become the least expensive energy and its price continues to decrease (making the cost of making and cracking ammonia less expensive) and (4) under some conditions ammonia can be directly combusted (thus used in combustion turbines) or used in fuel cells, with only water vapor and nitrogen as byproducts.

By using the excess energy that is currently being curtailed (see Introduction) for both green hydrogen generation and conversion to ammonia, long-term storage of ammonia requires much lower pressures than hydrogen (less than 100 bar / 1,450 psi). Ammonia can either be converted back to hydrogen or combusted directly.[6]

4. Thermophotovoltaic Energy Storage System

Just as solar cells generate electricity from sunlight, thermophotovoltaic cells do so from infrared light. Now, in a new study, scientists have revealed thermophotovoltaic cells with a record-high conversion efficiency of more than 40 percent, better than the average turbines used to generate power in the United States. These findings could help enable grid-scale thermal batteries for renewable energy, which could help make power grids carbon-free, the researchers say.[7]

The way in which most power plants generate electricity is with turbines. In a turbine, a fluid such as steam is driven by, say, the heat from combustion, nuclear energy, or solar heat to spin the rotor shaft of a generator, which converts the kinetic energy of the fluid to electricity.

The average efficiency of turbine-based power generation in the United States is less than 35 percent, says study lead author Alina LaPotin, a mechanical engineer at MIT.

[4] "A journey of a thousand miles…" Sep 2020, https://energycentral.com/c/ec/journey-thousand-miles%E2%80%A6

[5] Wikipedia article on Ammonia, https://en.wikipedia.org/wiki/Ammonia

[6] Wikipedia Article on Ammonia, see "Applications / Other / Fuel," https://en.wikipedia.org/wiki/Ammonia

[7] Charles Q. Choi, IEEE Spectrum, "Generating Electricity From Heat With No Moving Parts," April 10, 2022, https://spectrum.ieee.org/thermophotovoltaic

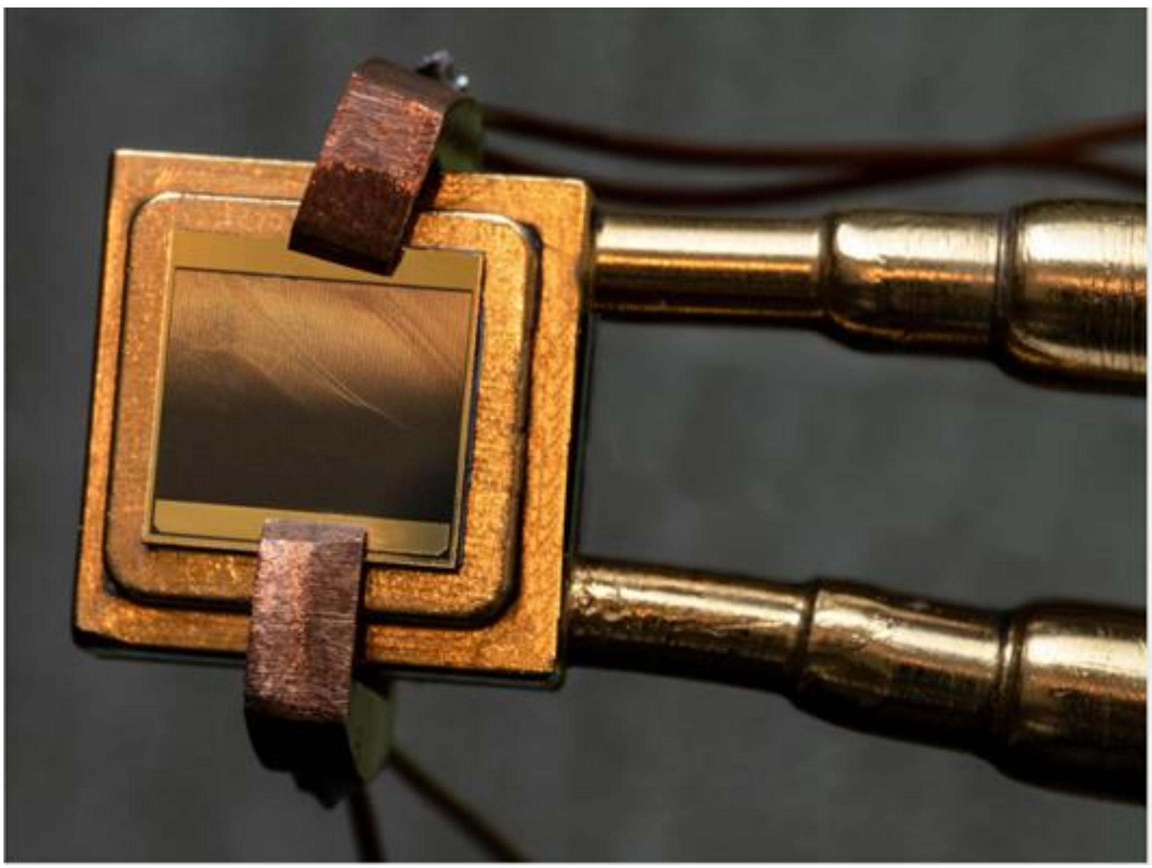
However, turbine costs and performance have reached full maturity, so there are limited prospects for their future improvement.

"A turbine-based power production system's cost is usually on the order of US $1 per watt. However, for thermophotovoltaics, there is potential to reduce it to the order of $0.10 per watt."

—Asegun Henry, MIT

In contrast, thermophotovoltaics are very early in their progress, and so may have numerous prospects to improve their efficiency and costs, LaPotin notes. For instance, whereas turbines depend on moving parts that can melt when they get hot enough, thermophotovoltaics are solid-state devices that can operate at higher temperatures, which can unlock a variety of benefits.

Scientists first created thermophotovoltaics with efficiencies of 29 percent roughly 40 years ago. However, despite predictions that their efficiencies would exceed 50 percent, for decades their efficiencies reached only as high as 32 percent.



This Thermophotovoltaic (TPV) cell, developed by a team of engineers at MIT. Has exceeded 40% efficiency in converting heat to electricity - FELICE FRANKEL

In the new study, the researchers experimented with thermophotovoltaic materials optimized for emitter temperatures of 1,900 to 2,400 °C and emitting infrared photons with energies between 1 and 1.4 electron volts. These single-photon energies are higher than those explored by previous thermophotovoltaic research, with the aim of avoiding efficiency-reducing voltage losses seen with thermophotovoltaics that exploit lower-

energy infrared photons. The present study also targets higher temperatures than those of prior thermophotovoltaics. The rule of thumb in this case, LaPotin says, is that the greater the temperature, the higher the power density of the devices and the lower their cost in relation to the power they generate.

The scientists also boosted the efficiency of their devices with highly reflective back surfaces that bounced lower-energy infrared photons back at the emitters. These reflected photons go on to heat the emitters, allowing them to emit the higher-energy infrared light that's more useful for the new thermophotovoltaics…

The efficiency of these devices can increase to more than 50 percent with better reflectors, the researchers say. A reflector in a study from another group in 2020 attained reflectivity of more than 98 percent. Combining such a reflector with the new thermophotovoltaics could lead to efficiencies of more than 56 percent at 2,250 °C, or more than 51 percent on average over a range of 1,900 to 2,400 °C, the scientists say.

With researchers at the National Renewable Energy Laboratory, Henry's team laid down more than two dozen thin layers of different semiconductors to create two separate cells stacked one on top of another. The top cell absorbs mostly visible and ultraviolet photons, whereas the lower cell absorbs mostly infrared. A thin gold sheet under the bottom cell reflects low-energy photons the TPVs couldn't harvest. The tungsten reabsorbs that energy, preventing it from being lost. The result, the group reports this week in Nature, is a TPV tandem that converts 41.1% of the energy emitted from a 2400°C tungsten filament to electricity.[8]

A key potential application for these new thermophotovoltaics is a grid-scale thermal battery. Such a system would absorb surplus electricity from renewable sources such as the sun and store that energy in heavily thermally insulated banks of a material such as silicon or graphite. When that energy is needed, thermophotovoltaic cells would convert this heat into electricity and dispatch the energy on demand to a power grid.[7]

"Thermal batteries are great applications for thermophotovoltaics because they need to be done at bigger scales to make the system efficiency equal to the device efficiency," Henry says.

Although such thermal energy-grid storage was initially conceived with molten silicon as the thermal battery material, graphite would prove even cheaper at roughly $0.50 per kilogram, resulting in a projected capital cost of less than $10 per kilowatt-hour…

"I think the most important implication is that thermal batteries can move forward to commercialization, even with the current cell performance we demonstrated here," Henry says.

The devices in the new study are about a square centimeter in size. For a grid-scale thermal-battery system, Henry envisions thermophotovoltaic cells roughly 1,000 square meters in size operating in climate-controlled warehouses…

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[8] Robert F. Service, Science, "Thermal batteries could back up green power," April 15, 2022, https://www.science.org/content/article/thermal-batteries-could-efficiently-store-wind-and-solar-power-renewable-grid

5. Molten-Salt Battery Freezes Energy

OK you have a rechargeable battery, any type of battery, and you charge it up to 100%, and you disconnect it. What happens to the energy in it? The answer, something called a self-discharge mechanism immediately starts to erode the energy. The speed of this depends on the battery technology. For Lithium-Ion batteries, it's pretty slow. *The self-discharge reaction occurring inside a lithium-ion battery is very complicated. The self-discharge rate of lithium-ion batteries is generally 2% to 5% per month.*

When an irreversible reaction occurs inside the battery, the resulting capacity loss is irreversible, mainly including:

1) Irreversible reaction between positive electrode material and electrolyte

It mainly occurs in two materials that are prone to structural defects, such as lithium manganate and lithium nickelate…

2) Irreversible reaction between anode material and electrolyte…

3) Irreversible reactions caused by impurities in the electrolyte itself…

These reactions irreversibly consume lithium ions in the electrolyte, resulting in battery capacity loss.[9]

But what if there was a way you could stop (or really slow down) self-discharge?

A recent study from the Pacific Northwest National Laboratory (PNNL) looks at molten-salt batteries that can "freeze" their charge for months until required. In their proof of concept, the researchers reported that the battery retained 92 percent of its capacity over three months. "We have some test cases ongoing for six months at this time," says Minyuan "Miller" Li, first author of the study. He expects the battery to retain over 80 percent of its charge in that period.[10]

Molten-salt batteries, as the name implies, use a liquid, molten-salt electrolyte, which freezes at room temperature, allowing the batteries to be stored in an inactive state. When activated, the cathode, anode, and electrolytes separate, with the molten electrolyte serving as a highly conductive medium for ionic exchange.

Batteries are generally unreliable for seasonal or long-term storage because they discharge when unused. However, in the PNNL team's demonstration, the freeze-thaw mechanism of the molten salt is able to circumvent that problem. They used nickel and aluminium as materials for the cathode and anode, respectively, with sodium aluminium tetrachloride ($NaAlCl_4$) as the molten-salt electrolyte—all relatively cheap, earth-abundant materials. This electrolyte has a melting point of around 157 ºC, and remains solid over a large spectrum of room temperatures.

"We want to charge this battery when renewables are abundant," explains lead researcher Guosheng Li, "and then we're going to keep the battery at ambient temperature, which will freeze [it]…and shut off the self-discharge for long storage."

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[9] Apogeeweb, "What is the Self-discharge of Batteries?" Oct 25, 2018, https://www.apogeeweb.net/article/1986.html

[10] Payal Dhar, IEEE Spectrum, "Molten-Salt Battery Freezes Energy Over a Whole Season," April 15, 2022, https://spectrum.ieee.org/long-term-energy-storage-molten-salt

When it's time to use the battery, he continues, there are a few different ways to heat it up. For example, "we can use waste heat, or…activate some of the battery in the beginning and then use that electricity to self-heat."

To demonstrate their concept, they built a relatively small, hockey-puck-size battery. But Li doesn't see any impediments to scaling up for practical use, given that the materials are easy to source. Even so, he says, "we know [these are] probably not the best materials, [so] our next target is to replace nickel with a lower-cost material."

Iron is one of the alternatives they are considering, as well as looking at other options for the electrolyte. The current melting point of 157 ºC of $NaAlCl_4$ *is higher than the researchers would like. "For future research, we are geared towards low-cost materials as well as relatively low operating temperature, but still above the ambient temperature," Li says. "We want to freeze the electrolyte at ambient temperature, right? So around 70 or 80 degrees [freezing point] would be ideal, which means we don't need to so much heat the battery to 180 degrees [as in the study]."*

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Authors comment: I assume the "…70 to 80 degrees…" and the "…180 degrees… directly above are degrees Celsius based on the context.

The PNNL team are trying to target a 2030 to 2035 time frame for commercial application, particularly for use in systems that are deployed and operational. A long road, in other words, lies ahead. As Li points out, this proof of concept was just to see if the technology was possible. "If we can perform a more elegant experiment, I do believe we can [bring down] the temperature, maybe to right above room temperature…and save a lot of energy."

Apart from bringing down operating temperatures and replacing the core with lower-cost materials, there are other challenges that the researchers feel will become more visible as they scale up. An important one, Sprenkle adds, is understanding the value of that stored energy. "A large part of our value is just resiliency… [and] we have difficulty accurately valuing resiliency… So there are some broader policy questions that come into play that are out of our control [but] still need to be addressed."