Zinc as versatile battery material for energy storage applications

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Zinc is a versatile, abundant, sustainable, safe, and very promising energy storage material that can be utilized in a wide variety of applications powered by zinc-based battery technologies. From small, printed, flexible batteries for sensors, to backup power batteries for data centres, to long-duration storage for commercial and industrial, residential and the electricity grid, zinc is increasingly likely to play a major part in future of the clean energy transition.

Zinc's history as battery material goes back more than 200 years to when Alessandro Volta built the world's first battery in 1799 (Fig. 1). The first primary battery, the Leclanché cell, was described by the French scientist, Georges Leclanché, in 1868. The first secondary zinc-bromine battery was patented in 1885, and the father of electricity Thomas Edison patented a nickel-zinc battery in 1901. The modern alkaline battery with pelletized cathode on the outside in contact with the battery canister and a center gelled zinc powder anode was introduced by K. Kordesch, P. Marsal and L Urry in 1960 (US Pat. 2,960,558).

Despite the phenomenal success of applying zinc in household primary batteries such as AA, AAA, C and D size for everyday use, they have not fulfilled their potential in secondary (rechargeable) battery applications due to challenges of short lifespans. Rechargeable technologies, such as the old lead acid battery, nickel cadmium, nickel metalhydride and then lithium-ion have been the chemistries of choice.

Fig. 1: Volta battery, at the Tempio Voltiano museum in Como, Italy.

With the advent of the electric vehicle (EV) revolution, the demand for lithium-ion batteries has skyrocketed, and the industry has realized that not everything can run on lithium, as there is a serious supply shortage on the horizon due to resource scarcity. Hence, various companies and research groups have taken on the challenges related to recharging zinc-based batteries over the last decade, and zinc battery developers have innovated their way around these challenges and are poised to compete effectively in the emerging energy storage market for the renewable energy transition.

A brief chemistry refresher demonstrates how zinc reacts in different electrolytes. For alkaline electrolytes, the simplified anodic discharge reaction is shown in equation (1) with its associated standard electrode potential E^0.

$$Zn + 2OH^- \rightarrow ZnO + H_2O + 2e^- \quad E^0 = -1.248\ V \qquad (1)$$

During charge, these reactions reverse. Equation (1) is a simplified reaction mechanism; it only shows the beginning state and the end state of the reaction. In reality, what happens in the initial discharge phase is the formation of soluble zincate ions described in equation (2), which will precipitate to zinc oxide once zincate saturation of the electrolyte is reached as shown in equation (3).

$$Zn + 4OH^- \rightarrow Zn(OH)_4^{2-} + 2e- \qquad (2)$$

$$Zn(OH)_4^{2-} \rightarrow ZnO + 2OH^- + H_2O \qquad (3)$$

Unlike for alkaline electrolytes, the anodic discharge reaction in a nearly neutral to mildly acidic electrolyte is simpler as shown in equation (4) with its associated standard electrode potential E^0.

$$Zn^- \rightarrow Zn^{2+} + 2e^- \qquad E^0 = -0.76\ V \qquad (4)$$

During the discharge process, no insoluble zinc oxide will form. Therefore, only reversibly stripping/plating of Zn^{2+} ions on the surface of the Zn anode will occur during the discharge and charge processes.

Zn metal electrodes in mild aqueous systems have an operating principle similar to Li metal electrodes in lithium-ion batteries. The key challenges of secondary (rechargeable) zinc batteries with alkaline electrolytes in the past have been the zincate solubility, shape change, gassing, dry-out, capacity loss and dendrite formation, which resulted typically in associated capacity fade and a limited cycle life. The aforementioned new research has led to a new breed of secondary (rechargeable) zinc batteries that have overcome these old problems with innovative solutions. The issue of shape change, capacity loss and dendritic growth has been resolved by applying engineered negative electrodes containing nucleation and migration stabilisation additives that work symbiotically with novel electrolytes to stabilise the zincate ion. The dry-out problem has been overcome by integrating gassing suppressant additives into the negative electrode and incorporating recombinant devices into the battery that facilitate the recombination of oxygen and hydrogen formed from the decomposition of water.
Another novel approach in development is the use of a 3D zinc micro-sponge electrode that overcomes the dendrite problem by providing a stable 3D electrode structure that does not change form and therefore avoids separator shorts and shape change. California-based Enzinc has developed this technology to achieve lithium-ion efficiencies without the safety, sustainability and scarcity concerns.
Solving these key issues puts zinc batteries in a much better position to compete in the stationary storage market and can help alleviate the supply chain problem lithium-ion batteries face these days from extraordinarily high demand.
Some new zinc battery developers have moved away from alkaline electrolytes altogether and are applying a mild acidic to neutral electrolyte and harnessing the reversible Zn^{2+} zinc ion reaction on stabilised zinc metal surfaces. For these mild electrolytes, it is of paramount importance to have stabilized zinc surfaces to overcome the challenges of electrochemical corrosion, surface passivation, and formation of insoluble by-products such as zinc hydroxy sulfate hydrates ($Zn(OH)_6SO_4$ x H_2O, $ZnSO_4Zn(OH)_{23}$ x H_2O).
Of course, the zinc anode is just half of the battery. The other half is the cathode, and there are plenty to choose from to fill the various application needs, including silver, nickel, manganese, bromine and air cathodes, each with its unique properties and features.

Silver-Zinc Batteries

Since the beginning of the Space Age, silver-zinc batteries have been trusted to power historical NASA launches. Silver-zinc batteries are lightweight, compact, powerful, reliable, and safe and therefore used for mission critical applications in space.
Silver-zinc batteries have a silver oxide cathode, a zinc anode, and an alkaline electrolyte (KOH solution), follow the discharge reaction shown in equation (5) and have an open circuit voltage of 1.85 V per cell. Their effective, practical specific energy density is 105 Wh/kg and 185 Wh/L.

$$Zn + AgO + H_2O \rightarrow Zn(OH)_2 + Ag$$
$$OCV = 1.85\ V \qquad (5)$$

Due to the high cost of these batteries, they are only used for space applications or in small button cells. Eagle Picher of St. Louis is a premier supplier of silver-zinc batteries to government and commercial launch vehicle applications.

Nickel-Zinc Batteries

Nickel-zinc batteries have a nickel hydroxide cathode, a zinc anode, and an alkaline electrolyte (KOH solution), follow the discharge reaction shown in equation (6) and have an open circuit voltage of 1.73 V per cell. Their practical specific energy density is in the range of 70 - 110 Wh/kg and 200 - 360 Wh/L.

$$Zn + 2NiOOH + 2H_2O \rightarrow Zn(OH)_2 + Ni(OH)_2$$
$$OCV = 1.73\ V \qquad (6)$$

Nickel-zinc batteries are safe, sustainable, and non-flammable. With lithium-ion batteries, a single cell failure can disable a storage system, but nickel-zinc batteries safely operate at a high range of temperatures. They also deliver higher power, operate in a wider temperature range, and require less maintenance. In addition to offering higher power density and better performance than lithium-ion and lead-acid batteries, nickel-zinc batteries present several other advantages. They are designed to last from 10 to 15 years and are both environmentally friendly and recyclable, enabling a 'cradle-to-cradle' approach to sustainability.
These batteries already are deployed in data centres as uninterruptible power supplies (UPS) for backup energy storage and for intelligent transportation systems by California-based ZincFive. The massive amounts of data being generated and stored each day mean that battery technology needs to evolve to support this crucial sector, as old lead acid batteries become more expensive to operate and lithium-ion batteries require extra fire protection and some cities are considering a ban on lithium-ion batteries for indoor use.
Further, because of the non-flammability, safety, and reliability, nickel-zinc batteries are even being used in critical military applications, such as powering US submarines and fighter jets. The fire risk issue is of paramount importance especially in submarine applications, and even a low risk of fire from thermal runaway in lithium-ion batteries cannot be tolerated in these use cases. ZAF Energy Systems of Joplin, MO has been successfully working with the US Navy, and their nickel-zinc batteries are undergoing rigorous testing and validation at the Naval Sea Systems Command (NASEA) Crane.

Manganese-Zinc Batteries

Manganese-zinc batteries have a manganese dioxide cathode, a zinc anode, and an alkaline electrolyte (KOH solution), follow the discharge reaction shown in equation (7) and have an open circuit voltage of 1.61 V per cell. Their practical specific energy density is in the range of 90 - 150 Wh/kg and 250 - 450 Wh/L.

$$Zn + 2MnO_2 + 2H_2O \rightarrow ZnO + 2MnOOH$$
$$OCV = 1.61\ V \qquad (7)$$

Building and home energy storage are two potential growth areas where zinc batteries offer a fire-safe and sustainable alternative to incumbent lead acid, lithium-ion batteries, and gas-powered generators. Manganese-zinc batteries, which use essentially the same safe, trusted, zinc-manganese dioxide chemistry found in AA household alkaline batteries used by the billions, prove ideal for backup power of homes or other buildings to provide power in the event of an outage for as long as two days when re-engineered for this purpose. Urban Electric Power of Pearl River, NY recently completed a pilot project in col-

Image: Imprint Energy

Fig. 2: Flexible, printed ZinCore battery from Imprint Energy.

laboration with EPRI (Electric power Research Institute) to investigate the performance characteristics of the company's zinc manganese battery storage system and assess suitability for utility use cases by third party Incubatenergy Labs [1]. Test results reveal in demonstrating discharge periods ranging from four to 16 hours applicable for long-duration energy storage use cases. In these types of applications, cost is a very important decision-making factor for home and business owners; the lower cost of abundant zinc and manganese makes this system a preferred choice, as the capital requirement to get into the system is already lower in addition to the total cost of ownership.

Silicon Valley startup Zēlos Energy was awarded a highly competitive multi-year $ 1.8 million grant from the California Energy Commission for research and development scale-up in low-cost, environmentally friendly alternatives to lithium-ion batteries. They have developed a sustainable, safe zinc-manganese battery designed as an alternative to lead acid and lithium-ion batteries in a variety of applications.

Another new and innovative use for zinc batteries has been developed by Imprint Energy (Fig. 2), which produces small, flexible, printed batteries for power labels on clothing and pill bottles, as well as other small devices comprising the Internet of Things (loT). Their latest ZinCore batteries provide ten times more power in the same volume than the previous zinc-based battery, ZincPoly, enabling applications with 5G radio demand with an extended operating temperature range of -35 ° C to 60 ° C [2].

Zinc-Ion Batteries

Zinc-ion batteries have an intercalation cathode, a zinc anode, and a mild, near neutral electrolyte (zinc sulfate solution), follow the simplified discharge reaction shown in equation (8) and have an open circuit voltage of 1.60 V per cell. Their practical specific energy density is in the range of 80 - 150 Wh/kg and 200 - 450 Wh/L.

$$Zn + MO_x \rightarrow ZnMO_x$$
$$OCV = 1.60\ V \qquad (8)$$

An intercalation cathode is a metal oxide with either layered or a tunneled structure that acts as a host for the zinc ions. The intercalation process is a topotactic reaction where the ions are reversibly removed or inserted into a host without significant structure change to the host. Examples for intercalation cathodes are manganese oxides, vanadium oxides, and Prussian blue analogous.

Canadian-based Salient Energy was one of five companies selected by the state of California to demonstrate a substitute for lithium-ion and will be demonstrating its zinc-ion in a residential energy storage system. Salient also is delivering a demo system to a sustainable homebuilder for inclusion in a model home. Enerpoly, a zinc-ion battery developer based in Sweden, is working with Polarium, an energy storage solution provider, to demonstrate the use of their zinc-ion battery cells in commercial and industrial systems.

By installing energy storage, residential and commercial customers may lower electricity costs. They can utilize zinc-ion batteries to store power generated with solar panels, and then consume the power stored in the zinc-ion batteries during periods of peak rates. This allows homes or businesses to increase the amount of their energy use that is powered by their self-generated solar.

Zinc-Bromine Batteries

Zinc-bromine batteries have a bromine cathode, a zinc anode, and a mild, near neutral electrolyte (zinc bromide solution), follow the discharge reaction shown in equation (9) and have an open circuit voltage of 1.85 V per cell. Their practical specific energy density is in the range of 65 - 75 Wh/kg and 60 - 70 Wh/L.

$$Zn + Br_2 \rightarrow ZnBr_2$$
$$OCV = 1.85\ V \qquad (9)$$

Zinc-bromine batteries are another category of zinc-based technologies that fit very well in the three-to-12-hour storage duration range. They come in two varieties: flow and non-flow configurations. Since the energy is stored in a zinc bromide solution, and the battery electrodes are mere means to facilitate the electrochemical redox reactions, they have a very long-life expectancy and don't have cycle life limitations per se.

An example for a recent zinc-flow installation is the deployment of a 2MWh energy storage system by Australian-based Redflow in California [3] (Fig. 3). The energy storage system is designed to store up to 2 MWh of energy and reduce peak energy

Image: Redflow

Fig. 3: 2 MWh of Redflow zinc-bromine flow battery energy storage and Dynapower inverters at the Anaergia biogas facility, California.

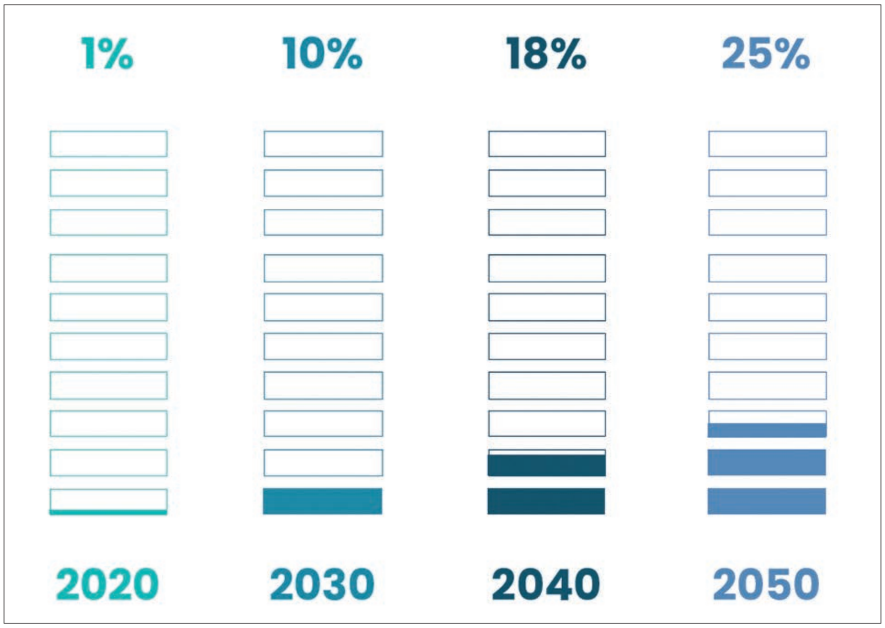

Fig. 4: Zinc market share forecast as percentage of battery energy storage market. Market share estimates based on consultation from Avicenne Energy.

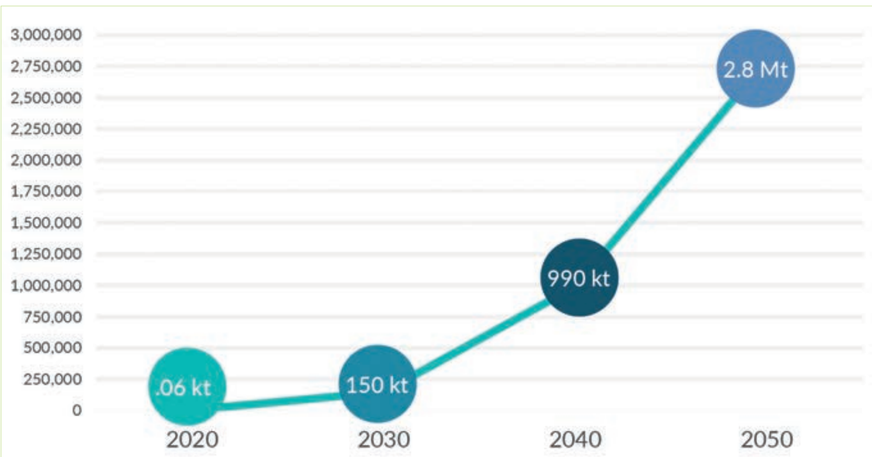

Fig. 5: Cumulative zinc tonnage consumption forecast in the battery energy storage market based on Bloomberg NEF energy storage market forecast, percentage of zinc market share from Figure 4, and an average zinc intensity of use at 2.5 mt Zn/MWh (1 mt = 1,000 kg)

use at Anaergia's Rialto Bioenergy Facility as part of the facility's microgrid.

Redflow Limited (ASX: RFX) recently announced that it has signed a non-binding Letter of Intent (LOI) with Anaergia's subsidiary SoCal Biomethane to collaborate on the potential installation of a new fully wrapped solar and 5.5 – 6.0 MWh Redflow battery storage solution at the SoCal Biomethane plant in Victor Valley, California. The Victor Valley plant is the first wastewater treatment plant in California to inject renewable natural gas made from co-digested wastewater sludge and food waste into a utility pipeline. The facility is a net generator of renewable fuel and provides long-term benefits through enhanced wastewater infrastructure delivered through a private-public partnership (P3). The new solar and storage project is designed to lower the plant's energy costs over the life of the system and reduce the carbon footprint of its industrial processes. The project is targeted for completion in the first half of 2023.

Non-flow zinc-bromine battery developers have booked orders for their systems in excess of 700 MWh for deployments starting this year [4].

Zinc-Air Batteries

Zinc-air batteries have a catalyzed air cathode, a zinc anode, and an alkaline electrolyte (KOH solution), follow the overall discharge reaction shown in equation (10) and have an open circuit voltage of 1.65 V per cell. The theoretical specific energy density of zinc-air batteries based on active material only is very high at 1,085 Wh/kg. Their practical specific energy density is in the range of 100 - 400 Wh/kg and 135 - 1,000 Wh/L based on application and implementation.

$$Zn + ½\,O_2 \rightarrow ZnO$$
$$OCV = 1.65\ V \qquad (10)$$

Zinc-air batteries also are finding their niche in large-scale, stationary storage applications, where development has entered the demonstration phase. Unlike competing lithium technologies that are limited for short duration energy storage due to high-cost issues, zinc-air batteries offer the ability to release power back into the grid for hours, or even whole days at a time, as their intrinsic low-cost, non-flammable, safe and abundant materials do not have the same cost-constraints.

For example, zinc-air flow batteries can be designed to fit any size system and provide the lowest cost of storage for long-duration applications, even up to 100 hours, as the duration can be easily selected by the size of the zinc storage tank.

Zinc8 Energy of Vancouver, Canada recently announced that it will demonstrate its zinc-air flow batteries for a 15-hour long duration storage demonstration project in a New York apartment complex that has solar renewable power [5].

Another type of zinc-air battery that is configured in a non-flow setup by Toronto-based e-Zinc will be put to the duration test in a demonstration project for the commercial and industrial (C&I) market funded by the California Energy Commission (CEC). A 125-acre commercial greenhouse site in Camarillo that presently hosts a 1 MW solar array will add 40 kW with 24 to 48 hours of storage duration.

During normal times, the zinc batteries will capture solar generation to discharge during peak hours and to power irrigation at night. When blackouts loom, they can shift to backup power mode in long-duration mode. This installation is expected to go into service by end of 2023.

Within the next few years, as more and more demonstration projects come online, zinc-air is expected to prove its ability to provide multi-day backup power and compete economically. As a truly green bonus, zinc-air offers a sustainable, eco-friendly alternative to the gas or diesel generators still commonly used for off-grid applications.

Sustainable, secure, and global supply chain

The biggest challenge facing all energy storage sources today is whether energy storage solutions available today can be scaled to the terawatt scale to meet growing demands. BloombergNEF's 2021 Global Energy Storage Outlook estimated that by 2030 one TWh of new stationary storage capacity needs to be added, and that is 20 times more than what was available in 2020.

Fortunately, abundant zinc is ready to meet this challenge. Unlike lithium and other elements, zinc is found around the world and in large supply.

The supply chain for zinc can be completely westernised if required, as it is globally mined and refined in 50 countries, establishing a secure, conflict-free, and sustainable supply chain. Further, zinc is very versatile when it comes to recycling, and many options are available for reuse or repurpose.

Given zinc's abundance and zinc battery innovation, the zinc battery market is expected to grow rapidly. Right now, the market share of zinc-based technologies is low, but the Zinc Battery Initiative predicts it will increase to 25 % by 2050.

This prediction is confirmed by the BloombergNEF New Energy Outlook report, which forecasts the energy storage market is expected to grow exponentially to 1.028 TWh by 2030. The percentage of zinc market share based on consultation with French company Avicenne Energy, is forecasted at 10 % in 2030, 18 % in 2040, and 25 % in 2050.

With so many opportunities, benefits and chemistries, rechargeable zinc batteries safely and sustainably can meet the world's energy storage needs in a manner fitting of zinc's 200-year battery history.

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