ADVANCED ELECTROCHEMICAL STORAGE RD&D AT PACIFIC NORTHWEST NATIONAL LABORATORY FOR RENEWABLE INTEGRATION AND GRID APPLICATIONS

Z. Gary Yang, Daiwon Choi, Greg Coffey, Jianzhi Hu, Cui Jun, Jin Yong Kim, Soowhan Kim, Michael, Kintner-Meyer, Dean Mattson, Kerry Meinhardt, Vijay Murugesan, Zimin Nie, John Lemmon, Guosheng Li, Liyu Li, Jun Liu, Xiaochun Lu, David Reed, Yuyan Shao, Vince Sprenkle, Vish Viswanathan, Wei Wang, Bao Wei, Xu Wu, and Gordon Xia

Pacific Northwest National Laboratory, Richland, WA, USA

ABSTRACT

Pacific Northwest National Laboratory (PNNL) has conducted extensive research and development in the past few years in electrical energy storage for renewable integration and grid applications. The efforts have been supported by the Department of Energy Office of Electricity and Energy Reliability (DOE-OE), Advanced Research Projects Agency–Energy (ARPA-E), and internal funding, with focus on electrochemical storage technologies or batteries that include redox flow, sodium (Na)-metal halide and unique lithium (Li)-ion batteries, as well as some new concepts. To transform science to technologies, PNNL is closely working with industries in developing advanced components, cells, and prototypes. Our grid analytics help define the needs with the U.S. grid, which also guides the storage technology research, development, and demonstration (RD&D). This paper offers an overview and update on the progress of our efforts in various battery RD&D for the stationary applications.

Keywords: redox flow battery, Na-metal halide battery, Li-ion battery, Na-ion battery, renewable integration

Electrical energy storage (EES) is a vital enabler for transforming the electrical grid into the 21st century. Energy storage provides grid stability to integrate intermittent renewable energy resources into the grid as well as improving the overall utilization of the entire electricity infrastructure. There are various potential storage technologies for the stationary applications. However, the current technologies are either constrained by specific site selection (pumped hydro or compressed air storage) and/or cannot meet the performance and cost requirements for broad market penetration. To address the cost and performance challenges for advanced energy storage systems, Pacific Northwest National Laboratory (PNNL) has utilized electrochemical devices and advanced materials development capabilities to advance the stationary electrical storage technologies or batteries with near-term and longer-term goals. Also, an integral part of our efforts is on grid system analytics that further define the needs of the storage with U.S. grids and help guide the battery research, development, and demonstration (RD&D).

The battery RD&D portfolio at PNNL, as shown in Figure 1, includes existing technologies that have evolved over the past few decades, but had issues to meet the performance and cost requirement matrices for broad market penetration [1]. Particularly we have

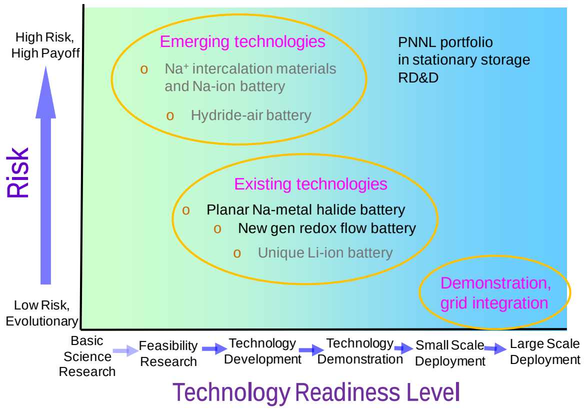

Fig. 1. PNNL portfolio of electrical grid energy storage research, development, and demonstration.

focused on three technology areas: aqueous based redox flow, sodium (Na)-metal halide, and unique lithium (Li)-ion batteries. In addition to accelerating commercialization of the existing technologies, PNNL has actively developed new EES concepts that can lead to transformational advances in performance and cost reduction. For example, in this past year, a Na-ion battery has been proved at room temperature, following discovery of Na-ion intercalation compounds.

NOVEL REDOX FLOW BATTERIES

With a redox flow battery (RFB) PNNL has aimed to develop low-cost, high-performance RFBs through collaboration with U.S. leading industries and universities (see Figure 2). In this past year, PNNL has made breakthroughs in the development of key component materials and chemistries for RFBs. New redox couples and supporting electrolytes based on halide and sulfate mixed chemistries have been discovered with significant advantages in stability, energy density, and cost, over the current all-vanadium sulfate systems. The mixed chloride and sulfate chemistries demonstrated a much improved stability, allowing for 75% increase in energy density and significant extension in operating temperatures (-5~55 ^{o}C) over the current technologies (10~35 ^{o}C), while being still highly reversible and efficient [2]. Alternatively, pairing of vanadium with iron, a more cost-effective replacement of vanadium, resulted in a substantially improved compatibility, allowing use of more cost-effective separators in the place of Nafion-membranes and avoiding gas release [3]. The ease in operation requirements, use of low-cost alternative components, and improved performance parameters all help reduce capital and life-cycle costs. In addition to electrolytes, PNNL has worked with DuPont, Daramic LLC, Fumatech, SGL, Graphtec, and others to screen and select the best membranes/separators and graphite felt electrodes. We have worked with Penn State University through subcontract to develop low-cost hydro-carbon alternatives to the Nafion membranes for RFB applications. Currently, bench-top systems are being assembled to further validate the new electrolytes and other components. Prototypes will be developed with collaboration with industries.

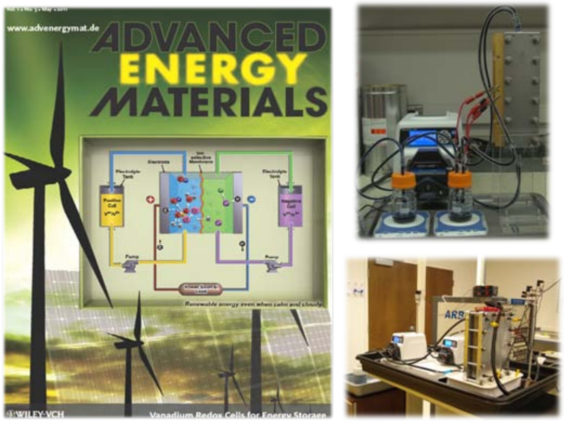

Fig. 2. Research and development of next-generation redox flow batteries at PNNL.

PLANAR NA-METAL HALIDE BATTERIES

The Na-metal halide battery was built in tubular designs and operated 300~350 ^{o}C since its invention a few decades ago. PNNL, teaming up EaglePicher Technologies LLC, is developing and demonstrating planar Na-metal halide batteries that can operate at lower temperatures with improved performance and allow use of more cost-effective stack materials. The team has successfully proved the concept of the planar design [4]. Interfaces and electrode chemistries have been optimized for the new designs (see Figure 3). Currently we are scaling up and assembling stacks to eventually deliver a 5-kW prototype. Meanwhile, efforts have been initiated to develop and optimize new cathodes, electrolytes, and interfaces to further reduce the operating temperatures.

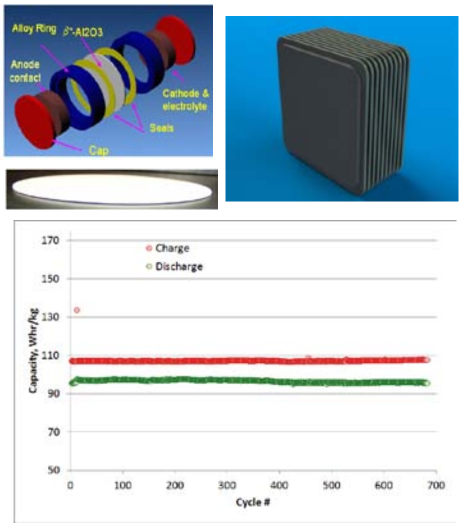

Fig. 3. Research and development of planar Na-metal halide batteries at PNNL.

UNIQUE LI-ION BATTERIES

PNNL has searched unique chemistries for Li-ion batteries that can demonstrate a longer cycle life and lower cost that the conventional ones currently of interest for vehicle applications. Our focus has been on developing low-cost electrode materials and demonstrating cells that are made from the cost-effective electrodes. Particularly, we have developed and optimized titanium dioxide (TiO_2) base anode and $LiFePO_4$ base cathode Li-ion batteries, intended for community storage. Nanocomposite electrode structures were developed to overcome the low electron conductivity issue of the materials. Over 1,000 deep cycles have been demonstrated for the Li-ion cells with only negligible capacity loss [5]. Currently we are developing new cathodes made from $Li(Mn,Fe)PO_4$ materials and evaluating the cells made from the cathodes.

EMERGING TECHNOLOGIES

Our efforts in emerging technologies have focused on proving new battery concepts that can lead to significant reduction in costs and performance. In this past year, we have developed single crystalline $Na_4Mn_9O_{18}$ nanowires as the positive electrode that allowed facile Na^+ intercalation and deintercalation. The Na-ion batteries (half-cells) made from the nanostructured material demonstrated a high reversible capacity and exceptional cycling performance. The $Na_4Mn_9O_{18}$ nanowire electrode material, after calcination at 750 ^oC, delivered a reversible capacity of 128 mAh g^{-1} at 0.1 C (1 C corresponds with 120 mA g^{-1}) with an excellent initial capacity retention capability of 77% even after 1000 cycles at 0.5 C (see Figure 4) [6]. Our current efforts are to search for new carbon-based negative electrodes so a full cell with commercial organic liquid electrolyte can be demonstrated in the future.

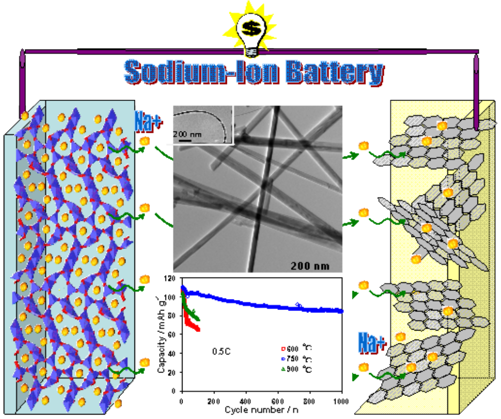

Fig. 4. Schematic and performance of a Na-ion battery made from a $Na_4Mn_9O_{18}$ nanowire electrode.

REFERENCES

[1] Yang et al., “Electrochemical Energy Storage for The Green Grid,” *Chem. Reviews* **111**, 2011, p. 3577.

[2] Li et al., “A Stable Vanadium Redox-Flow Battery with High Energy,” *Adv. Energy Mat.* **1**, 2011, p. 394.

[3] Wang et al., “A New Redox Flow Battery Using Fe/V Redox Couples in Chloride Supporting Electrolyte,” *Energy & Environ. Sci.*, available online.

[4] Lu et al., “High Power Planar Sodium-Nickel Chloride Battery," *ECS Transact*, **28**, 2011, p. 7.

[5] Choi et al., “Li-ion Batteries from $LiFePO_4$ Cathode and Anatase/Graphene Composite Anode for Stationary Energy Storage,” *Electrochem. Comm.* **12**, 2010, p. 378.

[6] Cao et al., “Reversible Sodium Ion Insertion in Single Crystalline Manganese Oxide Nanowires with Exceptional Long Cycle Life,” *Adv. Mat.*,**23**, 2011, p. 3155.

BIOGRAPHICAL NOTE

Conference presenter: Dr. Zhenguo (Gary) Yang is a Lab Fellow at Pacific Northwest National Laboratory (PNNL) of the U.S. Department of Energy, where he conducts applied research into advanced materials and energy conversion and storage. Currently, he is leading efforts in developing varied electrochemical energy storage technologies, in particular for renewable integration and grid applications. Previously he was a Chief Scientist and served as a technical lead in areas including solid oxide fuel cells, mixed conductive coatings, and hydrogen storage in nanostructured materials. Dr. Yang has authored/co-authored over 180 research papers and is an inventor/co-inventor of 16 U.S. patents. He is a fellow of ASM International. Dr. Yang received his Ph.D. in materials science and engineering from the University of Connecticut and worked as a postdoctoral fellow at Carnegie Mellon University before joining PNNL.