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Sector Review

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Liquid Battery Technologies

An Impending Deluge?

Liquid batteries

An Impending Deluge

- + The classic pumped hydroelectric storage application is energy accumulation on an epic scale to deal with the nighttime lows in energy demand and has achieved wide acceptance around the world
- + The last decade has seen major advances in utilising molten salts in liquid metals batteries for energy storage in grid (and off-grid) applications
- + The new technologies offer the potential to provide high-value new usages for Antimony, Lithium and Bismuth (and benefits for Tellurium), and even for Lead
- ✘ Corrosion remains an issue that academics are grappling with
- ✘ Antimony supplies are finite and constrained and greater usage would likely surge prices and maybe price out storage applications
- ✘ Bismuth supply is currently dominated by China

Conjuring with Liquids

Battery technologies have been proliferating in recent years like mushrooms after the rain. Despite this there are batteries and batteries. Many of the newly invented storage devices have specific usages and one new application is not necessarily a replacement for an existing type of battery. Unfortunately most parents still have reason to curse the ubiquitous *Double A* batteries that power Christmas gifts for children and never seemed to have an up-to-date, cost-effective or long-lasting alternative. Once a rip-off, always a rip-off.

Most of the buzz in the mainstream media is about battery options that extend the life of cellphones or laptops and other PDAs or with regard to hybrid or electric vehicles. However the really great economic leap forward has to do with mass storage devices which mesh with energy grids to provide off-peak storage of electricity. Industrial or natural gas has been stored since its inception in the industrial revolution in massive tanks, caverns or gasometers, while a solution to massive electricity storage has been much more elusive. With conventional dry-cell battery using two electrodes separated by an electrolyte, it would require thousands of individual cells, the size of soft drink cans, to be strung together in a massive installation to create a mass storage battery of any usefulness to be attached the grid.

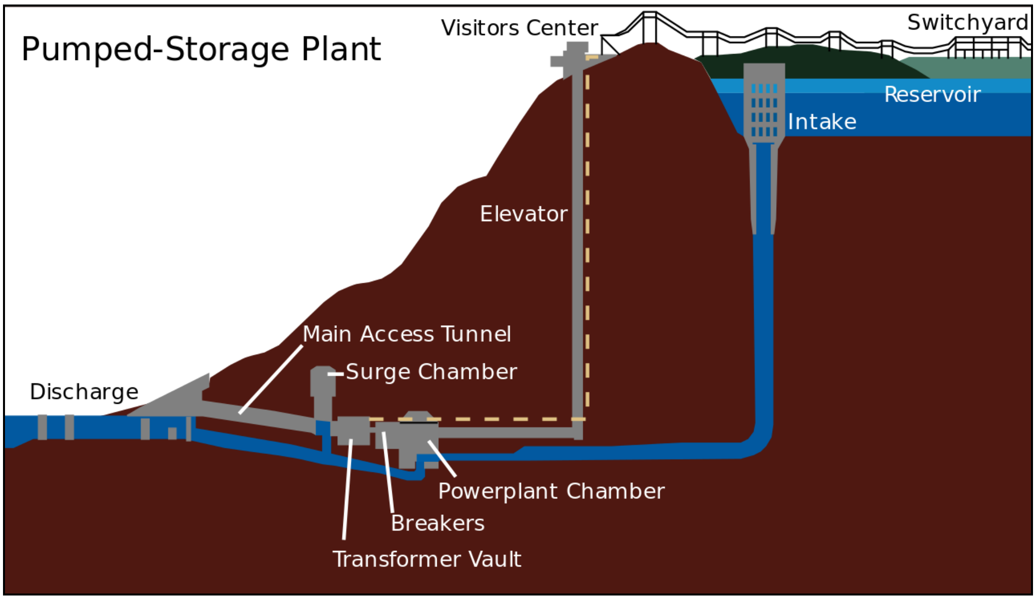
The relevance of this has been heightened with the burgeoning of alternative energy sources (wind and solar) that are irregular in their generating periods and do not always coincide with peak demand.

Mass Storage Devices

The important consideration is that mass storage devices do not even need to be connected to the grid and thus can be in the middle of nowhere bridging the infrastructure gap (and cost) that weighs on emerging economies (and isolated minesites).

In recent years the principal mass storage device we have concerned ourselves with has been the Vanadium Radox battery with its shipping container-sized housing. This is a very real and efficient alternative for those isolated locations we mentioned.

When one goes beyond the physical "battery", the only widely used system for utility-scale storage of electricity is pumped hydro, in which water is pumped uphill to a storage reservoir when excess power is available, and then flows back down through a turbine to generate power when it is needed.



One mine developer we are acquainted with, King Island Scheelite (KIS.ax) has a Tungsten project on an isolated island between the Australian mainland and Tasmania. They had mentioned this storage method as a way they were considering of using the abundant (yet erratic) wind source at the location to make electricity (from pumping seawater uphill to a dam) and thereby liberating their project from dependence upon expensive imported diesel. The dam is essentially a big battery.

Therefore pumped hydro can be used to match the intermittent production of power from irregular sources, such as wind and solar power, with variations in demand. Because of inevitable losses from the friction in pumps and turbines, such systems return about 70% of the power that is put into them This "round-trip efficiency" may not be ideal but considering that the power source if "free" it is indeed a viable option.

And then there are liquid metal batteries…

Molten Salts

One of the greatest remaining challenges is storing electricity that interacts with the grid. The latest technology to grapple with this issue is the liquid metal battery with relies upon the field of the study of molten salts. The origin of using these salts for storing energy goes back to the Second World War.

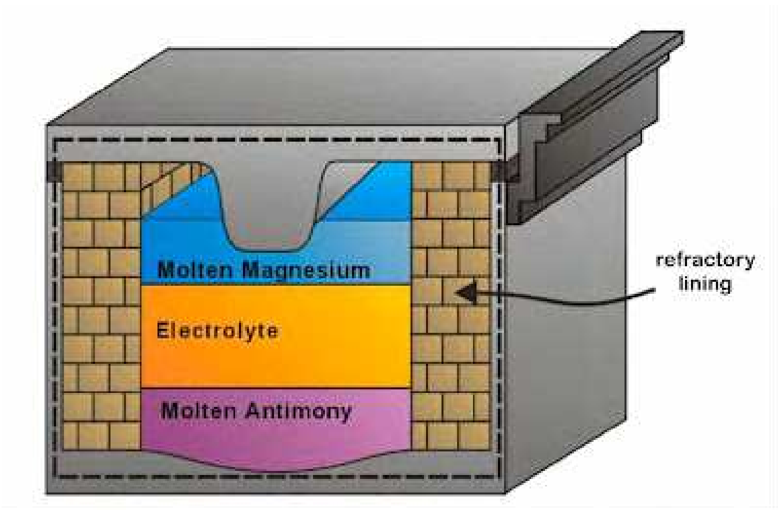
Molten salt is salt which is solid at standard temperature and pressure but enters the liquid phase due to elevated temperature. A salt that is normally liquid even at standard temperature and pressure is usually called a room temperature ionic liquid, although technically molten salts are a class of ionic liquids.

Liquid Metal Batteries (LMBs)

Liquid metal batteries use an electrolyte that is solid and inactive at ambient temperatures. They can be stored indefinitely (over 50 years) yet provide full power in an instant when required. Once activated, they provide a burst of high power for a short period (a few tens of seconds to 60 minutes or more), with output ranging from watts to kilowatts. The high power is due to the high ionic conductivity of the molten salt, which is three orders of magnitude (or more) greater than that of the sulphuric acid in a Lead–acid car battery.

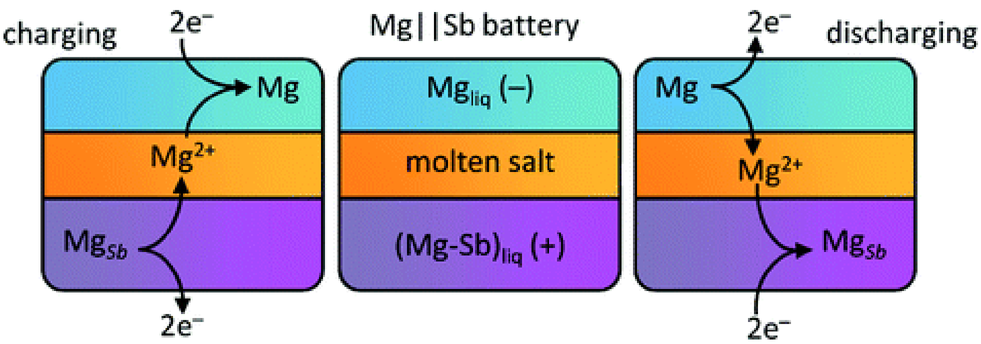
It seems most new battery innovations emerge from academia rather than commercial R&D. Researchers at MIT (led by Professor Donald Sadoway) have been working on a liquid battery system that could enable renewable energy sources to compete with conventional power plants. The research has been funded to the tune of $15mn by the likes of Bill Gates, energy giant Total, the US Department of Energy's Advanced Research Projects Agency and Khosla Ventures (run by Sun Microsystems co-founder Vinod Khosla).

The MIT team's Mg||Sb liquid metal battery is comprised of three liquid layers (as shown at right) and operates at 700 °C.



During charging, Mg is electrochemically extracted from the Mg–Sb alloy electrode and deposited as liquid Mg on the top (negative) electrode. During discharging, the Mg electrode is consumed, and Mg is deposited into the Mg–Sb liquid bottom (positive) electrode. During charging, the battery consumes energy and upon discharge, the battery supplies energy.

The schematic that follows shows a Mg||Sb liquid metal battery and the chemical reaction between the different elements and how it first stores then releases the charge.



Source: Bradwell et al.

The music to our ears in all this is the use of Antimony, and seemingly in quantity, thus providing an important new application for the metal.

The Innovation

The more recent MIT battery design substitutes different metals (mainly Lead and Lithium) for the molten layers used in the team's previously developed battery with a strong Magnesium component.

The latest iteration involves a Lithium/Antimony/Lead liquid metal battery comprising a liquid lithium negative electrode, a molten salt electrolyte, and a liquid Antimony/Lead alloy positive electrode, which self-segregate by density into three distinct layers owing to the immiscibility of the contiguous salt and metal phases. The difference in composition between the two liquid metals gives rise to a voltage.

Their latest formula replaced the Magnesium with Lithium and allowed the battery to work at a temperature more than 200 degrees Celsius lower than the previous formulation. The all-liquid construction confers the advantages of higher current density, longer cycle life and simpler manufacturing of large-scale storage systems (because no membranes or separators are involved) relative to those of conventional batteries.

The researchers found that while Antimony could produce a high operating voltage, and Lead gave a low melting point, a mixture of the two combined both advantages. In addition to the lower operating temperature, which should simplify the battery's design and extend its working life, the new formulation will be less expensive to make. However when they make that comment it leaves us wondering whether they are factoring in how much Antimony, which has a delicate supply/demand balance might rise if suddenly a new application that absorbs more metal starts to get traction.

Reports of the extensive testing indicate that even after 10 years of daily charging and discharging, the system should retain about 85% of its initial efficiency. This would be a major attraction for electric utilities, who have been largely watchers, rather than initiators, in new battery technologies. The MIT team has speculated that it may be possible to build giant batteries using 50-100 fewer individual cells this way, than would be possible with a conventional battery array, reducing cost and complexity.

The Cost Benefits

The use of Sb as the positive liquid electrode in a liquid metal battery offers a low-cost chemistry, below the threshold cost required for broad-scale adoption of a large-scale electricity storage technology. *Bradwell et al.* in their paper noted that Antimony could potentially drop the cost of the active components by a factor of five (Table S3), while providing similar voltages for analogous chemistries.

Bradwell offered a summary of the candidate electrode material costs and world reserves. The price data though is somewhat old from 2012 information collected from USGS Mineral Commodity Summaries.

Metal	Electrode	Cost ($/kg)	Cost ($/mol)	World reserves (10^3 tons)
Li	negative	65[13]	0.4	9,900
Na	negative	1.6[14]	0.04	>1,000,000
Mg	negative	5	0.13	>1,000,000
Bi	positive	24	4.4	330
Te	positive	150	19	21
Sb	positive	7	0.74	2,100

Some of these metals are now even cheaper than they were then. It is interesting to note the potential usages for Bismuth and Tellurium as well.

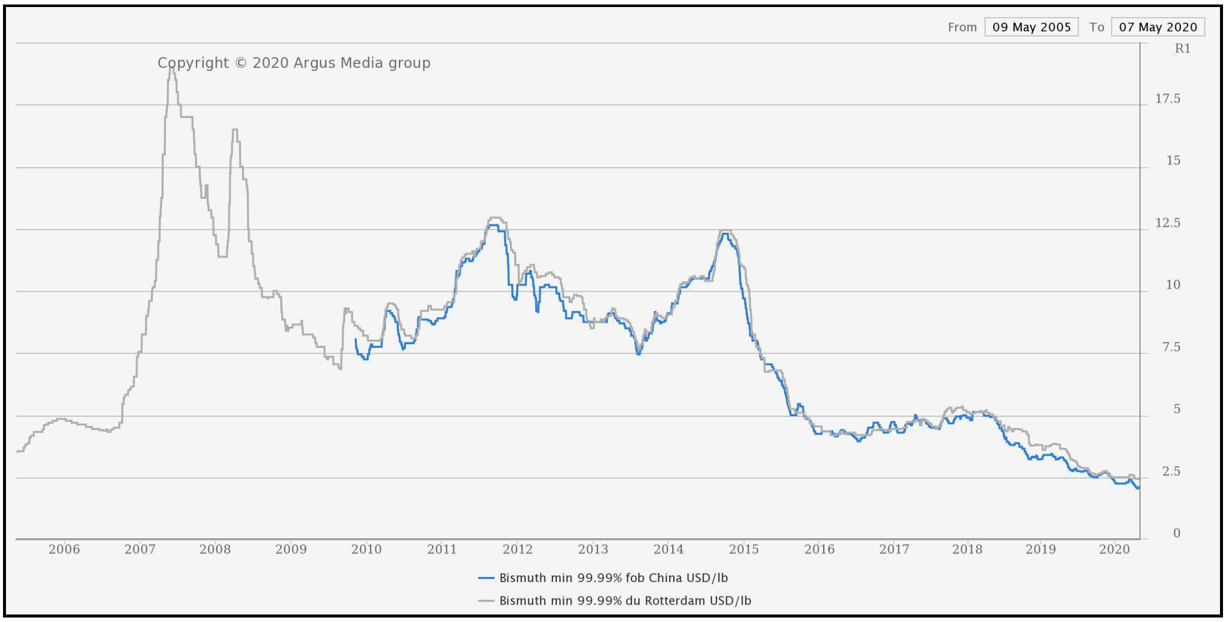
Inexpensive molten chloride salts, such as $MgCl_2$, KCl, and NaCl are suitable as the electrolyte, providing high conductivity, a suitable density and liquid range, and stability with reactive metals.

The Lead-Bismuth Option

The high operation temperature, caused by the high melting temperature of both the molten salt electrolyte and metal electrodes in some of the examples mentioned, can induce critical issues related to the maintenance cost and degradation of electrochemical properties resulting from the thermal corrosion of materials.

A team of South Korean researchers, led by Junsoo Kim, proposed a new liquid metal battery format focused on Bismuth and Lithium, with a chemistry of a LiCl-LiI electrolyte and a Bi-Pb positive electrode to lower the operation temperature of Li-based LMBs and achieve the long-term stability. The cell (Li|LiCl-LiI|Bi-Pb) is operated at 410 °C (much lower temperature than the Magnesium model) by employing the LiCl-LiI electrolyte and Bi-Pb alloy positive electrode. In their study the cell shows excellent capacity retention at 86.5%.

This might provide a new usage for the seldom talked about metal, Bismuth. Global bismuth mine production (largely as a by-product of lead/zinc mines) was around 10,700 tons by 2018. China holds nearly 65% of the bismuth reserves and continues to dominate the global market accounting 75% of the global bismuth consumption.



Source: Argus Metals

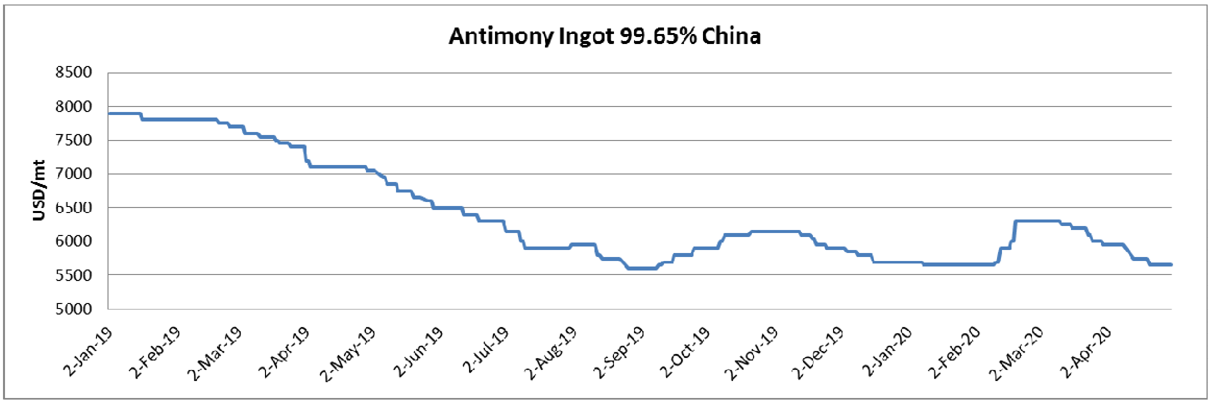
The price of this metal has never recovered since its 2008 highs and it could do with some more applications to enhance its demand picture.

Antimony - Let the Benefits Flow

The liquid metal battery finds new uses for two of metals of interest to us, Antimony and Lithium. The former, in particular could do with attracting more innovative uses.

We are well-known as unalloyed (pardon the pun) fans of Antimony but it must be admitted that while in a critical supply situation (which puts it near the top of most strategic metals rankings) the applications for Antimony are scarcely "high-tech" in the way Rare Earths are. The main traditional use was as a hardening alloy with lead in bullets and ammunition as lead batteries. The newer innovation was as a fire retardant, but there has been scarcely any new application of note for several decades.

The price of Antimony has been battered in recent years with 2019 being particularly poor as a nascent recovery in the preceding year was nipped in the bud by the EU's odious REACH program casting aspersions against Antimony on safety grounds.



Source: Argus Metals

Meanwhile, Chinese production of the metal continues to decline due to over-exploitation and it has come increasingly to rely on supplies generated by its neo-colonialist efforts in Burma. All this achieves is to run down that source even more rapidly than would normally be the case for a well-priced and well-husbanded resource.

Conclusion

One might view technically pumped energy as just one gigantic "liquid battery", but that is obviously not what the scientists are proposing here. VRBs have become a well-rehearsed discussion for energy storage and Elon Musk would have us believe that superannuated Tesla batteries have a "life after death" but we remain unconvinced on the latter.

If Liquid Metal Batteries become the killer application in grid-linked storage (or non-grid linked) then it adds further feathers to the cap of Lithium, adds a bit of spice to the eternally balanced and unpromising Lead scene and potentially lights a fire under Antimony demand and pricing.

The issue though is the availability of metal supplies. Lithium seemingly has a supply situation with little in the way of constraints for a long way out. Lead has ongoing production and also conventional Lead-Acid battery recycling as a source. Antimony though does have a finite supply at the moment and more likely a switch to using this metal, even in a limited way, would light a fire under currently depressed prices. If it rose too high (for instance over $12,000 per tonne) then it might choke off demand or usage as Vanadium did with its "own-goal" in 2018 when its price shot too high, too fast.

To mix some metaphors, molten salt batteries have flown under the radar thus far but definitely have a place in the evolving battery universe and hopefully will take the Antimony (and maybe Bismuth) market along for the ride.

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