Case Western Reserve University

Final Scientific/Technical Report

High Energy Storage Capacity Low Cost Iron Flow Battery

Contract Number: DE-AR0000352

Award:	DE-AR0000352
Lead Recipient:	Case Western Reserve University
Project Title:	High Energy Storage Capacity Low Cost Iron Flow Battery
Program Director:	Grigorii Soloveichik
Principal Investigator:	Robert F. Savinell
Contract Administrator:	Advanced Research Projects Agency-Energy (ARPA-E), U.S. Department of Energy AR-1, 1000 Independence Avenue, SW, Washington, DC 20585
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X This Report contains no Protected Data.

Public Executive Summary

A new flow battery was proposed that utilizes low cost materials: iron as the only active element, cheap aqueous electrolytes, and inexpensive separators. During charging, ferrous iron (Fe^{2+}) is oxidized to ferric iron (Fe^{3+}) at the positive electrode while it (Fe^{2+}) is reduced to form iron metal (Fe^{0}) at the negative electrode. Because iron is plated at the negative electrode during charging, conventional electrode structures couple the energy storage capacity and the power rating of the battery. In order to decouple the energy and power ratings and regain the economic advantages of a flow battery, a slurry electrode design was proposed for use as the negative electrode. The slurry electrode is made by flowing electrically conductive particles in an electrolyte containing the dissolved iron species. On charging, iron is plated onto the particles. The particles can then carry the iron metal out of the cell to be stored in external reservoirs. This project looked to develop a slurry for the negative electrode of the all-iron flow battery that can operate at 200 mA/cm^2 with <100 mV overpotential, be pumped with parasitic energy costs < 10%, and promote plating on the particles. A scalable and stackable cell design of 1100 cm^2 was developed. The project was initially under contract in mid-January 2013. The project was converted from a one-year proof of concept seedling to an additional two-year program, then extended with an 18-month plus-up, and finally with an additional 6-month approved cost-overrun.

During the seeding project, the concept of plating on carbon particles in a slurry was demonstrated. However, this was accomplished with high-cost multi-walled carbon nanotubes as the slurry material. The following two-year program discovered several low-cost carbon blacks that could also be used in this application. These findings were supported by an analysis that demonstrated the effectiveness of the carbon that takes into account not just the effective electronic conductivity of the slurry, but also the surface area per volume of the slurry. It was demonstrated that stable, flowable slurries could be created with these carbons, even when the carbons where fully loaded with iron during charging. During the two-year program, laboratory-scale 50 cm^2 single-cells demonstrated charge-discharge cycling at current densities of 150 mA/cm^2 and energy efficiencies of >50%. Meanwhile, cost modeling continued to show promise for this energy storage approach.

Following the conversion period, the overall objective of the nominally 18-month plus up period was to close the technical gap of a 25X scale-up and reduce risk to enable commercial investment required to develop a slurry iron flow battery product. A specific objective was to demonstrate 150 cycles of performance exceeding 70% energy efficiency with a 10-cell stack of 1156 cm^2 cells operating at 100 mA/cm^2. The 10-cell short stack was designed to have a power delivery rating of approximately 1 kW, which represents a size commensurate with the requirements of our commercialization partner at that time. A complete battery support system for the full-size cell was designed, fabricated, and tested. This includes pumps (multiple types were considered, and constant volume hose pumps were found to be acceptable for performance and cost), electrolyte rebalance reactor, and sensors and control systems. The support system proved to be well-behaved and worked well. A new low-cost membrane was developed for this system based on a microporous polymer support with a layer of hydrogel polymer. The membrane had low resistivity, and significantly reduced pressure driven fluid flow across the membrane (as compared

to the un-coated microporous support). This membrane approach was scaled-up in conjunction with a commercial toll coating company, and a large amount of membrane was manufactured to support large cell and stack testing. A new concept for an electrolyte rebalance reactor to react hydrogen gas from the negative electrolyte (from plating inefficiency) with excess ferric ion in the positive electrolyte was developed. This design was very simple, low cost, and effective.

The full scale 1156 cm^2 single-cell was designed, modeled, fabricated and tested. Modeling showed that uniform flow-distribution should be obtained with the designed flow distributor. The design took into consideration the need to stack the cells, and components were fabricated for a ten-cell stack. Testing of the cell for charge and discharge demonstrated current densities of 50 mA/cm^2 with efficiencies of 50%. However, optimization and long cycling could not be accomplished because the slurry electrode would plug within the cell and block the flow. This would shut down the cell after several charge-discharge cycles. Various approaches were pursued to address this problem with some progress. However, there was not adequate time to find solutions to the problem although several promising approaches were identified for future work.

The final deliverable for this proposed 18-month effort was to be a 1 kW, 6 kWh slurry flow battery, with complete balance of plant, ready for testing at an ARPA-E 'Charges' site with an estimated capital cost less than $45/kWh for a six-hour system (excluding power electronics). The deliverable milestone was not achieved for reasons mentioned above related to the slurry plugging. At the completion of this project, it was determined that the cost targets are achievable. The cost estimate for a 1 MW system with a one-hour capacity was estimated at $140/kWh (including power electronics) and for a six-hour system was estimated at $40/kWh (including power electronics). These costs include the battery, the balance of plant, the power conditioning and a concrete pad. This program resulted in three patents including the slurry-based iron flow battery, the rebalance reactor, and the membrane separator. At the time of this report, slurry-based iron flow battery patents have been issued in the US, China, Japan, Korea, and Europe. The other patent applications were under various stages of examination. A licensee was identified and the company initiated a scale-up and development program to take this technology to the marketplace, and CWRU staff have transferred their know-how and knowledge base to the company. This technology will enhance the economic and energy security of the United States by enabling the use of intermittent renewable energy technology, such as wind and solar power, as dispatchable resources. This report summarizes the results of this research and development program.

Acknowledgements

This project was funded by the DOE Advanced Research Projects Agency- Energy (ARPA-E) through contract number DE-AR0000352. Financial and administrative support was provided by Case Western Reserve University. Cost-share research and financial support also was provided by Fusion Power System.

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Table1. Key Milestones and Deliverables

Accomplishments and Objectives

This award allowed Case Western Reserve University to demonstrate a number of key objectives. The focus of the project was on demonstrating the concept and building a working prototype of a slurry-based iron flow battery. This potentially very low cost approach to large-scale energy storage would have significant implications for improving energy conversion efficiency of conventional electrical power plants as well as to facilitate the introduction of substantial amounts of renewable energy sources into the US grid such as wind and solar.

A number of tasks and milestones were laid out in Attachment 3, the Technical Milestones and Deliverables, at the beginning of the project and updated with the conversion, plus-up, and approved cost overrun periods. The actual performance against the stated key milestones is summarized here:

Table 1. Key Milestones and Deliverables

The table follows the body of this report

Project Activities

A new flow battery was proposed that utilizes low cost materials: iron as the only active element, cheap aqueous electrolytes, and inexpensive separators. During charging, ferrous iron (Fe^{2+}) is oxidized to ferric iron (Fe^{3+}) at the positive electrode while it (Fe^{2+}) is reduced to form iron metal (Fe^{0}) at the negative electrode. Because iron is plated at the negative electrode during charging, conventional electrode structures couple the energy storage capacity and the power rating of the battery. In order to decouple the energy and power ratings and regain the economic advantages of a flow battery, a slurry electrode design was proposed for use as the negative electrode. The slurry electrode is made by flowing electrically conductive particles in an electrolyte containing the dissolved iron species. On charging, iron is plated onto the particles. The particles can then carry the iron metal out of the cell to be stored in external reservoirs. The project demonstrated the feasibility of the slurry electrode and performance in battery prototypes at the laboratory-scale size. The cell was then scaled-up to a full-size cell and support system. The full-size cell was demonstrated to function, although performance was not optimized. Challenges to slurry flow within the cell was observed, and although various approaches to resolve the issues were promising, a full solution was not possible within the time constraint of the project. The integrated flow, control, and electrolyte rebalance support system was demonstrated to successfully operate. A cost below $45/kWh for an large scale energy storage system (1 MW,with six hours of storage) was shown to be achievable. IP patent protection were filed for several inventions resulting from this work, and one patent has been granted at the time of this report in numerous countries, while two other patent applications are under various stages of examination.

During the seeding project, the concept of plating on carbon particles in a slurry was demonstrated. This was followed by a two-year conversion of the program, where laboratory-scale 50 cm^2 single-cells demonstrated charge-discharge cycling and a rebalance reactor and new low-cost membrane was invented. Following the conversion period, there was an 18-month plus up period with the objective to close the technical gap of a 25X scale-up and reduce risk to enable commercial investment required to develop a slurry iron flow battery product. Several tasks performed during this period were successful including scaling-up membrane manufacturing and the rebalance reactor, and designing, fabricating and testing the tank and flow system with sensors and controller. However, there were significant challenges uncovered with scaling up the laboratory cells to a full scale 1156 cm^2 cell. Achieving continuous charge and discharge cycling was hindered by slurry plugging the cell and blocking further slurry flow. During a six-month approved cost-overrun period solutions to these challenges were pursued, and although progress was made, a complete solution was not developed. However, a commercialization partner was identified and the company is pursuing resolving these issues with the aim of bringing this technology to the market place.

Project Outputs

A. Journal Articles and Ph.D. Dissertations

Ke, Xinyou, Alexander, J. Iwan, and R.F. Savinell, "Flow distribution and maximum current density studies in redox flow batteries with single passage of the serpentine flow channel", Journal of Power Sources, 270, 646-657 (2014).

N. C. Hoyt, J. S. Wainright, R. F. Savinell, "Mathematical Modeling of Electrochemical Flow Capacitors", *J. Electrochem. Soc*., **162** (4) A652-A657 (2015).

N.C. Hoyt, J. S. Wainright, R.F. Savinell, "Current Density Scaling in Electrochemical Flow Capacitors", *J. Electrochem. Soc.*, **162** (6) A1102-A1110 (2015).

T. J. Petek, N. C. Hoyt, J. S. Wainright, R. F. Savinell, "Characterizing Slurry Electrodes Using Electrochemical Impedance Spectroscopy", *J. Electrochem. Soc.*, **163**, A5001-A5009 (2015).

T. J. Petek, N. C. Hoyt, J. S. Wainright, R. F. Savinell, "Slurry Electrode for Iron Plating in an All-Iron Flow Battery", *Journal of Power Sources*. **294**, 620-626 (2015).

Ke, Xinyou, Alexander, Iwan D., Prahl, Joseph M. and Robert F. Savinell, "A simple analytical model of coupled single flow channel over porous electrode in vanadium redox flow battery with serpentine flow channel", Journal of Power Sources, 288, 303-312 (2015).

Hoyt, N.C., Savinell, R.F. and J.W. Wainright, "Modeling of Flowable Slurry Electrodes with Combined Faradaic and Nonfaradaic Currents", *Chemical Engineering Science*, **144**, 288-297 (2016)

S. Selverston, R. Savinell and J. Wainright , "In-tank Hydrogen Ferric Ion Recombination", *Journal of Power Sources* **324**, (2016), pp. 674-678, DOI: 10.1016/j.jpowsour.2016.05.126

Ke, X. Prahl, J.M., Alexander, J.I., and R.F. Savinell, "Mathematical Modeling of Electrolyte Flow in a Segment of Flow Channel over Porous Electrode Layered System in Vanadium Flow Battery with Flow Field Design", Electrochimica Acta, 223, 124-134 (2017)

Hoyt, N.C., Agar, E., Nagelli, E.A., Savinell, R.F., and J. Wainright, "Electrochemical Impedance Spectroscopy of Flowing Electrosorptive Slurry Electrodes", J. Electrochem, Soc., 165 (10), E439-E444 (2018); DOI: 10.1149/2.0051810jes

Ke, Xinyou, Prahl, Joseph M., Alexander, J.Iwan, and Robert F. Savinell, "Redox flow batteries with serpentine flow fields: Distribution of electrolyte flow reactant penetration into the porous carbon electrodes and effects on performance", J. Power Sources, 384, 295-302 (2018).

Tyler Petek, "Enhancing the Capacity of All-Iron Flow Batteries: Understanding Crossover and Slurry Electrodes", Ph.D. Dissertation, Case Western Reserve University, 2015.

Steven Selvertson, "Iron Based Flow Batteries: Improving Lifetime and Performance", Ph.D. Dissertation, Case Western Reserve University, 2017.
http://rave.ohiolink.edu/etdc/view?acc_num=case1495709157583731

Xinyou Ke, "Fundamental Studies on Transport Phenomena in Flow Batteries, Flow Field Structures and Slurry or semi-solid electrodes: Modelling and Experimental Approaches", Ph.D. Dissertation, Case Western Reserve University, 2018.
http://rave.ohiolink.edu/etdc/view?acc_num=case1543883710323558

B. Papers

Petek, Tyler, "Enhancing the Capacity of All-Iron Flow Batteries: Understanding Crossover and Slurry Electrodes: Electronic Dissertation, Case Western Reserve University, 2015, Ohio Link Electronic Thesis and Dissertation Center, 01 Feb 2019.

A poster of the project was presented at the 2013 ARPA-E Summit, and at the March 2013 San Diego Energy Storage Workshop and Kick-off meeting,

A poster, "High Energy Capacity Low Cost Iron Flow Battery" by Tyler J Petek, Jesse S Wainright, and Robert F Savinell, was presented at the 2013 ARPA-E Summit at the Gaylord National Hotel and Convention Center on 25-27 February 2013.

A poster, "High Energy Capacity Low Cost Iron Flow Battery" by Tyler J Petek, Jesse S Wainright, and Robert F Savinell, was presented at the ARPA-E Energy Storage Workshop and Kick-off meeting in San Diego 27-28 March 2013.

A poster, "High Energy Capacity Low Cost Iron Flow Battery" by Tyler J Petek, Jesse S Wainright, and Robert F Savinell, was presented at the CWRU Research ShowCASE on 12 April 2013 at Case Western Reserve University.

A poster, "High Energy Capacity Low Cost Iron Flow Battery" by Tyler J Petek, Jesse S Wainright, and Robert F Savinell, was presented at the 2013 OFCC Conference at Lorain County Community College on 01-02 May 2013.

A poster, "High Energy Capacity Low Cost Iron Flow Battery" by Tyler J Petek, Jesse S Wainright, and Robert F Savinell, was presented at the ECS chapter meeting at the Yeager Center at Case Western Reserve University on 10 May 2013.

A poster, "High Energy Capacity Low Cost Iron Flow Battery" by Tyler J Petek, Jesse S Wainright, and Robert F Savinell, and video of the project was presented at the 2013 Washington DC CWRU Alumni event on 22 May 2013. The project goals and status were shared in detail with Ohio Senator Sherrod Brown, US Representative Marcy Kaptur from Ohio's 9th district, and US Representative David Joyce from Ohio's 14th district. This event was held in the Library of Congress

Presentation, "Iron-Based Flow Batteries for Grid-Scale Energy Storage", Northeastern University and Sandia National Lab Workshop on Challenges in Energy Storage, August 2013.

Presentation, "Iron-Based Flow Batteries for Grid-Scale Energy Storage", Department of Mechanical Engineering, Massachusetts Institute of Technology, August 2013.

A poster, "High Energy Capacity Low Cost Iron Flow Battery" by Tyler J Petek at the CWRU Engineering Dean's Alumni Reception in Cleveland 27 September 2013.

Presentation and Poster – EESAT 2013 Meeting – 24 October 2013: T. Petek, J. Wainright, and R. Savinell, "High Energy Storage Capacity Low Cost Iron Flow Battery: Developing A Slurry Electrode".

Presentation – 2013 AIChE Annual Meeting – 03 November 2013: Tyler Petek, Robert F. Savinell, Jesse Wainright, "High Energy Storage Capacity Low Cost All-Iron Flow Battery: Developing a Slurry Electrode".

Presentation and Poster – 2nd Industrie De Nora Research Symposium – 12 November 2013: J. Wainright, R. Savinell, presentation "Flow Battery Research at EEELab-CWRU"; T. Petek, poster "High Energy Storage Capacity Low Cost Iron Flow Battery: Developing A Slurry Electrode".

Presentation – MRS Fall Meeting & Exhibit – 02 December 2013: RF Savinell, JS Wainright, TJ Petek, NS Sinclair, HN Hoyt, KL Hawthorne, IL Escalante-Garcia, MA Miller, "Iron-Based Flow Batteries for Grid-Scale Energy Storage".

Booth – NASA Northern Ohio Energy and Innovation Summit – 10 December 2013: T. Petek, J. Wainright, R. Savinell, "A Low Cost All-Iron Flow Battery".

Booth and Poster – Ohio Fuel Cell Coalition Symposium – 10-11 June 2014: T. Petek, N. Hoyt, N. Sinclair, J. Wainright, and R. Savinell, "High Energy Storage Capacity Low Cost Iron Flow Battery: Development of a Slurry Electrode".

Booth and Poster – Ohio Fuel Cell Coalition Symposium – 10-11 June 2014: T. Petek, N. Hoyt, N. Sinclair, J. Wainright, and R. Savinell, "High Energy Storage Capacity Low Cost Iron Flow Battery: Development of a Slurry Electrode".

Invited Presentation at Ohio University. September 8th, 2014. J. Wainright, “Recent Advances in Electrode Design for an All-Iron Flow Battery”

Invited Presentation at the Battery Show. Novi, Michigan. September 17, 1014. Robert F. Savinell, “Iron-Based Flow Batteries for Grid Scale Energy Storage”.

Poster – NY-BEST and JCESR Energy Storage Technical Conference – 5 November 2014. T. Petek, E. Nagelli, J. S. Wainright, R. F. Savinell, “High Energy Storage Capacity Low Cost Iron Flow Battery: Developing a Slurry Electrode”.

Poster – De Nora Research Symposium – 11-12 November 2014. E. Agar, E. Nagelli, N. S. Sinclair, J. S. Wainright, R. F. Savinell, “Conductivity Enhancement of Carbon Slurry Electrode for All-Iron Redox Flow Battery”.

Poster – De Nora Research Symposium – 11-12 November 2014. N. Hoyt, J. S. Wainright, R. F. Savinell, “Mathematical Modeling of Electrochemical Flow Capacitors”.

Poster – De Nora Research Symposium – 11-12 November 2014. S. Selverston, J. S. Wainright, “Passive, Internal Electrolyte Balancing in Aqueous Flow Batteries”.

Presentation at the Fall ECS Meeting, Cancun Mexico, October 4th, 2014 Krista Hawthorne, “Recent Advances in Electrode Design for an All-Iron Flow Battery

Booth – ARPA-E Energy Innovation Summit, Feb 2015, Washington, DC, N. Sinclair, E. Agar, E. Nagelli

E. Agar, N. S. Sinclair, E. A. Nagelli, T. J. Petek, N. C. Hoyt, J. S. Wainright, R. F. Savinell, High Energy Storage Capacity Low Cost Iron Flow Battery. *ARPA-E Bi-Annual Stationary Energy Storage Meeting*. May 28-29, 2015, Chicago, IL.

E. Agar, E. A. Nagelli, N. S. Sinclair, N. C. Hoyt, E. A. Striker, R. F. Savinell, J. S. Wainright. “Cost-Effective All-Copper Flow Battery Using Flowable Slurry Electrode for Large-Scale Energy Storage”. *228th ECS Meeting.* October 11-16, 2015, Phoenix, AZ.

N. C. Hoyt, E. Agar, E. A. Nagelli, R. F. Savinell, J. S. Wainright, “Characterization of Carbon Black Particles for Use in Aqueous Slurry Electrodes”. *228th ECS Meeting.* October 11-16, 2015, Phoenix, AZ.

E. Agar, E. A. Nagelli, N. S. Sinclair, N. C. Hoyt, E. A. Striker, R. F. Savinell, J. S. Wainright. “Cost-Effective Redox Flow Batteries using a Flowable Slurry Electrode”. *2015 MRS Fall Meeting & Exhibit.* November 29 – December 4, 2015, Boston, MA.

N. S. Sinclair, E. A. Nagelli, J. S. Wainright, R. F. Savinell, “High Energy Storage Capacity Low Cost Iron Flow Battery”, *Electrical Energy Storage Applications and Technologies (EESAT) 2015 Technical Conference*, September 21-24, Portland, OR (2015)

E. Agar, N. S. Sinclair, E. A. Nagelli, T. Petek, N. Hoyt, J. S. Wainright, R. F. Savinell, “High Energy Storage Capacity Low Cost Iron Flow Battery”, *ARPA-E Bi-Annual Stationary Energy Storage Technology Meeting*, May, 28-29, Chicago, IL (2015)

E. Agar, E. A. Nagelli, N. S. Sinclair, N. C. Hoyt, E. A. Striker, R. F. Savinell, J. S. Wainright. “Cost-Effective All-Copper Flow Battery Using Flowable Slurry Electrode for Large-Scale Energy Storage”. *228th ECS Meeting.* October 11-16, Phoenix, AZ (2015)

N. C. Hoyt, E. Agar, E. A. Nagelli, R. F. Savinell, J. S. Wainright, “Characterization of Carbon Black Particles for Use in Aqueous Slurry Electrodes”. *228th ECS Meeting.* October 11-16, Phoenix, AZ (2015)

E. Agar, E. A. Nagelli, N. S. Sinclair, N. C. Hoyt, E. A. Striker, R. F. Savinell, J. S. Wainright. “Cost-Effective Redox Flow Batteries using a Flowable Slurry Electrode”. *2015 MRS Fall Meeting & Exhibit.* November 29 – December 4, Boston, MA (2015)

E. A. Nagelli, R. F. Savinell, J. S. Wainright, “Slurry Electrodes for Industrial Processes” *Pathways for Sustainable Manufacturing (EPSuM) Innovation Workshop*, July 6, Columbus, OH (2015).

R. F. Savinell and J. S. Wainright, “CWRU All Iron Flow Battery”, *ARPA-E Bi-Annual Stationary Energy Storage Technology Meeting*, May, 28-29, Chicago, IL (2015) *(invited)*

R. F. Savinell, “Flow Batteries for Grid Scale Energy Storage”, Department of Physics and Energy, University of Limerick, June 8, Limerick, Ireland (2015) *(invited)*

. Agar, E. A. Nagelli, N. S. Sinclair, N. C. Hoyt, E. A. Striker, R. F. Savinell, J. S. Wainright. “Cost-Effective All-Copper Flow Battery Using Flowable Slurry Electrode for Large-Scale Energy Storage”. 228th ECS Meeting. October 11-16, Phoenix, AZ (2015)

N. C. Hoyt, E. Agar, E. A. Nagelli, R. F. Savinell, J. S. Wainright, “Characterization of Carbon Black Particles for Use in Aqueous Slurry Electrodes”. 228th ECS Meeting. October 11-16, Phoenix, AZ (2015)

E. Agar, E. A. Nagelli, N. S. Sinclair, N. C. Hoyt, E. A. Striker, R. F. Savinell, J. S. Wainright. “Cost-Effective Redox Flow Batteries using a Flowable Slurry Electrode”. 2015 MRS Fall Meeting & Exhibit. November 29 – December 4, Boston, MA (2015)

R.F. Savinell, “Commercializing the CWRU Iron Flow Battery: A Technology with Promise for Commercial Utility Energy”, Energy Storage and Integration Workshop-Emerging Technologies from the Region, NASA Glenn Research Center, Cleveland, Ohio, October 29-30, 2015.

Booth, ARPA-E Summit, Feb 2016, Washington, DC, “High Energy Storage Capacity Low Cost Iron Flow Battery,” N Sinclair, E Nagelli, A Bourke, J Wainright, R Savinell

Booth, ARPA-E Summit, Feb 2017, Washington, DC, “High Energy Storage Capacity Low Cost Iron Flow Battery,” N Sinclair, Joe Murphy, J Wainright

“Slurry Electrodes, Iron Flow Batteries, and Other Approaches to Grid-Scale Energy Storage”, Invited Lecture, University of Virginia, April 6, 2017

“Scaling Considerations in All-Iron Flow Batteries,”
Nicholas Sinclair, ECS Meeting Spring 2017, New Orleans.

Poster Presentation “Hydrogen Diffusion Transport in an All-Iron Flow Battery System,”
Xinyou Ke, ECS Meeting Spring 2017, New Orleans

Oral presentation “slurry Electrodes, Iron Flow Batteries, and Other Approaches for Grid-Scale Energy Storage” Robert F. Savinell, International Society of Electrochemistry, Fall Meeting in Providence, Rhode Island, 2017.

C. Status Reports none

D. Media Reports

These sites posted stories based on the press release sent by CWRU. Some are word-for word based on the original CWRU article, others edited and did some reporting.

Featured article on the phase 3 program.
http://phys.org/news/2016-12-battery-prototype-augment-grid.html

CWRU Article
http://thedaily.case.edu/researchers-building-flow-battery-prototype-augment-grid/

Featured article and news clip on an ABC affiliate station.
http://www.news5cleveland.com/news/e-team/spending-bill-could-cut-funding-to-renewable-energy-research-at-case-western-reserve-university

E. Invention Disclosures

An invention disclosure has been filed with Case Western Reserve University on the all-iron flow battery including the slurry negative electrode. (Referred to in Patent Applications as ***Iron Flow Battery***.)

An invention disclosure has been filed with Case Western Reserve University with regards to flow batteries utilizing alternative metal halide chemistries (e.g. iron or copper with chloride, bromide, or iodide). This invention disclosure stemmed both from this ARPA-E funded project and the DOE-OE project in the same facilities. (Referred to in Patent Applications as ***Halide Flow Battery***.)

An invention disclosure has been filed with Case Western Reserve University for in-tank electrolyte rebalancing in sealed aqueous flow battery systems. (Referred to in Patent Applications as ***Hydrogen Recombination Reactor***.)

An invention disclosure has been filed with Case Western Reserve University pertaining to development of a coated microporous separator that is both highly conductive and is able to minimize hydraulic crossover. (Referred to in Patent Applications as ***Composite Membrane***.)

An invention disclosure has been filed with Case Western Reserve University pertaining to the internal flow structure of a slurry flow battery. (Not patented.)

F. Patent Applications

Iron Flow Battery

US Provisional Application 61/491,973 filed on June 1, 2011. PCT/US2012/040429 filed on June 1, 2012. US Application 14/122,885 filed on Dec. 1, 2013 and published as US 2014/0227574 A1 on Aug. 14, 2014. Issued on Jan. 31, 2017 as US 9,559,375 B2.

European Application EP 12 792 876.0 filed on Nov. 15, 2013 and published as EP 2 715 841 B2 on May 23, 2018. EP Decision to Grant December 6, 2017 as EP 2 715 841 A2; validated in UK, DE, FR, NL and DK in April 2018. EP/DK 2715841, issued July 23, 2018 ("Kongeriget Denmark").

Chinese Application CN 201280027075.8 filed on Dec. 2, 2013 and published as CN 103748709 A on Apr. 23, 2014. Notice of grant received March 1, 2017; fees paid and patent granted, May 2017.

Japanese Application JP 2014-5153737 filed on Nov. 20, 2013 and published as JP 2014-519168 A on August 7, 2014. Granted as JP 6013463 B2 on October 25, 2016.

Korean Application KR 10-2103-7034154 filed on June 1, 2012 and published as KR 10-2014-00051180 on April 30, 2014. Granted as KR 101824032 B1 on Jan. 25, 2018.

Halide Flow Battery

US Provisional Application 62/051,817 was filed on Sep. 17, 2014. PCT/US2015/050676 was filed on Sep. 17, 2015 and nationalized as US Application 15/512,079 on Mar. 17, 2017. This application was published as US 2018/0233763 A1 on Aug. 16, 2018.

Hydrogen Recombination Reactor

US Provisional Application 62/239,469 was filed on Oct. 9, 2015. PCT/U2016/056230 was filed on Oct. 10, 2016 and published as WO 2017/062936 A1 on Apr. 13, 2017. US Application 15/766,121 was filed on April 5, 2018 and published as US 2018/0294502 A1 on Oct. 11, 2018.

Australian Application AU 2016 334 392 was filed on Oct. 10, 2016 and published as AU 2016334392 A1 on Apr. 26, 2018.

Chinese Application CN 201680070054.2 was filed on May 30, 2018 and published as CN 108292771 A on July 17, 2018.

European Application EP 16854529.1 was filed on Apr. 30, 2018 and published as EP 3 360 193.

Japanese Application JP 2018-517725 was filed on June 5, 2018 and published as JP 2018536968 A on Dec. 13, 2018.

Korean Application KR 10-2018-701298 was filed on May 8, 2018 and published as KR 10-2018-0073592A on July 2, 2018.

<u>Composite Membrane</u>

US Provisional Application 62/300,323 filed on Feb. 26, 2016. PCT/US2017/019644 filed on Feb. 27, 2017 and published as WO 2017/147568 A1 on Aug. 31, 2018.

US Application 16/080,080 filed on Aug. 27, 2018 and published as US 2019/0067725 A1 on Feb. 28, 2019.

Australian Application AU 2017224129 filed on Feb. 27, 2017 and published as AU 2017224129 A1 on Aug. 31, 2018.

Chinese Application CN 201780025725.8 was filed on Oct. 25, 2018 and published as CN 109075369 A on Dec. 21, 2018.

European Application EP 17757410.0 was filed on Aug. 30, 2018 and published as EP 3 420 610 A0 (cover sheet of WO 2017/147568 A1) on Jan. 2, 2019.

Japanese Application JP 2018-545167 was filed on Aug. 27, 2018.

Korean Application KR 10-2018-7027791 was filed on Sep. 27, 2018 and published as KR 10-2018-0118712A on Oct. 31, 2018.

G. Licensed Technology

A license agreement is in place with Fusion Power Systems for the all iron flow battery using slurry technology. A sponsored research agreement is also completed as cost share for the ARPA-E phase three stack development of the technology.

H. Networks/Collaborations Fostered

A conference call with the leaderships of the Electrochemistry Innovation Laboratory of University College London and a representative of the British Consulate in Chicago about a collaboration between UCL and CWRU on electrochemistry and flow battery research. There is much interest and plans have been made to exchange information, and to apply to the British Consulate for funds to facilitate establishing a collaboration including but also beyond flow battery research. However, there was no follow-up in the part of UCL.

George Crabtree PI of the Argonne led energy storage hub (JCSER) visited CWRU to discuss collaboration opportunities between CWRU and JCSER. Dr. Crabtree will recommend that CWRU be included as an affiliate of JCSER.

Craig Evans of Energy Storage Systems in Oregon visited CWRU to discuss common interests in commercializing the iron flow battery and to tour the CWRU labs. There were several follow-up discussions during the project about further collaboration, but ESS felt that because of its commitment to the hybrid iron flow battery concept they did not have the band-width to pursue the slurry iron flow battery in parallel.

A collaboration was initiated between our research group and Keithley Instruments. This effort focused on developing software routines to allow Keithley's 'source meter' instruments to be used for electrochemical measurements and for battery and supercapacitor testing in particular. Kiethley provided funding for one researcher from our group to write the necessary code, which was tested on cells in our laboratory.

A collaboration with XG Sciences had been developed in which XG Sciences provided particles for testing.

A conference call and visit were held with ITN Energy Solutions in which ITN expressed interest in the project and requested an exchange of on-site visits. Initial talks with a United Mineral Resources and TDM focused on the possibility of collaboration, forming a new start-up company, and raising venture funding. These did not end up with a collaboration.

Discussions were had with principals of RTP Consulting of Chicago, IL and Flagship Ventures of Cambridge, MA. Both of these potential partners did their due diligence studies regarding licensing the IFB technology. Serious discussions continued with Flagship Ventures for over a year about the status of the technology and licensing arrangements. CWRU eventually terminated these discussions after deciding to partner with Fusion Power Systems (see below).

Discussions were initiated with Concurrent Technology Corporation. CTC was viewed as a potential manufacturing partner with experience in stack design. Multiple visit between the groups took place, and an agreement for a collaboration involving the Phase III of the program was established. However, with new management at CTC, the agreement with respect to cost-share fell apart.

After several discussions with Fusion Power Systems, a license agreement was put in place for the all iron slurry technology. A sponsored research agreement was also completed as cost share for the ARPA-E phase three (stack development) of the technology.

I. **Websites Featuring Project Work Results: none**

J. **Other Products (e.g. Databases, Physical Collections, Audio/Video, Software, Models, Educational Aids or Curricula, Equipment or Instruments):** none

K. Awards, Prizes, and Recognition

Robert F. Savinell, awarded Fellow of the International Society of Electrochemistry (only ~50 Fellows globally at the time of his award)

Robert F. Savinell, awarded Distinguished University Professor of Case Western Reserve University (CWRU highest recognition to faculty, and only 21 DUPs had been awarded at that time)

Follow-On Funding

There was no follow-on funding to CWRU after the end of this award. However, Fusion Power Systems which spun out a separate company called Mobius invested (do not know amount) in its own prototype development program and was also seeking external investment capital.

TABLE 1: Key Milestones and Deliverables

TASKS

Phase 1

1 Understand Slurry Properties

1.1 Characterize phase behavior, stability and rheology of electronically conducting slurries

1.2 Understand, predict, measure electrical conductivity of slurry electrodes

Milestones and Deliverables

Q1 Milestone: Slurry viscosity < 10X that of 2 M $FeCl_2$

- We have demonstrated that, at flow rates equal to or larger than 5 times stoichiometric flow rates in a 1000 cm^2 cell at 150 mA/cm^2, the slurry viscosity is less than 10 times the base electrolyte due to the shear thinning behavior.

Q2 Milestone: Slurry stable for > 2 hours without agitation.

- Slurries made of multi-walled carbon nanotubes and slurries made of 20µm natural carbon flakes were investigated in stagnant beakers.
  - Over 2 hours, a volume fraction gradient was visually observed in both slurries; there was a higher fraction of particles at the bottom than the top of the slurry. However, there was minimal phase separation observed.
  - This effect was much more noticeable with the flakes than the MWCNTs.
  - With the MWCNTs, any pumping action was sufficient to immediately redistribute the slurry.

Q1 Milestone: Slurry electronic conductivity > 0.5 S/cm

- This goal was not reached. We have extensive data on the electronic conductivity of different particle sizes, shapes, and concentrations as well as stagnant and flowing results Investigate slurries with different particle properties:
  - Different particle materials, i.e. metals such as nickel, iron, and copper, and metalized carbon particles.
  - Different particle size ranges and shapes – MWCNTs and nanofibers as well as with particle sizes in the 200-500µm range.

	Q2 Milestone: Slurry ionic conductivity > 0.1 S/cm. • This goal was reached. We have extensive data on the ionic conductivity of different electrolyte compositions containing $FeCl_2$ and $FeCl_3$ with 1.0 M NH_4Cl. o Depending on the state of charge (from 25:75 to 75:25) and total iron content, the ionic conductivity ranged between 0.10 and 0.16 S/cm. Q2 Milestone: Slurry electronic conductivity > 1.0 S/cm. • This goal was not reached. In addition to investigating natural flake carbon reported last quarter, many different slurries were investigated. The most promising slurry to date is made with multi-walled carbon nanotubes and displays an electronic conductivity as high as 85 mS/cm initially. After an initial charge to 35 mAh/g of MWCNT, the electronic conductivity increased to over 0.6 S/cm. • Later in the program a model was developed that showed lower effective slurry electrical conductivity could be off-set by high surface area in order to keep plating off the current collector. Therefore, this target level of conductivity was not necessary.
1.3 Measure electrochemical kinetics of reactions of interest for slurry electrodes	Q2 Milestone: Activation overpotentials < 20 mV at 200 mA/cm^2 for $Fe^{2+/3+}$ redox reaction • This goal has been reached. Through analysis of polarization data and impedance spectroscopy, the activation overpotentials in the positive slurry electrode have been determined to be about 13 mV at 200 mA/cm^2. Q3 Milestone: Demonstrate kinetic overpotential <100mV at 200mA/cm^2 for $Fe^{2+/0}$ • This milestone was accomplished. A $Fe^{2+/0}$ slurry was shown to have an exchange current density of 170 mA/cm^2, corresponding to 30 mV of kinetic overpotential at 200 mA/cm^2. • This result was achieved only when monitoring and adjusting the pH of the slurry during the initial charge. While the electronic conductivity of the slurry is low, the cell voltage is high and hydrogen evolution can occur. If the pH rises above 5, ferrous hydroxides can precipitate on the particles and passivates the particles to the reaction. However, if the initial metal deposition on the particles can occur without a significant pH shift, the slurry becomes more conductive and the reactions can proceed at lower potentials and hydrogen evolution is less likely to occur.
1.4 Measure and correlate mass transfer to slurry electrodes	Q2 Milestone: Demonstrate a slurry with a limiting current >1 A/cm^2 for $Fe^{2+/3+}$ redox reaction • This goal was reached. For the positive slurry electrode made with MWCNTs in 0.5M $FeCl_2$, 0.5M $FeCl_3$, and 1M NH_4Cl, the limiting current was found to be >1.2A/cm^2.

2 Mathematical Models

2.1 Flow/Pressure Drop Models

Q3 Milestone: Demonstrate a slurry with a limiting current >2 A/cm^2 for the iron plating reaction

- A dramatic increase in the limiting current was observed when the pH was maintained below 5. The overall cell polarization is mostly linear through +/-0.15 A/cm^2 suggesting a limiting current of at least 0.5 A/cm^2.

Q1 Milestone: Model pumping costs to be less than 20% of a 5kW stack

- A half-cell flow field, as well as a feeder pipe, was designed and modeled and the pressure drop was found to be significantly less than 1.2 watts for all of the scenarios tested.
- The flow field design showed appropriate pressure drops to control the distribution of the slurry in the stack and within the cell.

Q4 Milestone: Demonstrate less than 10% pumping losses via modeling.

- This milestone has been achieved. Modeling predicts the combined parasitic losses due to pumping and shunt currents to be less than 2% of a 5 kW stack.

2.2 System level model

Q4 Milestone: Demonstrate via modeling an efficiency of greater than or equal to 70% round trip energy efficiency. Predict overall efficiency for a decoupled all-iron flow battery for different power ratios; including pumping loses.

- The total overpotential of an all-iron battery with slurry electrodes as both the positive and negative electrodes was estimated by independently measuring the system overpotentials. The estimated voltaic efficiency at 200 mA/cm^2 is 73%. With 2% parasitic losses, due to pumping and shunt currents, the coulombic efficiency has to be > 98% to achieve a round trip efficiency > 70%.

Q4 Milestone: Demonstrate negative electrode polarization of <100 mV at 200 mA/cm^2

- This milestone has been achieved. The total overpotential in a slurry electrode, 6wt% industrial grade MWCNTs, has been measured relative to a reference electrode during copper deposition. Copper instead of iron, was used in these studies as a model system to avoid complexities of hydrogen evolution. The total overpotential was consistently about 80 mV after 50 mAh/g C of copper was

3 Prototype Development

3.1 The objective of this task is to develop a 50 cm^2 hardware set and validate its performance

4 Technology to Market

4.1 Update T2M Plan

deposited. Plating 50 mAh/g C is equivalent to 10% of the total charge of a 1M Fe^{2+} negative slurry. A 1M Fe^{2+} battery could be cycled 10%-90% SOC without affecting the initial copper deposited.

Q4 Milestone: Demonstrate slurry electrode performance of 95% coulombic efficiency at 200 mA/cm^2 for a 50 cm^2 half-cell for third cycle. Demonstrate 100 cycles at C/3 rate with 80% of initial capacity retained and 80% utilization of Fe^{2+} in reservoir.

- While the 50 cm^2 cell is operational, testing in this system was suspended in order to focus efforts on pre-metallizing natural flake carbon particles (particles which will, according to the CAPEX analysis, allow the system to achieve $100/kW). Pre-metallizing the particles will raise the electronic conductivity enough so that the more economic particles can effectively operate as a slurry electrode.

Q1 Milestone: Complete and present T2M Plan that details roadmap and identifies key T2M gaps for future analysis.

- The Technology to Market (T2M) Plan for the "High Energy Storage Capacity Low Cost Iron Flow Battery (0670-5371) was finalized on December 19, 2012.

Q1 Milestone: Meet with Energy Storage Systems in Oregon to discuss collaborations, interests, and opportunities with their ARPA-E flow battery project; Visit at least one other potential collaborator/commercialization partner.

- Met with ESS at the ARPA-E Summit and at the San Diego Kick-off meeting. There is interests in collaboration but will need to find a way to protect the IP of each other's' technology. ESS visited CWRU. Also met with Watt-Joule at the ARPA-E Summit and the company's principals expect to visit CWRU in the near future. Had conference call with A123, and an NDA will be initiated before further detailed discussions commence. Visited EnerVault in California to learn about their redox flow battery technology. They are not likely to collaborate directly on the all iron flow battery since they have invested and continue to pursue their iron/chrome technology.

Q2 Milestone: Preliminary market evaluation; Define market and performance requirements.

- This task was subcontracted to Strategen Consulting LLC. A preliminary market assessment had begun, and we continue discussion with them about the expected product.

Q2 Milestone: Complete preliminary cost-performance model

4.2 Market assessment and outreach to potential collaborators/advisors 4.3 Complete preliminary cost-performance model	• The effect of various parameters (current density, voltaic efficiency, carbon particle cost, and electrolyte utilization) on the capital cost of a 1MW/4MWh system was estimated. Q3 Milestone: Identify possible paths, funding, and appropriate partners for next stage of development • Under contract, Strategen Consulting has delivered a comprehensive market assessment. Three top focus areas have been identified of highest priority and ease of deployment/lead time. The report has been used as a "pitch deck" to engage companies in sectors of the energy storage industry and will continue to be refined next quarter. To date, an extensive list of companies has been assembled and 16 contacts have been made.
4.4 Establish Transition Plan 4.5 Final cost-performance model	Q4 Milestone: Refine the cost-performance model with updated CAPEX/OPEX, including sensitivity analysis and competitive benchmarking. • With component pricing consistent with the PNNL Redox Flow Battery Interactive CAPEX model, the CAPEX for the all-iron battery is estimated to be as low as \$100/kW. A sensitivity analysis has been prepared on the cost of the carbon as well as current density. Competitive benchmarking has been completed by STRATEGEN, LLC.
4.6 Next-stage agreement secured	Q4 Milestone: Engage potential end-of-project transition partners and establish agreement. • Many high-potential partner targets, e.g. ABB, BASF, Parker Hannifin, S&C Electric, and Xtreme Power, are engaged in continuing conversations but to date no agreements have been finalized.
Phase 2 **1 Understand Slurry Properties** 1.1 Pursue strategies (various l/d substrates, pre-metallization) to develop slurry electrode with required electrical characteristics and rheology properties using non-MWNT starting materials	Q6 Milestone: Slurry that is > 300 mS/cm in battery negative electrolyte • A list of readily available slurry substrates has been compiled with corresponding inherent conductivities. • Metal has been plated onto cost effective starting materials using a dilute electrolyte method. Pre-metallization by electroless deposition was determined to be not cost effective. Q6 Milestone: Slurry that is > 300 mS/cm in battery negative electrolyte • Work is being done to investigate a new source of particles from XG Sciences. Work is also being done to investigate the electrochemical pretreatment of particles. • Heat treatment has shown to improve the conductivity of Nano27 particles.

- During pre-metallizing of heat treated Nano27 particles it has been observed that copper was not plated onto the current collector but agglomerates were formed.

Q8 Milestone: Slurry that is >30 mS/cm electrical conductivity and a slurry surface area/volume > 200,000 cm^2/cm^3

- This milestone has been achieved. Two carbon particles have been identified that meet the goal thus far: Regal 660R (Cabot) and xGnP graphene nanoplatelets.

1.2 Focus research on selected low-cost substrate materials and characterize electrochemical and rheology properties

Q8 Milestone: Slurry that is >30 mS/cm electrical conductivity and a slurry surface area/volume > 200,000 cm^2/cm^3, still flowable after stand > 2 hrs, and flow viscosity < 100 cP

- This milestone has been achieved. Two carbon particles have been identified that meet the goal thus far: Regal 660R and Monarch 800 (both Cabot).

Q9 Milestone: Slurry that is >30 mS/cm electrical conductivity and a slurry surface area/volume > 200,000 cm^2/cm^3, still flowable after stand > 2 hrs, and flow viscosity < 100 cP and CAPEX <$500/kW

- This milestone has been achieved. Two carbon particles have been identified that meet the goal thus far: Regal 660R and Monarch 800 (both Cabot).

Q11 Milestone: Slurry electrical conductivity > 30 mS/cm and a surface area/volume > 200,000 cm^2/cm^3, still flowable after stand > 2 hrs, flow viscosity < 100 cP and CAPEX < $100/kW

- Achieved. Previous reports have confirmed electrochemical and rheological milestones have been met utilizing the Cabot R660R particle. Current cost estimates for battery component CAPEX with the R660R particle place a one-hour megawatt scale system at $95/kW and approximately $10/kWh for each additional kWh.

1.3 Understand slurry properties over 10-90% SOC

Q10 Milestone: Slurry electrical conductivity > 300 mS/cm, still flowable after stand > 2 hrs, flow viscosity < 100 cP and CAPEX < $500/kW with metal loadings of 0.4 Ah/g of C and 0.8 Ah/g of C

2 Prototype Development

2.1 Fabricate low aspect ratio cell design with commercially realistic bipolar plates (50cm^2)

2.2 Fabricate four 50 cm^2 prototype cells of second generation

2.3 Fabricate a 400 cm^2 prototype cell

- Achieved. Measurement of rheological properties of the slurry electrolyte as a function of SOC (i.e. metal loading) has been carried out. Negligible pressure and viscosity changes were observed with SOC.

Q6 Milestone: Complete second generation 50 cm^2 cell fabrication and test slurry flow

- This milestone is in progress. A scalable prototype has been created with a 25cm^2 electrode.
- The design is capable of housing a 50cm^2 electrode but due to power supply limitations is not currently being utilized.

Q7 Milestone: Cells fabricated and integrated into test stands

- This milestone has been achieved. Cells have been fabricated and received. The cells have been received from Tanzola Design and Manufacturing and have been integrated into the test stands.

Q9 Milestone: Cell fabricated and integrated with controls and test integrity of flow

- The 400 cm^2 hardware is being designed to include inlets designed to minimize shunt currents as well as using flow pathways which have demonstrated even flow distribution in the 50 cm^2 hardware.

Q9 Milestone: Cell fabricated and integrated with controls and test integrity of flow

- Achieved. Cell has been received, assembled and integrated with controls. No loss of flow integrity was observed and symmetric cell tests indicate no significant contact resistances in the hardware.

Q6 Milestone: Complete design of test stations, build test stations, and test the test stations.

- The test stations have been designed and all components have been received with the exception of the Bio-Logic battery cycler.

Q6 Milestone: Complete design of test stations, build test stations, and test the test stations.

- This milestone has been achieved. Construction on four test stations has been completed and tested for leaks

3 Prototype Electrochemical Performance 3.1 Design stations for simultaneously testing four 50 cm^2 prototype cells 3.2 Experimentally characterize electrochemical performance of string of four 50 cm^2 prototype cells 3.3 Experimentally test 400 cm^2 prototype cell	*Q8 Milestone: Demonstrate >60% voltaic efficiency and >90% coulombic efficiency at >150 mA/cm^2 over 10 cycles of 40-60% SOC* • This milestone has been achieved. 22 cycles of 40-60% SOC have been achieved in the iron chemistry with >90% coulombic efficiency at 150 mA/cm^2 with voltaic efficiency of 62% after accounting for 10 mΩ of contact resistance in the cell. The 22 charge-discharge cycles were achieved with an average voltaic efficiency of 54%, and if we assume 10 mΩ is from contact resistance alone still meets the >60% voltaic efficiency milestone. A 10 mΩ correction is a conservative estimate considering our measured contact resistance from our series of symmetric cell experiments is ca. 20 mΩ.
4 Mathematical Modeling 4.1 Simulate and optimize design for 50 cm^2 cell flow fields and cell configuration 4.2 Simulate and optimize 400 cm^2 cell flow fields and cell configuration	Q5 Milestone: Complete 1st generation design and performance simulation This milestone has been achieved. A scalable and stackable design has been created. The design was confirmed as easily manufactured and stackable by a commercial manufacturer. Q6 Milestone: Complete 2nd generation design and performance simulation • This milestone has been completed. Design and performance modeling was outlined in the quarter 5 report. *Q8 Milestone: Complete design and performance simulation* • Performance testing is being carried out on the second generation of 50-cm^2 hardware prior to the design of 400-cm^2 hardware
5 Technology to market 5.1 Refine cost-performance model to drive R&D to focus on most important components, parameters, metrics	Q6 Milestone: Complete 1st iteration system-level cost-performance model based on 50cm^2 cell prototype development. Analyze and pinpoint areas to increase performance and reduce costs to guide team's R&D. Model flow battery systems for mainstream and different possible first markets. • CAPEX as low as $150/kW, including the voltaic and coulombic efficiencies as a function of membrane thickness, can be achieved with particles that cost <$120/$m^3$ of electrolyte. The modeling efforts predict round trip energy efficiencies >66%. To date, all work has fixed the volume

of the positive electrolyte as twice that of the negative electrolyte. Future work will investigate how changing the negative electrolyte volume (which dictates the amount of slurry particles) affects the total system CAPEX.

Q8 Milestone: Complete 2nd iteration system-level cost-performance model with best to date designs, cell materials and fabrication estimates, and membrane and slurry materials. Highlight further techniques to increase performance and reduce CAPEX.

Q8 Milestone: Complete 2nd iteration system-level cost-performance model with best to date designs, cell materials and fabrication estimates, and membrane and slurry materials. Highlight further techniques to increase performance and reduce CAPEX.

- This milestone has been achieved. The second iteration cost-performance model has been completed and currently being utilized to determine the most crucial areas in which CAPEX can be reduced.

5.2 Establish IP strategy and secure IP

Q6 Milestone: Develop comprehensive IP strategy and plan (patents vs. trade secrets; if/when/ where to file, what patents to maintain, etc.). Patents filed in Europe, China, S. Korea, and Japan.

- This milestone was completed in quarter 5 and outlined in the quarter 5 report.

Q8 Milestone: Prepare invention disclosure for pre-metallization techniques. Revisit IP plan.

- This milestone is no longer applicable to the project. It has been shown through modeling in the previous quarter and demonstrated in this quarter that pre-metallization is not necessary to ensure favorable current distribution. The IP plan has been revised to include this change.

Q10 Milestone: Prepare invention disclosure for scalable cell design. Revisit IP plan.

- Achieved. An invention disclosure has been prepared for the scalable 400 cm^2 hardware design.

Q11 Milestone: Evaluate invention disclosures for patentability. File patent applications per IP plan.

- In progress. Four invention disclosures from this project have been filed with the University Technology Transfer Office, and two have been already filed for patent application, while two are being considered for application. Cell designs are still being evaluated for patentability.

5.3 Publishing and presenting results consistent with IP strategy	Q6, Q7….. Milestone: Per IP plan, present results at National and international professional society meetings and ARPA-E organized meetings. • Journal publications at national/international meetings, posters, dissertations, etc. are itemized in this final report.
5.4 Engage commercialization partners	Q6 Milestone: Identify 4 potential partners for collaborating on cell design for manufacturing. Identify other possible strategic partners and develop plans for potential engagement of these partners. The Engagement Plan will include: outreach strategy (contacts + timing) for potential supply chain, development, and manufacturing partners and funders. • Potential partners identified to date include Arotech (Ann Arbor, MI); Electric Fuel Battery (Auburn, Alabama); FuelCellsEtc (College Station, TX); Giner (Newton, MA); Lynntech (College Station, TX); Proton OnSite (Wallingford, CT); Teledyne Energy Systems (TESI) (Hunt Valley, MD). Initial contact has been established with Lynntech, Proton OnSite, and TESI. • An "evergreen" document ("Company Target List") has been developed to easily record any identified potential partners and monitor progress with them. The document is updated whenever there are changes in the degree of engagement with any of the target companies in order to monitor the partner engagement process. Q7 milestones • Discussions have been initiated with UL and EPRI regarding collaborations leading to commercializing an iron flow battery. UL has an interest because of the safety issues related to large scale energy storage. EPRI has entered into discussions because of interest expressed by a Utility (FirstEnergy). • An NDA was executed on December 17, 2014 with ITN Energy Systems to foster exchange of confidential information and collaboration efforts towards cell stack design and testing. A conversation will be scheduled in late-January 2015. • Recontacted Alstom for the status of their interest on Nov. 18, 2014 and Jan. 13, 2015. • Recontacted Pangaea Ventures, who deferred from evaluating the IFB due to ongoing "due diligence with a startup company developing an all-iron flow battery." The contacted stated that "a term sheet has been signed" (with the other company). • Younicos acquired Xtreme Power in April. Xtreme Power had indicated interest and good feedback with respect to the IFB system when contacted in October 2013. • An "evergreen" document ("Company Target List") has been developed to easily record any identified potential partners and monitor progress with them. The document is updated whenever there are

changes in the degree of engagement with any of the target companies in order to monitor the partner engagement process.

Q8 Milestone: Progress against Engagement Plan reported

- This milestone has been achieved. This quarter, a conference call was held with ITN Energy Systems to discuss the technology and on-site visits are being scheduled. We have also begun conversations with a metals company about the potential for a start-up company and venture funding for a prototype demonstration project. Conversations with Alstom Power have been re-initiated and a visit to CWRU in the summer is being planned.

Q9 Milestone: Secure a partnership for collaborating on cell design for manufacturing. Present a post-project transition plan that includes a proposed commercialization pathway (licensing, partnership, or start-up), an outreach plan to customers, partners, and/or investors based on anticipated strategy, key technological risks and mitigations, and next steps and actions with associated timeline. If a start-up is the likely preferred pathway, include expected first markets of entry, expected business model, and target partners and customers. In the case of a start-up or partnership, also include identified funding needs for next steps and potential funding sources. Develop pitch deck for potential strategic partners and/or funders.

- This milestone is in progress. This quarter, a visit with ITN was conducted in order to assess ITN's capabilities and discuss future partnership opportunities. We have continued conversations with United Mineral Resources and Tanzola Design and Manufacturing about the potential for a start-up company and venture funding for a prototype demonstration project. Discussion this quarter with two other potential partners were started and are still on-going. One of these potential partners is a principal of RTP Consulting of Chicago, IL and with whom we are initiating an NDA. The other is a principal of Flagship Ventures of Cambridge, MA. Both of these potential partners are in various stages of performing due-diligence
- Achieved. We have secured TDM as our manufacturing partner.
- Our post-project transition plan includes securing venture funding for a start-up along with funding though the SBIR/STTR program.
- The expected first markets of entry are customers requiring energy storage for their businesses and private properties for renewable energy storage and time-shift.

Q10 Milestone: Refine transition plan choosing the most appropriate commercialization model based on the level of technology development, refine pitch deck appropriate for given pathway selected and continue to engage next-stage partners. Report on progress against post-project transition.

- Achieved. A startup has been determined to be the most likely commercialization path. A manufacturing partner has been identified (TDM) and is currently helping to secure startup

Phase 3

1 Stack Scale Up and Demonstration

1.1 Cell and Stack Design, Simulation, Fabrication, and Testing

funding. Additionally, a letter of intent is being prepared for the upcoming round of Department of Energy SBIR/STTR funding. A pitch deck has been refined specifically for a small business commercialization approach and additional next stage partners are being engaged.

Q11 Milestone: Refine transition plan adding key manufacturability, and scale-up risks and mitigations, refine pitch deck as appropriate and continue to engage next-stage partners. Report on progress against post-project transition.

- Achieved. Transition plan has been refined specifically for either license to Flagship Ventures or formation of a startup company as post project transition options pending evaluation of the technology by Flagship Ventures.

Q14: Cell Fabrication - Fabricate first generation 1156 cm^2 cell prototype and test flow distribution.

- First generation 1156 cm^2 cell has been designed based on testing conducted in fourth generation 50 cm^2 hardware during this quarter. The hardware design was sent for manufacturing.

Q14: Stack Simulation - Complete simulation and design of 10-cell short-stack (1156 cm^2 area/cell) with less than 20% flow variation cell to cell, less than 5% combined pump and shunt losses.

- Completed. The current design has less than 20% flow variation from cell to cell. Shunt and pumping loss has been estimated to be 1%.

Q14: Cell Fabrication - Fabricate first generation 1156 cm^2 cell prototype and test flow distribution.

- Our preferred manufacturer determined that the designs sent to them were too large to be machined on the CNC machines available. Additionally, significant clogging was observed with the Cabot Regal 660R particle in the current hardware that was the basis for the full-scale cell design. A redesign was completed based on modular 50 cm^2 hardware normally used for non-slurry batteries. This design utilizes flat gaskets as spacers, which will eliminate several o-rings and will require less material to produce. It will be able to be machined on the available CNC machines. A ramped insert was created and preliminary testing was done with slurry in the 50

cm^2 hardware. Changes were made to the ramp insert design to support the gasketing over a large area and these inserts are being machined for testing.

Q15 Milestone stack leak test - Fabricate and test 10-cell short-stack (1156 cm^2 area/cell) for leak integrity, demonstration leakage (liquid) in 24 hours and H_2 leak rate < 1 mol H_2/day at 5psig.

- The bipolar stack design has been completed and has been modeled for flow. Careful consideration has been placed on the distribution of slurry to each individual cell in the stack. The transition from the manifold into and out of the individual cells is a potential failure point with the slurry electrode. Fabrication of the stack has been delayed due to the issues noted above

Q15 Milestone single cell performance - Single cell testing completed, incorporate design/materials changes in next-generation cell design. Meet performance target: 70%EE at 0.1 A/cm^2, 20 cycles at 50% DOD.

- This milestone has been delayed due to issues with the cell design as well as clogging observed with R660R particles. New cell designs have been completed and are being tested on a 50 cm^2 scale.

Q16 Milestone stack performance go/no go - Short-stack testing completed, incorporate design/materials changes in next-generation stack design, demonstrate 70% EE at 0.1 A/cm2 , 20 cycles at 50% DOD

- Header design testing has been completed on the 50 cm^2 hardware. Designs for the 1156cm^2 cell have been submitted to the manufacturer and we are awaiting the completion of the hardware.

Q17 Regarding Q16 Milestone stack performance go/no go

- 1156cm^2 cell hardware has been received and initial single cell leak testing has been completed. A leak due to the construction of the graphite has been identified and is being corrected by the manufacturer.

Q17 regarding Q15 Milestone stack leak test.

- Stack components have all been fabricated. Some design changes were initiated as a result of findings from leak testing a single full-size cell, and single cell is now lead tight.

Q18 regarding Q15 Milestone single cell performance

- The single cell testing has been completed, and operated continuously with the R660 activated carbon with surfactant. Multiple cycles have been demonstrated at over 80% SOC and .05 A/cm2 with over 60%VE.

Q19 Regarding Q16 Milestone stack performance go/no go –

- The 1156cm^2 cell hardware has been received and initial single cell leak testing has been completed. Modification to the flow distributing inserts were made to improve flow and the pump used for slurry has been changed to a peristaltic pump that prevents densification of the slurry and the corresponding clogs. Initial cycling test have been completed with cycles from 40-50% SOC and 20-80% SOC. A full charge has also been performed with no increase in cell pressure from 0-100% SOC.

Q20 Regarding Q16 Milestone stack performance go/no go -

- The 1156cm^2 cell hardware has been received and initial single cell leak testing has been completed. An issue with the shunt control ports has been identified and an insulating coating has been tested on small scale hardware to alleviate the issue. Corresponding modifications will be made to the stack hardware in the next few weeks. Initial cycling test have been completed with cycles from 40-50% SOC and 20-80% SOC (the % amount of iron II chloride converted to iron III or iron 0). A full charge has also been performed with no increase in cell pressure from 0-100% SOC. New milestones have been negotiated to end of project.

Q21 Regarding Q16 Milestone stack performance go/no go -

- The 1156cm^2 cell hardware has been received and initial single cell leak testing has been completed. An issue with the shunt control ports has been identified and an insulating coating has been tested on small scale hardware to alleviate the issue. This solution has been

	implemented on the 1156 cm^2 stack hardware. Several cycling tests have been run with a repeating deformation of the membrane causing the cell to clog after time.
1.2 Membrane fabrication scale-up	Q14 milestone Membrane Performance - Validate membrane performance; demonstrate areal resistivity <0.6 ohm-cm^2 in iron electrolyte; pressure driven permeability < 1E-14 cm^2 in iron electrolyte. • Completed Q15 milestone: Membrane received- Fabricate 30 membrane pieces for prototype 1156 cm^2 cell and stack testing with areal resistivity <0.6 ohm-cm^2 in iron electrolyte; pressure driven permeability < 1E-14 cm^2 in iron electrolyte. • Samples of a roll to roll process adapted from our coating procedure by Chemsultants have been received and tested. The scaled coating procedure meets all membrane performance milestones. The coater is being scheduled to run a full roll. Processing at this scale can be done at a rate of 0.5 m^2 per minute and a cost of \$20/m^2.
2 Scale-up and Testing an Electrolyte Rebalance and Hydrogen Recombination System 2.1 Develop a mathematical model of a multi-electrode CGR and optimize a design	Q16 reactor performance - Validate performance of CGR with 50mA/cm^2 of catalyzed area in a simulated hydrogen evolving system at 2 psi H_2 and iron electrolyte tank with 0.5M Fe^{3+}. • This milestone has been met and exceeded. Recombination reactor performance of greater than 80 mA/cm^2 has been demonstrated in a simulated in-tank system. A more convenient out of tank system in which transport should be enhanced has been designed and is being machined currently. This modification should further enhance performance, thus reducing the reactor size and reduce the amount of platinum needed for this system.
2.2 Develop and test a full-size prototype CGR for the prototype battery system	Mid- Q16 Milestone CGR lifetime performance - Fabricate full-size CGR and complete life test with less than 1% decay in the H2 consumption rate over 30 days. • A 1/10th scale prototype had been fabricated and is being tested in a flow loop with a Mazzei injector for flow and sealing. Design was modified with a vapor barrier to prevent an unforeseen condensation issue that has the potential to flood the catalyzed surface with time. Full scale design will be created with an included vapor barrier upon confirmation in 1/10th scale prototype. Q18 Regarding Mid-Q16 Milestone CGR lifetime performance

2.3 Deliver the prototype CGR for integration into the balance of plant system	• A 1/10th scale prototype had been fabricated and is being tested in a flow loop with a Mazzei injector for flow and sealing. A 4X increase in performance using 8X lower platinum loading has been seen in the CGR when gas phase transport is designed appropriately. Q22 Regarding Mid-Q16 Milestone CGR lifetime performance • A 1/10th scale prototype had been in successful operation for several weeks of cycling with an 1156 cm^2 single cell. Q22 Regarding Mid- Q16 Milestone CGR lifetime performance. • A recombination system is implemented in the balance of plant but issues with cell clogging have prevented a 30-day test.
3 Balance of Plant Prototype Development 3.1 Develop a process and instrumentation design for the balance of plant	Q14 BOP milestone - Down select and order tanks, pumps, sensors, and control hardware for BOP. • Complete.
3.2 Spec and acquire pumps, tanks, sensors, controls 3.3 Integrate BOP	Q16 BOP fab and test - Complete fabrication and testing of BOP. Demonstrate one-week uninterrupted stand-alone operation. • Completed – Individual components have been acquired and tested in parts with the exception of full scale tanks. The tank design is partially dependent on the final design of the recombination reactor and has not been ordered until the reactor design is finalized.
4 Prototype Battery System Testing 4.1 Test integrated short-stack with balance of plant system	Q19 Regarding Q16 BOP fab and test • Completed – Individual components have been acquired and tested in parts with the exception of full scale tanks. The system has been outfitted with pH probes this quarter. Q20 Regarding Q16 BOP fab and test

This task was never completed due to challenges with continuous operation with the single cell. **5.Technology to market** 4.2 Refine cost-performance models	• Completed – Individual components have been acquired and tested with the exception of full scale tanks. The system has been outfitted with pH probes this quarter. Additionally, temperature control has been added to the system through the use of titanium heat exchangers and a recirculating hot/cold water system. New milestones have been negotiated to end of project. Q15 Waterfall Presentation - Waterfall presentation and sensitivity analysis of cost model approved by ARPA-E. The model includes estimation of membrane fabrication and stack costs, and the iteration of full system cost at different production volumes. • Complete and ready for approval by ARPA-E. Cost models have been developed on the 1 kW / 6 kWh scale and the 1 MW / 6 MWh scale. Membrane substrate and fabrication, felt, carbon particles, electrolyte, and balance of plant have been considered for each scale. Q16 cost projections GO/NO GO - Go/no go waterfall presentation of cost model projection less than $100/kWh for 6 hr system for high production volume. • Completed- Projected cost for the first megawatt scale, six-hour system are $330/kW and $55/kWh, including power conditioning. Cost for concrete pad has been added based on talks with system installers. Additional installed costs are being refined with assistance from GEM Energy, a custom solar/storage system provider. Q16 Milestone BOP - Complete cost estimate of BOP, <$20/kWh based on experimental data and vendor quotes. • Completed - The complete list of balance of plant components has been completed and the total cost of the BOP system for the 1 kW system totals $17,000. This system is comparable to the system required for the 1 MW system and will cost approximately the same, or $17/kWh.

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