



MANAGEMENT PERSPECTIVE

The attached paper, "Alternative Batteries to Lithium-ion," is a technical review of battery platforms that could potentially replace lithium-ion batteries. This is actually in response to a question recently posed by a potential investor.

It should be understood that the lithium-ion battery, while experiencing a number of issues including battery "wear-out" and the potential for safety concerns, has become the dominant power supply for everything from consumer electronics to electric vehicles and to other forms of transportation. To that extent, there is a considerable entrenched infrastructure for lithium-ion batteries. Additionally, the future prospects of the lithium-ion battery are illustrated by the building of the Gigafactory by Elon Musk.

Millions of dollars are being spent in federal laboratories, universities and in industry to research and develop new forms of energy storage systems. None to date have been successfully commercialized. Further, additional millions are being spent in the lithium-ion battery area seeking the "breakthrough" technical innovation to enable higher voltage and energy density and thus more practical use in the key market segments of transportation and electric vehicle systems, utility applications and energy storage systems.

However, a significant portion of the research and development being performed is focused on new materials for high energy electrodes and separator materials (physics solutions), rather than addressing the fundamental issue, the chemistry of the electrolyte. New Dominion Enterprises holds the IP for a series of inorganic electrolyte materials that will not only address thermal related issues confronting current lithium-ion batteries but will also help to enable the research into high energy electrodes leading to longer lasting, safer and higher energy density lithium-ion batteries.

Alternative Battery Types to Li-Ion Systems

Throughout recent years, several alternative energy storage systems have been proposed to fill the need for electrical energy storage/use. In this brief, Li-ion batteries will be summarized and compared to other storage device types. Li-ion batteries are easily the most widespread and fastest growing electrical storage batteries, outside of lead-acid batteries for SLI applications. The principal limitations for this type of battery are: safety problems, shorter lifetimes, and a limited voltage capability. These limitations can all be traced to a single weakness in the technology – the electrolyte. Electrolytes employed commercially are all variants based upon light, low viscosity organic carbonates.¹ While these electrolyte systems do function well, significant improvement is needed to supply the ever-growing demand for portable power.

The first failure in these systems is safety. Organic carbonates are inherently highly volatile, boiling near room temperature, and also highly flammable. This is the reason that so many safety incidents have been reported over recent years, as coupling a hazardous liquid to a high energy battery system can, and has, produced disastrous results.² Many engineering approaches have been employed to overcome this obvious incompatibility, all with rather limited success, as proven by the fact that these incidents continue to occur on a fairly frequent basis. NDE technology is based upon an inorganic related series of compounds that do not boil and do not burn – a chemistry solution for a chemistry problem.³⁻⁷

The second problem with conventional organic electrolytes is that they are not only flammable and volatile compounds, they are quite understandably not very tolerant to heat. They break down readily at even modest temperatures, fouling the electrodes in the battery and becoming more viscous. That is the battery works less and less well over time as more decomposed electrolyte is formed. NDE technology is very thermally robust and is able to transfer some stability to a conventional electrolyte mix, even as a small percentage additive, significantly lengthening useful battery lifetimes. This is especially true when the battery is expected to perform at higher energy rates, such as for transportation applications; or in harsh environments where external temperatures are normally expected to be elevated over room temperature.^{8,9}

The third shortcoming of conventional electrolytes is in its lack of electrical stability.^{9,10} These carbonate-based organic compounds simply cannot withstand the higher voltages

desperately desired in the next generation of energy storage devices. This is the principal reason that while a myriad of higher voltage electrodes have been discovered and examined,¹¹ they are as of yet unrealized in the commercial market due to electrolyte instability. Again, NDE technology overcomes this problem as it is electrochemically stable over a much wider voltage range, and as in the case of the thermal protection, confers electrical stability to the organics as well.⁸

The next logical phase of battery development to meet upcoming energy needs is to devise a li-ion system that replaces the less than ideal organic electrolyte. This will not only enable Li-ion systems to reach their full potential as energy sources, it leverages the already enormous infrastructure in the other (non-electrolyte) materials that already exists. NDE technology provides such a replacement. Further improvements in Li-ion type systems can readily be realized by switching from lithium (+1 ion) to magnesium¹² (+2 ion) or aluminum¹³ (+3 ion), to increase to available power of the devices. Due to the similar nature of the electrolyte requirements, it is logical to see how NDE improvements to Li-ion electrolytes will smoothly transition to these multi-valent systems, without having to resort to solid-phase composite electrolytes.¹⁴

Other energy storage systems have been proposed over the years without much success beyond an enhanced academic understanding of the nature of these alternate technologies. One such as these is based on what has become collectively known as beta batteries, one that has been known for quite some time.¹⁵ There are several practical reasons that these systems were never adopted for widespread use. The first is the nominal operating temperature. These systems function only at elevated temperatures wherein the active metal, in this case sodium, is fluid. Even after much scientific and engineering research, to this day these systems still need to be heated to approximately 300 °C to function.¹⁶ Beyond this extreme limitation for nearly all applications, there is the nature of the other materials required to construct such a system. These typically include molten sodium metal or anhydrous NiCl₂, both of which are extremely hazardous, corrosive, and flammable. A subset of this type of system is also a high operational temperature system and is known as molten sulfur batteries. This too has been known for years, and has found little to no practical application for reasons very similar to the ones enumerated above for beta batteries.¹⁷

A different approach has been taken to eliminate the failings of conventional electrolytes. These are collectively known as reactive metal-air batteries, and the concept has been around for

over 50 years.¹⁸ The overall effort was considerably reduced by the 1980's due to materials problems at the air electrode, thermal management, and miscellaneous technical problems associated with the various anodes evaluated. More recently, new energy storage device proponents, like Fluidic Energy, have been trying to resurrect these systems, particularly zinc-air.¹⁹ While the system has attractive features – “no” cathode and a flexible electrolyte systems – there are still fundamental problems. The energy storage capacity is one of the lowest for this type of battery (658 Ah/Kg), and the nominal voltage is a mere 1.65V.²⁰ For comparison, voltage for Li-ion is over 4.2 V and, with a better electrolyte than the aforementioned carbonates, experimental electrodes are already poised to go to 5V and higher.²¹ Further, the need for continuously free flowing air to the cathode has cast considerable doubt on battery lifetimes, as fouling – an unavoidable occurrence over extended use, would make it difficult for the device to “breathe” and cause early onset of poor performance.

Redox flow batteries are another energy storage technology that has been around for many years, without finding practical application. This is due to the relatively complex engineering that is required to operate such a system versus a typical battery system. As shown in Figure 1, multiple liquid reservoirs must be maintained and the liquid media circulated with precision. This is an energy input cost as well as a potential source of exposure to the environment of large amounts of toxic materials, as Vanadium and Chromium give the best operating voltages.²²

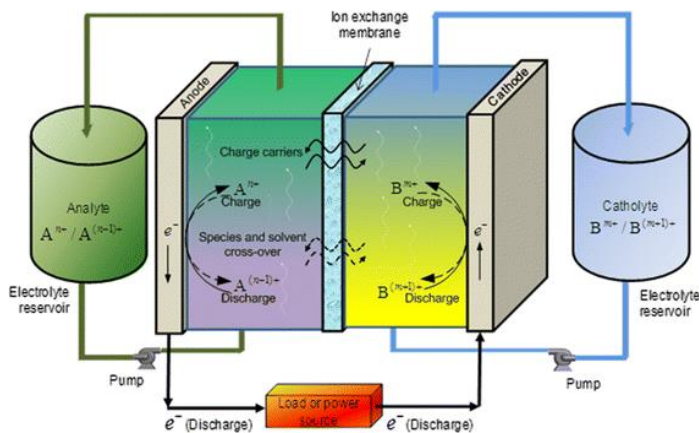


Figure 1. A typical redox flow battery system.

A recent workshop convened by Sandia, PNNL, and the Minerals, Metals, and Materials Society (TMS) for the US Department of Energy, suggests the following cost performance targets for key utility applications, and identify cost targets for flow batteries of \$250/kWh in

capital costs in 2015, decreasing to \$100/kWh by 2030. Current estimates of costs for flow batteries are significantly higher than the required targets: a 2008 estimate of RFB costs suggested nearly \$2500/kW, albeit without specification of duration or sizing. Regardless of detail, however, significant cost reduction must be achieved: technological improvements, material development, and economies of scale must be achieved first before success in the marketplace could ever be realized.²²

Beyond these technologies described above, there are a few more esoteric electrical energy storage methods that are similarly well known having been first discovered decades ago. Among these are compressed air storage, flywheels, thermal-swing, and pumped hydro-power.²³ None of these have found any foothold in the market for as many technical reasons as there are alternative technologies. Ion shuttle systems, chief among them Li-ion systems are the future for electrical storage and will remain firmly so for the foreseeable future. As such, NDE technology is one that will enable, in stages, the realization of Li-ion batteries' full potential. This is valid over a wide range of applications; from small portable devices (cell phone, laptop) to large stationary ones (grid-scale, power back-up) and most others in-between. With the thermal and electrochemical robustness of NDE technology, it is also applicable to a variety of specialty applications that currently go unmet today.

References:

1. Qi Li, Juner Chen, Lei Fan, Xueqian Kong, Yingying Lu; "Progress in Electrolytes for Rechargeable Li-based Batteries and Beyond" *Green Energy & Environment*; 1 (1), 18, **2016**.
2. "Aviation Cargo and Passenger Baggage Events Involving Smoke, Fire, Extreme Heat or Explosion Involving Lithium Batteries or Unknown Battery Types"; FAA Office of Security and Hazardous Materials Safety, **2018**.
3. Harrup, M. K.; Stewart, F. F.; Delmastro, J. R.; Luther, T. A.; "Safe Battery Solvents" *U. S. Patent #7,285,362*, October 23, **2007**.
4. Gering, Kevin L.; Harrup, Mason K.; Rollins, Harry W.; "Ionic Liquids, Electrolyte Solutions Including The Ionic Liquids, And Energy Storage Devices Including The Ionic Liquids" U. S. Patent #9,206,210, December 8, **2015**.
5. Harrup, Mason K.; "All-Inorganic Solvents For Electrolytes" U. S. Patent Pending, November, **2016**.

6. Klaehn, John R.; Dufek, Eric J.; Rollins, Harry W.; Harrup, Mason K.; Gering, Kevin L.; “Electrolyte Solutions Including A Phosphoranimine Compound, And Energy Storage Devices Including Same” U. S. Patent #9,761,910 September 12, **2017**.
7. Harrup, Mason K.; “All-Inorganic Solvents For Electrolytes” European Patent Pending, February, **2018**.
8. Sazhin, S. V.; Harrup, M. K.; Gering, K. L.; “Characterization of Low-flammability Electrolytes for Lithium-ion Batteries.” J. Power Sources, v. 196 **2011**, 3433.
9. Rollins, H. W.; Harrup, M. K.; Dufek, E. J.; Jamison, D. K.; Sazhin, S. V.; Gering, K. L.; Daubaras, D. L.; “Fluorinated Phosphazene Co-Solvents For Improved Thermal And Safety Performance In Lithium-Ion Battery Electrolytes” Journal of Power Sources, 263, **2014**.
10. Sazhin, S. V.; Harrup, M. K.; Gering, K. L.; “Characterization of Low-flammability Electrolytes for Lithium-ion Batteries.” J. Power Sources, **2010**.
11. Meng Hu, Xiaoli Pang, Zhen Zhou; “Recent progress in high-voltage lithium ion batteries” J. Power Sources, **2013**.
12. Mohtadi, R.; Mizuno, F.; “Magnesium batteries: Current state of the art, issues and future perspectives” Beilstein J. Nanotechnol. (5) **2014**.
13. Li, Q.; Bjerrum, N. J.; “Aluminum As Anode For Energy Storage And Conversion: A Review”, J. Power Sources 110, **2002**.
14. Di-Yan Wang, Chuan-Yu Wei, Meng-Chang Lin, Chun-Jern Pan, Hung-Lung Chou, Hsin-An Chen, Ming Gong, Yingpeng Wu, Chunze Yuan, Michael Angell, Yu-Ju Hsieh, Yu-Hsun Chen, Cheng-Yen Wen, Chun-Wei Chen, Bing-Joe Hwang, Chia-Chun Chen, and Hongjie Dai, “Advanced Rechargeable Aluminium Ion Battery With A High-Quality Natural Graphite Cathode” Nat. Commun. 8: **2017**.
15. J.T. Kummer, in: *Beta-Alumina Electrolytes*, ed. H. Reissand; J.O. McCaldin; (NewYork: Pergamon Press, **1972**).
16. Xiaochuan Lu; John P. Lemmon; Vincent Sprenkle; Zhenguo Yang; “Sodium-beta Alumina Batteries: Status and Challenges” JOM, 62(9), **2010**.
17. J.L. Sudworth and A.R. Tilley, *The Sodium Sulphur Battery* (London: Chapman & Hall) **1985**.
18. Keith F. Blurton; Anthony F. Sammells; “Metal/air batteries: Their status and potential — a review”, Journal of Power Sources, Volume 4(4), **1979**.
19. Katie Fehrenbacher; “A Battery Made From Metal and Air Is Electrifying the Developing World”, FORTUNE.COM, **2016**.
20. Xin Zhang; Xin-Gai Wang; Zhaojun Xie; Zhen Zhou; Recent Progress in Rechargeable Alkali Metal–air Batteries”, Green Energy & Environment; 1 (1), **2016**.
21. Hu, M.; Pang, X.; Zhou, Z.; “Recent Progress in High-voltage Lithium Ion Batteries”, Journal of Power Sources 237:229, **2013**.
22. Adam Z. Weber, Matthew M. Mench, Jeremy P. Meyers, Philip N. Ross, Jeffrey T. Gostick, Qinghua Liu; “Redox Flow Batteries: A Review”, J. App. Elect., 41(1137), **2011**.

23. Report of the Energy Storage Association (ESA), **2018**.