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Why Grid Scale Energy Storage

An Electrical grid equipped with energy storage system allows companies to manage and deploy the electrical energy in a much more efficient and flexible way. Key features such as peak shaving, frequency regulation and time shifting can be realized via such systems to enhance power quality and reliability. Moreover, a grid-scale energy storage system is able to serve as a buffer between the electric grid and an ever increasing demand for renewable energy generation such as solar and wind. These systems smooth out the climate-dependent intermittency and allow the harvested energy to be distributed as needed. It has long been a global desire to increase renewable energy penetration in order to reduce the electricity sector's carbon footprint as well as the fossil fuel consumption. To date, available technologies such as pumped hydro energy storage (PHES), compressed air energy storage (CAES), flywheel energy storage (FES), supercapacitors, superconducting magnetic energy storage (SMES) and electrochemical energy storage (EES) have been developed to meet different power and duration needs, as shown in Figure 1.

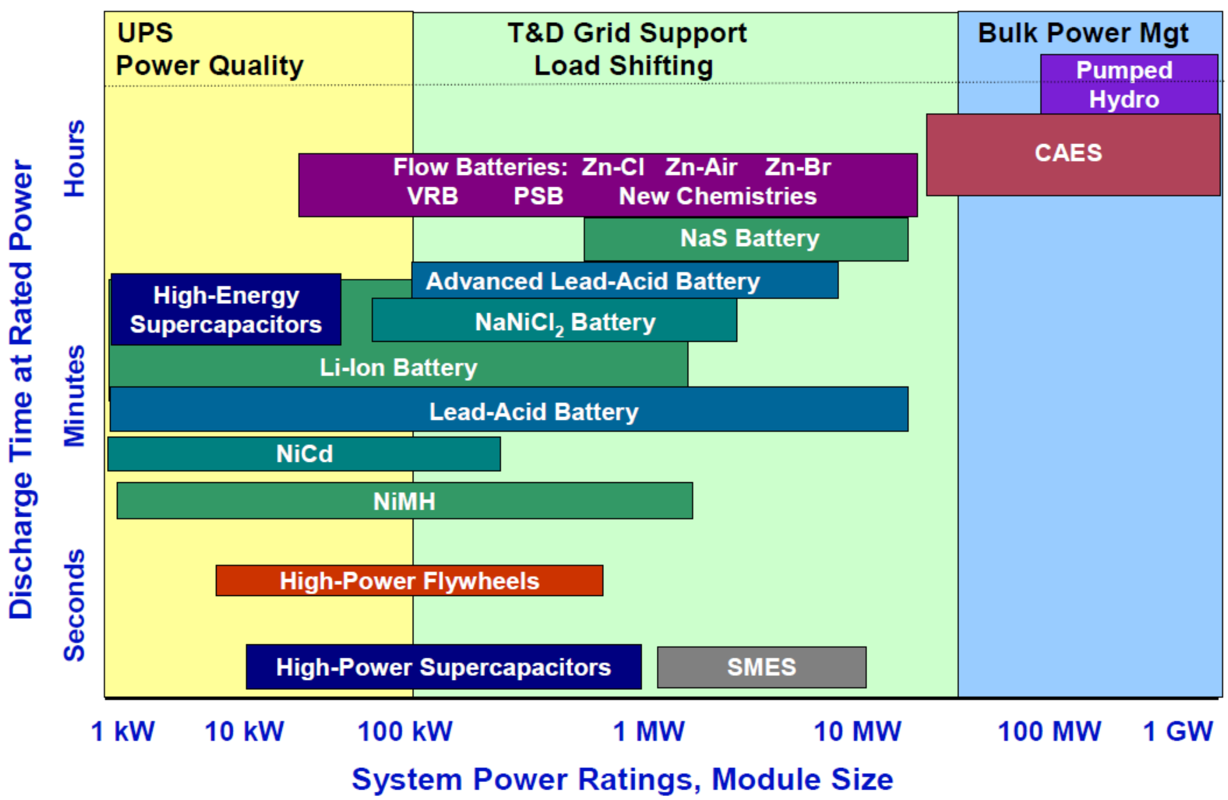

Figure 1: Position of energy storage technologies[1]

[1] Rastler, D. "Electric Energy Storage Technology Options: A White Paper Primer on Applications, Costs, and Benefi ts" EPRI, Palo Alto, CA 2010 . 1020676 .

We need efficient, reliable and cheap energy storage systems

Among the available technologies, electrochemical energy storage (EES or battery) is probably the most versatile option covering a wide range of power and energy demands. Conventional EES systems including lead-acid, and sodium-sulfur batteries have been demonstrated and commercialized with limited market penetration. More recently, Li-ion batteries have also been investigated for applications beyond the size of portable devices and transportation systems. In general, most of the conventional batteries are recognized for their simplicity and are well-suited for fast response and low duration (15 to 60 min) applications (e.g. frequency regulation). However, adopting conventional batteries as high capacity energy storage systems (e.g. 100MWh power plant with peak power 10MW and 10 hours duration) seems impractical because of the high capital cost. Emerging EES systems such as redox flow batteries (RFB) are attractive due to their potential to overcome some of these limitations and can be configured to provide both high power and high energy capacity. At the moment, cost is probably the largest barrier hindering broad commercial success of the RFB technology. Recent Advanced Research Projects Agency-Energy (ARPA-E) target capital costs of $100/kWh installed for a grid-scale battery, whereas cost of the present state-of-the-art RFB systems is in the range of $300-$700/kWh depending on the adopted chemistry. Some of the advantages and limitations of several EES systems are summarized Table 1.

Table 1 Main applications, advantages and limitations of different EES.[2]

Technology	Main Application	Advantages	Limitations
Li-ion battery	transportation; portable electronics; power application on grid is being investigated	near 100% efficiency; high energy density; high power	high capital cost (~$700/kWh); safety and reliability problems due to heat management issues; small temperature range of operation
Pb-acid battery	current automobile and electrical bikes, buses; backup power; industrial applications	least expensive in terms of capital cost ($/kWh)	short cycle life; high maintenance; hHigh lifecycle cost ($/kWh/cycle); low specific energy due to insufficient materials utilization
Na-S and Na-metal halide battery	research targets grid-scale storage	efficiencies up to 90%; energy densities comparable to current Li-ion batteries	operating range of 300–350 °C; safety and durability concerns (e.g., fire in case of membrane and package failure); high production cost; current specifications (weight and size) limit potential applications
Redox flow battery (RFB)	grid-scale storage	MW storage system; power and energy capacity are independently tunable and adjustable; potential long cycle life	high capital cost; long term durability not proven; capacity loss issues like self-discharge over time; electrolyte stability at different temperatures; stack design and grid integration challenges

Why Redox Flow Cell Batteries are special?

Among the EES systems, Redox Flow Cell Batteries (RFBs) are unique because of there inherent flexibility. Unlike conventional batteries, the chemical energy of the RFB is stored in the external reservoirs as liquid electrolytes, shown in Figure 2. As the RFB operates, electrolytes are pumped from external tanks to the electrochemical cell to facilitate the battery charge and discharge. This operation allows the decoupling of energy capacity (size of the electrolyte tank) and power capability (size of the cell stack). This is a unique feature of RFB and as a result offers

[2] Liu, L. et al "Materials Science and Materials Chemistry for Large Scale Electrochemical Energy Storage: From Transportation to Electrical Grid" Adv. Funct. Mater. 23 (2013) 929-946

considerable freedom in system scale design as well as allowing versatility in redox chemistry selection to meet different application needs. The RFB cell stack, in this case, simply provides the platform for the active chemicals to perform electrochemical reactions and typically the electrodes are not participating in the redox reaction. This characteristic avoids the electrode deformation as often seen in the conventional Li-ion battery allowing deeper cycles and longer cell life time. Additionally, storing active chemicals externally minimizes the battery self-discharge or side reactions as well as enhances the system safety, which is particularly critical for large-scale energy storage systems.

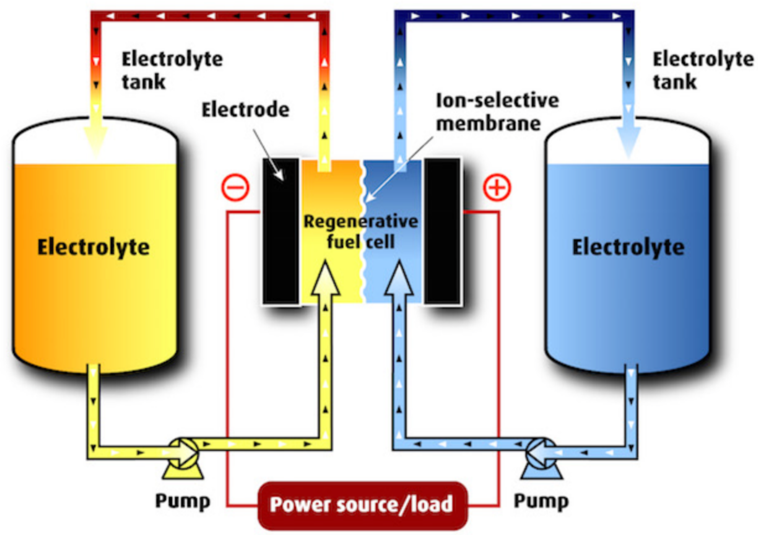

Figure 2 Schematic diagram of the redox flow cell battery system.

History of Redox Flow Cell Batteries and Current Developments

In the 1970s, L. H. Thaller of the National Aeronautics and Space Administration (NASA) in the United States presented the first iron-chrome redox flow battery.[3] At a similar time, New Energy and Industrial Technology Development Organization (NEDO) in Japan established "Moonlight Project" supporting Meidensha Electric Company's zinc–bromine battery, Furukawa Electric Company's zinc–chlorine battery, and Mitsui Engineering and Shipbuilding Corporation's iron–chrome redox flow battery.[4] These early developments were successful in pilot-scale prototypes; however, the large-scale deployment was very limited primarily due to the high capital cost. Around 1985, Professor Maria Skyllas-Kazacos at the University of New South Wales in Australia proposed an all-vanadium redox flow battery (VRB) which adopts vanadium ion for both positive and negative sides which mitigates species cross-contamination and allows easier rebalancing (which is accomplished by simply remixing the catholyte and anolyte).[5] Among the current RFBs, the VRB is probably the most extensively studied system and has attractedseveral companies

[3] Thaller, L. H. U.S. Patent 3,996,064, 1976.
[4] Shigematsu, T "Redox Flow Battery for Energy Storage" SEI TECHNICAL REVIEW 73 (2011) 4-13
[5] Skyllas-Kazacos, M. et al "New All-Vanadium Redox Flow Cell" J. Electrochem. Soc. 133 (1986) 1057-1058

such as Avalon Battery, UniEnergy Technologies and Sumitomo Electric Industries (SEI, Japan) for commercial development. Another example of large-scale RFB development is Regenesys' polysulfide-bromine battery (PSB) built in Columbus, Mississippi and Little Barford, UK (Figure 3) in the 1990s. At that time, Regenesys' PSB was probably the world's largest electrochemical storage device everattempted, designed to deliver 10-20MW of power with c.a. 100MWh of capacity. Despite the promising advances made in developing the PSB technology, RWE, the parent company of Regenesys, decided to cease funding of the project in 2004 .

Most of the early RFB developments encountered significant challenges and the large-scale implementation was very limited. However, with the growing interest to increase renewable energy penetration toward a low-carbon society, RFB technology has recently attracted substantial industrial attention. Start-up companies are emerging in the effort to realize commercial deployment and have made significant progress. The advances in the current RFB industry will be highlighted in this article.

Figure 3 Regenesys' polysulfide-bromine flow battery in Little Barford, UK.

When it comes to design a RFB system, the most critical starting point is probably the redox chemistry selection. Ideally, the designated redox couples should have the following characteristics: (1) High open circuit voltage (OCV); (2) Reversible and fast reaction kinetics; (3) High solubility; (4) High stability of the electrolyte over a wide SOC range; (5) Multi electron transfer; (6) Low cost; (7) Environmentally benign. Although RFB allow a wide selectrion of chemistries, only a few redox couples fulfill most of the requirements and have been chosen for commercial demonstration. To date, iron-chrome, all-vanadium and zinc-bromine RFBs are the three most successful systems developed in the RFB industry.

Iron-chromium RFB

Iron Chrome Battery (ICB) uses Fe^{2+}/Fe^{3+} and Cr^{2+}/Cr^{3+} redox couples typically in hydrochloric acid solution which yield a standard cell potential at 1.18V. The electrode reactions presented in discharge mode are:

$$\text{Positive:} \quad Fe^{3+} + e^- \xrightarrow{discharge} Fe^{2+} \qquad E^0 = 0.77V\ vs\ SHE$$

$$\text{Negative:} \quad Cr^{2+} \xrightarrow{discharge} Cr^{3+} + e^- \qquad E^0 = -0.41V\ vs\ SHE$$

The iron-chrome chemistry possesses significant cost and safety advantages as iron and chrome are earth abundant and non-toxic elements. Early ICB development started in the US (NASA) and Japan (Kansai Electric Power Co., Inc. (KEPCO) and SEI) around 1970s. Here we summarize some of the challenges encountered: In ICB, Fe^{2+}/Fe^{3+} redox couple is highly reversible and the reaction kinetics are fast on carbonaceous electrodes. However, the Cr^{2+}/Cr^{3+} couple would require the aid of catalyst and elevated operating temperatures (~65^{o}C) to facilitate the reaction rate. Moreover, hydrogen evolution is prone to occur at the Cr^{2+}/Cr^{3+} electrode as a competing reaction and causes capacity loss due to asymmetrical state-of-charge (SOC) in each individual electrolyte. Ideally the catalyst used should exhibit high hydrogen overpotential while facilitating the Cr^{2+}/Cr^{3+} redox reaction. The rate of hydrogen evolution, however, might also be sensitive to the electrolyte quality since trace amount of metal impurities could be electrochemically reduced on the electrode surface and alter the reaction kinetics. To minimize the effect caused by hydrogen evolution, accessories such as rebalancing systems have been proposed to stabilize the SOC over the long term operation. Note that the need for a catalyst, heating and rebalancing systems for operating ICB would add cost and parasitic losses to the system. In addition, cross-mixing of iron and chromium species could occur at elevated temperature due to loss in membrane selectivity. To mitigate species cross over, the concept of using mixed reactant solution was proposed allowing Fe ions and Cr ions to be present in both electrolytes.[6] In this case, the ion selective membrane can be replaced with cost-effective microporous separator thereby taking advantage of lower resistance and reduced stack cost. Also, if required, solution maintenance can be performed by simply remixing of discharged catholyte and anolyte. The disadvantages of using mixed solution are reduced coulombic efficiency and cell OCV.

EnerVault Corporation, a recent ICB developer, was founded in California in 2008 targeting multi-MW systems for grid-scale application. Since 2010, EnerVault has progressively demonstrated the ICB from laboratory prototype (2kW, 2010), pilot system (30kW, 2012) to recent field demonstration (250kW/1MW-hr, 2014) located in Turlock, California. In the process of developing the ICB, the company has claimed technical advances including hydrogen suppression and the so-called Engineered Cascade™ design where cells/stacks are fluidically connected in series and the configuration in the individual cell/stack is tailored and optimized based on the expected SOC in the cascade system. In Turlock, the 250kW ICB system, which comprised nine 30kW modules, was coupled with a 150kW solar array to power an irrigation pump thereby helping farmers reduce electricity expenses. One important task of running the Turlock system was to verify the reliability of the hydraulic pumping system which is projected to last several thousand hours but can be replaced in the matter of hours. The 250kW/1MW-hr ICB is the largest ICB to date and the total

[6] Randall F. "Single Cell Performance Studies on the Fe / Cr Redox Energy Storage System Using Mixed Reactant Solutions at Elevated Temperature" 18th Intersociety Energy Conversion Engineering Conference Orlando, Florida, August 21-26, 1983

$9.5 million of funding is supported by US Department of Energy ($4.7 million) and California Energy Commission ($4.8 million). Unfortunately, at the time of writing, EnerVault is restructuring and seeking for new owner.

All-vanadium RFB

Vanadium Redox Flow battery (VRB) adopts V^{2+}/V^{3+} as negative couple and V^{4+}/V^{5+} as positive couple dissolved in concentrated acid (e.g. 2-5M sulfuric acid) and yields ~1.4V cell OCV. The electrode reactions presented in discharge mode are as follows:

$$\text{Positive: } VO_2^{\ +} + 2H^+ + e^- \xrightarrow{discharge} VO^{2+} + H_2O \quad E^0 = 1.00V\ vs\ SHE$$

$$\text{Negative: } V^{2+} \xrightarrow{discharge} V^{3+} + e^- \quad E^0 = -0.26V\ vs\ SHE$$

The primary advantage of using the VRB system is that the cross-contamination of the two electrolytes is eliminated allowing effortless rebalancing as VRB uses the same element for both sides of the battery. Typically, VRB possesses 20-25Wh/L energy density with vanadium concentration ~1.7M in the electrolyte.

High capital cost has been the major barrier in commercializing the VRB. A recent report[7] estimates $600-$700/kWh for VRB when used in a large renewable application (250MWh) indicating challenges remain for VRB to meet the cost target toward broad market penetration. As suggested by few recent studies, significant portion of cost in the VRB system are contributed by the vanadium electrolyte (~40%) and the cell materials (~30%).[8,9] It is therefore to be expected that the major focus of research groups will be to reduce the cost of these components.

Among the chemistries that have been successfully implemented in the RFB technologies, vanadium is one of the more expensive elements and requires innovative ways of extracting the maximum energy from the electrolyte. In an effort to minimize the vanadium cost impact, developers have tried to use less expensive sources of vanadium including recycled materials.[10] Some developers have suggested that the use of less pure (less expensive) starting materials is possible but further modifications to the system are required to ensure efficient operation.[11] Conventional electrolytes have a temperature stability window of 10°C-40°C and as a result, additional thermal management systems may be required for the long-term operation; this inevertably leads to extra cost and energy loss. In this regard, research groups in University of New South Wales, Sumitomo Electric Industries and Pacific Northwest National Laboratory have found that the stability of the high vanadium concentration electrolyte can be further extended by

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[7] Rastler, D. “Electric Energy Storage Technology Options: A White Paper Primer on Applications, Costs, and Benefi ts” EPRI, Palo Alto, CA 2010 . 1020676 .
[8] Zhang, M. et al “Capital Cost Sensitivity Analysis of an All-Vanadium Redox-Flow Battery” J. Electrochem. Soc. 159 (2012) A1183-A1188
[9] Viswanathan, V. et al “Cost and performance model for redox flow batteries” J. Power Sources 247 (2014) 1040-1051
[10] http://www.imergy.com/press-releases/2014/7/imergy-power-systems-achieves-technological-breakthrough-in-energy-storage-flow-batteries-made-from-recycled-vanadium
[11] Keshavarz, M. et al “Vanadium flow cell “ US patent application US20130095362 A1

introducing chemical additives to the electrolyte.[12,13,14] The challenge of using the additive is to stabilize the vanadium ion in it's four different oxidation states over wide temperature range without deteriorating the system performance e.g. retarding the reaction kinetics or promoting side reactions and corrosion. Nevertheless, it remains to be seen whether these electrolytes containing additives are viable in the long-term or if they introduce additional issues.

In VRBs, porous carbon felts are commonly used as electrode materials to provide a high surface area for the electrochemical process. A membrane, sandwiched between two felts, allows charge transfer (mostly H^+) while at the same time minimizing vanadium ion crossover, i.e. battery self-discharge. Since conventional perfluorinated ion exchange membranes (e.g. Nafion) are rather costly for large-scale implementation, the possibility of using low cost membranes (e.g. hydrocarbon polymer) has been investigated and several materials are reported to have promising performance.[15]

In addition to to reducing the cost of the material components used in the cell, another way to reduce the cell cost is to improve the cell performance thereby reducing the size of cell stack required for a given application. In the past few years, significant improvements have been made to enhance the VRB performance by refining electrode, membrane and cell configuration.[16] Advances for VRB are ongoing in order to meet the cost targets required for board market penetration. At the moment, there are several start-up companies in North America focusing on the VRB development and commercialization.

UniEnergy Technologies (UET), a current VRB developer, was funded by Mukilteo, WA in 2012. One of the core technologies in UET is the mixed-acid electrolyte developed by PNNL which claims high energy density and high stability. This advance allows UET to pack a 600kW/2.2MW-hr VRB system into five 20-foot containers and multiple containers can be connected and double-stacked to achieve 40MW/acre. In addition, UET partners with Rongke Power (China) and Bolong New Material (China) for low cost stack manufacturing and electrolyte production. The current system design yields 19.5Wh/L energy density and 65%~70% AC/AC efficiency. As of 2014, the capital cost is about $875/kWh of storage, or about $3,500/kW of peak power capacity.[17] UET is currently collaborating with Snohomish Public Utility District, Puget Sound Energy and Avista for demonstrating renewable integration via a $14.3 million matching grants storage program funded by Washington State. In 2015, UET announced the commissioning of a 1 MW energy storage system with a maximum energy capacity of 4MWh in Pullman, Washington. This is one of the largest capacity flow battery operating in North America and Europe and will be used by Avista Utilities for grid applications.

Imergy Power Systems (IPS), formerly known as Deeya Energy, has been developing energy storage system in Fermont, CA since 2004. In 2013, the company switched its focus to VRB

[12] Roe, S. "A High Energy Density Vanadium Redox Flow Battery with 3 M Vanadium Electrolyte" J. Electrochem. Soc. 163 (2015) A5023-A5028

[13] Kubata, M. "Electrolyte for redox flow battery, and redox flow battery " US patent US7258947 B2

[14] Li, L. et al "A Stable Vanadium Redox-Flow Battery with High Energy Density for Large-Scale Energy Storage" Adv. Ener. Mat. 1 (2011) 394-400

[15] Sun, C. "Evaluation of Diels–Alder poly (phenylene) anion exchange membranes in all-vanadium redox flow batteries" Electrochem. Comm. 43 (2014) 63-66

[16] Aaron, D. "Dramatic performance gains in vanadium redox flow batteries through modified cell architecture" J. Power Sources 206 (2012) 450-453

[17] http://www.xconomy.com/seattle/2014/07/07/unienergy-technologies-goes-from-molecules-to-megawatts/2/

technology development with a new name, IPS. With the goal of reducing capital cost, IPS has developed the high performance chloride-containing electrolyte which they claim allows the use of less pure vanadium (98%) recovered from environmental waste (mining slag, oil field sludge, fly ash). As a result, cheaper vanadium source together with lower processing cost allows 40% reduction on the electrolyte cost. IPS claims this advance would lower the system capital cost from \$500/kWh to \$300/kWh. However, some of the drawbacks of using electrolyte with higher impurity level are that the side reactions (e.g. hydrogen evolution, chlorine formation) might be facilitated. Based on the filed patents,[18] it seems IPS is developing methods to suppress these side reactions by plating certain metals (e.g. bismuth) onto the electrode. By teaming up with Foxsemicon (Taiwan) for manufacturing, IPS provides 5kW/15-30kWh, 30kW/120-200kWh, and 250kW/1MWhr systems for various application requirements. IPS is participating in several micro-grid projects based in California[19] and has around 100 units in the field. In addition, SunEdison recently announced plans[20] to purchase 1000 of the 30kW/120-200kWh systems (>100MWh) from IPS to bring the solar-generated electricity to rural India.

Zn/Br_2 battery

The Zn/Br_2 battery, pioneered by Gould Inc., Exxon and Energy Research Corporation in 1980s, uses a zinc-bromide solution as the electrolyte. During battery charging, the zinc ions are plated as zinc metal at the negative electrode and bromide ions are oxidized to dissolved (complexed) bromine at the positive electrode. On discharge, the zinc and bromine are consumed forming zinc and bromide ions returning to the electrolyte. The electrode reactions presented in discharging mode are:

$$\text{Positive:}\quad Br_2 + 2e^- \xrightarrow{discharge} 2Br^- \qquad E^0 = 1.07V\ vs\ SHE$$

$$\text{Negative:}\quad Zn \xrightarrow{discharge} Zn^{2+} + 2e^- \qquad E^0 = -0.76V\ vs\ SHE$$

Because zinc plating is involved, the energy of Zn/Br_2 battery depends not only on the size of the reservoir but also the size of the electrode in the cell/stack. Because the energy and the power are not fully decoupled, Zn/Br_2 battery is generally considered as hybrid flow battery. Combining high OCV with 2-electron process, Zn/Br_2 battery offers high energy density ~60-70Wh/L.[21] Furthermore, ion-selective membranes and temperature control are not critcal in the Zn/Br_2 battery. Due to the low cost materials together with low cost reactants and high energy density, the Zn/Br_2 battery system is projected to cost \$290-350/kWh for a 250MWh application. However, some challenges remain regarding the bromine management. During battery operation, bromine-rich stream at the positive side could increase bromine crossover rate and encourage battery self-discharge. Moreover, low solubility of bromine in the aqueous solution would lead to high vapor pressure raising possible environmental concerns. As a result, use of a bromine complexing agent, e.g. Methyl Ethyl Morpholinium Bromide (MEM) or Methyl Ethyl Pyrrolidinium Bromide (MEP), was discovered to mitigate these concerns. During battery charging, the bromine complexing agent would interact with bromine forming a immiscible dense ploybromide phase at the bottom

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[18] Keshavarz, M. et al US patent application US20130095362 A1

[19] http://www.imergy.com/press-releases/2014/12/imergy-power-systems-flow-batteries-selected-for-navy-california-energy-commission-microgrid-demonstration-project

[20] http://www.imergy.com/press-releases/2015/3/sunedison-purchases-1-000-energy-storage-systems-from-imergy-to-bring-electricity-to-villagers-in-rural-india

[21] http://www.sandia.gov/ess/publications/SAND2000-0893.pdf

of the tank resulting in a low bromine concentration in the aqueous layer. In contrast, the bromine has to be liberated sufficiently fast from the complexed phase upon discharge, usually via vigorous mixing or directly pumping the complexed phase into the cell.[22] At the negative electrode, there are challenges around the zinc deposition which could form dendritic structures or have other non-uniform distributions possibly leading to battery shorting. In an effort to mitigate this, stripping process may be needed to strip the residual zinc from the electrode on a regular basis.

EnSync Energy System (formerly known as ZBB) is the current Zn/Br_2 battery developer located in Menomonee Falls, WI. The company offers two commercial systems: the hybrid system (Zn/Br_2 battery+Li-ion battery) for commercial and industrial application and the scalable flow battery system (55kWh/unit) for utility application. EnSync has also developed energy management and control system providing solutions for various needs as well as power purchase agreements. Some of the complete/ongoing projects include: replacing diesel generator as elevator power back-up system in Hawaii and taking Cayman Technology Center off-grid by integrating Zn/Br_2 flow batteries, energy management system, a 380kW solar system and an 800kW diesel generator. Moreover, EnSync developed strategic partnership with Lotte Chemical (South Korea) for cell components and chemicals and SPI solar (China) for 80-120MWh of PV energy storage.

Reseach efforts over the past decade have led to significant improvements in Redox Flow Cell batteries making their commercial deployment more attractive. Despite some remaining challenges, we anticipate that RFBs will be an important technology facilitating the incorporation of renewable energy sources onto the electric grid. As our societies move toward a lower carbon footprint, these technologies will become all more important.

Che-Nan (Josh) Sun is a Research Scientist at Eectrosynthesis Company. His research interest focus on energy storage/conversion devices such as fuel cells, flow batteries, Li-ion and Na-ion batteries. His professional skills include electrochemical impedance spectroscopy, electrode characterization, membrane development and cell performance optimization. His research contributed 20 peer-reviewed journal articles, 7 professional presentations and 1 US patent. Dr. Sun received his Ph.D. in Materials Science and Engineering from Case Western Reserve University in 2011, and was a post-doc at Oak Ridge National Labs, TN. Contact Josh at info@electrosynthesis.com

The Electrosynthesis Company has had a long history of developing redox flow cell batteries including the Regenesys polysulfide-bromine redox flow systems, VRBs as well as other RFBs. The team at Electrosynthesis is very capable of performing thorough battery development, testing, characterization and optimization at both lab and pilot scale. We have previously demonstrated RFB technologies at up to 30 kW and 100kWh in our existing facilities. Furthermore, the Electrosynthesis Company has broad experience in industrial electrochemistry successfully demonstrating the scale-up of electrosynthetic and membrane separation processes from laboratory, to pilot plant and production.

[22] Richards, L. "Zinc-Bromine Battery Development Sandia Contract 48-8838 Final Report" 1009