

PNNL REPORT

PNNL-23819-4

Unlimited Release

High Current Density Redox Flow Batteries for Stationary Electrical Energy Storage

Milestone Report for the DOE-OE Energy Storage Systems Program

(FY16 Quarter 4: October 2015 through September 2016)

**David Reed, Ed Thomsen, Vilayanur Viswanathan, Wei Wang, Zimin
Nie and Vincent Sprengle**

Prepared by
Pacific Northwest National Laboratory
Richland, Washington 99354

Pacific Northwest National Laboratory is a multi-program laboratory managed and operated by Battelle Memorial Institute for the U.S. Department of Energy under contract DE-AC05-76RL01830.

Approved for public release; further dissemination unlimited.

Issued by Pacific Northwest National Laboratory, operated for the United States Department of Energy by Battelle Memorial Institute

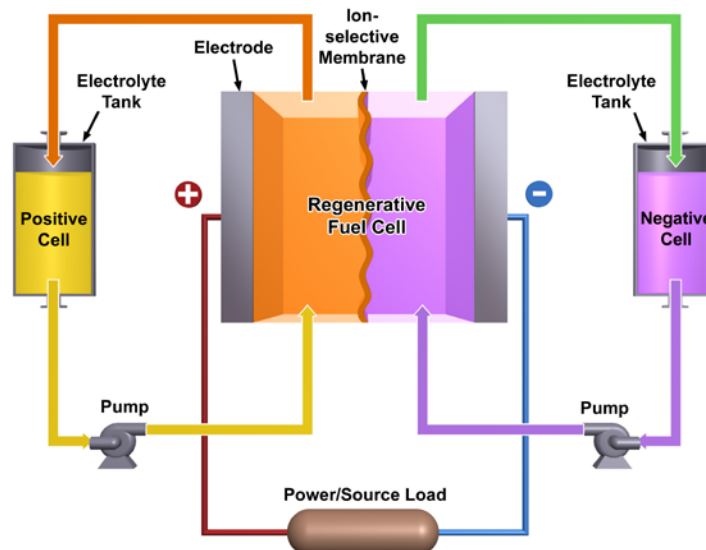
NOTICE: This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government, nor any agency thereof, nor any of their employees, nor any of their contractors, subcontractors, or their employees, make any warranty, express or implied, or assume any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represent that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise, does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government, any agency thereof, or any of their contractors or subcontractors. The views and opinions expressed herein do not necessarily state or reflect those of the United States Government, any agency thereof, or any of their contractors.

High Current Density Redox Flow Batteries for Stationary Electrical Energy Storage

Milestone Report for the DOE Energy Storage Systems Program
(FY16 Quarter 4: October 2015 through September 2016)

David Reed, Ed Thomsen, Vilayanur Viswanathan, Wei Wang, Zimin Nie and Vincent Sprengle

Energy and Environmental Directorate
Pacific Northwest National Laboratory
Richland, WA 99354



A schematic illustration of the structure of a redox flow battery

Abstract

This report describes the status of advanced redox flow battery research being performed at Pacific Northwest National Laboratory for the U.S. Department of Energy's Energy Storage Systems Program.

In FY16 we target a redox flow battery system operating with 25% increased current density over FY15 targets. The redox flow battery system will be developed and designed to maximize the stack energy efficiency at 400 mA/cm². A prototype kW scale system will be demonstrated to show the targeted improvements in performance. Cost projections for a 1 MW/ 4 MWh commercial system will be based on the performance and materials used in the demonstration stack.

- **Target reached:** A 3-cell redox flow battery was constructed and tested using the all vanadium mixed acid electrolyte developed under the OE program. The 3-cell stack was operated at 400 mA/cm², a 25% increase over the FY15 target (320 mA/cm²). A thinner, lower resistant membrane, Nafion® NR-211, was utilized along with a new monolithic bipolar plate design with an interdigitated flow pattern. Both additions to the FY16 stack improved performance and lowered the cost of the stack design. The resulting 3-cell stack exceeded target metrics by achieving an average power of 1.1 kW and a stack energy efficiency of ~ 74% when operated at 400 mA/cm². The prototype stack maintained similar stack energy efficiency (~74%) in comparison to FY15 targets. The system cost for a commercial 1MW/4MWh redox flow battery system is projected to be ~\$290/kWh for the all vanadium mixed acid electrolyte.

Q1 Milestone: Evaluate performance of existing redox flow battery technology at 400 mA/cm² and determine efficiency/performance tradeoffs.

- Milestone completed. A single cell with active area of 780 cm² was constructed using the FY15 design and evaluated at 25% greater current density (400 mA/cm²) to determine the impact on the stack energy efficiency. When operated at the FY15 current density target of 320 mA/cm², the stack energy efficiency was ~75% with a flow rate of 800 cc/min/cell and a temperature of 35°C. The stack energy efficiency was decreased by ~ 5% at the same flow rate and temperature when the current density was increased to 400mA/cm². The pressure drop was maintained below 10 psi and was nearly identical for both current densities evaluated. Optimization of components will be further investigated in FY16 to increase the stack energy efficiency at 400 mA/cm².

Q2 Milestone: Complete evaluation of experimental 3-cell stacks with component improvements to improve stack performance at higher current density.

- Milestone completed. A new single cell with active area of 780 cm² was fabricated with the FY15 design with a thinner Nafion 211 membrane. The Nafion 211 membrane is approximately 1 mil thick in comparison to a 2 mil thick Nafion 212 that was used in FY15. The stack demonstrated in Q1 operated at 400 mA/cm² had a stack energy efficiency of 70% at ~35°C with a flow rate of 800 cc/min/cell. The new cell fabricated in Q2 utilizing the Nafion 211 membrane had a stack energy efficiency of 73% when operated under similar conditions. Cost performance projections and additional design changes to increase performance and to reduce the cost will be evaluated and described in detail in Q3 and Q4 of FY16.

Q3 Milestone: Evaluate cost performance models based on Q2 results.

- Milestone completed. The redox flow battery cost model was validated using performance data from a 3-cell stack. At a current density of 400 mA/cm², the new redox flow stack with an optimized design and flow rate can achieve a stack energy efficiency of 70% with projected system costs of \$290/kWh. Approximately 60% of the total cost is associated with the chemicals attributed to the price of vanadium.

Q4 Milestone: Develop and demonstrate a kW scale redox flow battery system capable of meeting projected cost targets of < \$300/kWh for a projected 4-hour system.

- Milestone completed. A 3-cell prototype stack was demonstrated and fabricated using a thinner, less-resistant Nafion® NR-211 membrane. In addition, a monolithic bipolar plate design with an interdigitated flow pattern was used in the 3-cell stack. The bipolar plate is a vinyl ester/graphite composite material applicable to low cost, high volume manufacturing. The resulting 3-cell stack exceeded target metrics by achieving an average power of 1.1 kW and a stack energy efficiency of ~ 74% when operated at 400 mA/cm². The system cost for a commercial 1MW/4MWh redox flow battery system is projected to be ~\$290/kWh for the all vanadium mixed acid electrolyte.

Introduction

The demand for large-scale electrical energy storage (EES) devices has been growing for both improved efficiency and flexibility of the current grid infrastructure and to enable a higher penetration of stochastic renewable sources such like solar and wind onto the grid. Among the most promising technologies for the grid-scale EES are redox flow batteries (RFBs), which are capable of storing a large quantity of electricity (multi-MWs/MWhs) in a relatively simple and straightforward design.^{1,2}

There are several RFB technologies including polysulfide/bromide,^{3,4} all vanadium,⁵⁻⁸ Fe/Cr,⁹ and etc², however, the all-vanadium redox flow battery (VRFB) has received significant attention because of its excellent electrochemical reversibility, high round-trip efficiency, and negligible cross-contamination between positive and negative electrolytes.¹⁰ Systems up to multi-MWs have been demonstrated for grid applications and renewable integration.¹⁰

Even though the VRFB technology has several advantages over the conventional Li ion or lead acid batteries, high capital cost is one major challenge for the widespread deployment of VRFB's. The high cost of these systems can be attributed to several factors, including the use of expensive vanadium, costly Nafion[®] membrane and the need of an additional heat exchanger system to help maintain the electrolyte temperature between 25 and 35 °C in order to prevent precipitation of the conventional pure sulfate electrolyte.

Recently, PNNL scientists¹¹ made a dramatic improvement in the thermal stability and solubility of the conventional pure sulfate VRFB system by developing a mixed acid (hydrochloric and sulfuric acid) supporting electrolyte. In small-scale, single flow cell tests, electrolytes with up to 2.5 M vanadium in the mixed acid electrolyte (vs. < 1.6 M for the conventional VRFB) demonstrated stable charge/discharge cycling operation over a temperature range of -5 ~ 50 °C. In addition to the increased concentration, the addition of chloride ions also reduced the viscosity of the electrolyte¹², potentially reducing the power consumption required for pumping the electrolyte through the cell.

In FY12, PNNL demonstrated a 1 kW / 1 kWh scale prototype stack and system in order to validate the improved mixed acid electrolyte in a larger scale system. This system successfully increased the maximum operating current density of the stack from 50 to 80 mA/cm² (>50% increase) while achieving a ~ 25% increase in the energy density of the system through the enhanced vanadium solubility of the mixed acid electrolyte. As tested, the 1.0 kW /1.0 kWh prototype system was able to deliver a continuous power of 1.1 kW in the operating range of

15 to 85 % SOC at 80 mA/cm² with an energy efficiency of 83% and an energy content of 1.4 kWh. A picture of the assembled and tested redox flow battery system is shown in Figure 1.

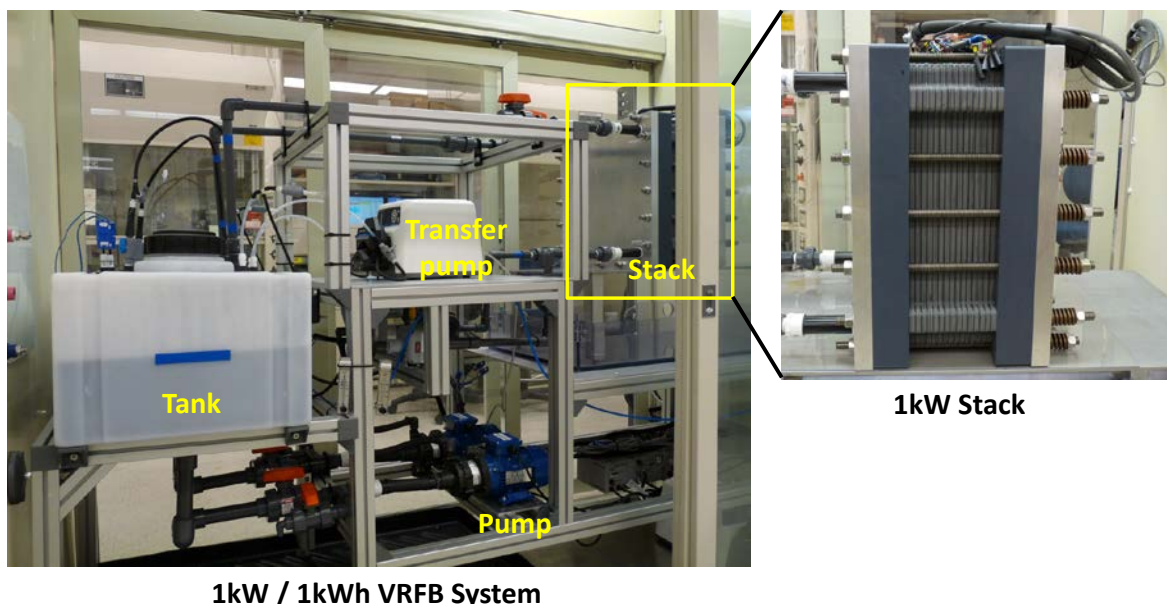


Figure 1. 1 kW / 1 kWh VRFB system and 1 kW stack

The kW scale VRFB with the PNNL mixed acid electrolyte successfully demonstrated stable, reliable and efficient operation without any precipitation - even at electrolyte temperatures > 45°C. This high temperature operability provides several unique advantages including: 1) high electrochemical stack efficiency due to better kinetics and low electrolyte resistance, 2) low viscosity resulting in lower pump power loss, and 3) no need of heat exchanger system. The aforementioned benefits also increase the system energy efficiency and enable simplification of system designs and control, resulting in overall cost reductions. Cost analysis for a 1.0MW / 4.0 MWh system were based on the performance of the prototype stack and project to a system level cost of \$540 /kWh when assuming a 20% installation cost and current material technologies. Overall, the prototype system exceeded the performance goals of 1.0 kW at 80mA/cm² and energy efficiency of > 70%- while meeting the cost target of < \$560/kW.

In FY 13, PNNL demonstrated a 1 kW/ 1kWh scale prototype stack and system with double the previous current density (160 mA/cm² vs 80 mA/cm²). The stack utilized a Nafion 212 membrane which is approximately half the thickness and cost of the conventional Nafion 115 used in state of the art redox flow battery systems. A new interdigitated flow concept was also developed using modeling and experimental techniques to attain an increase flow of up to 3-4 times the original design while maintaining the same pressure drop. The resulting stack exceeded target metrics by achieving 2.4 kW at 160 mA/cm² with an energy efficiency of 79%, nearly 5% greater than previous stacks, and a system efficiency of 72%.

In FY 14, PNNL demonstrated 4 kW/ 1 kWh scale prototype stack and system with 50% greater current density than FY 13 (240 mA/cm² vs. 160 mA/cm² in FY13). The battery utilized the OE developed all-vanadium mixed acid electrolyte and a Nafion 212 membrane. At 240 mA/cm², the stack achieved ~ 5X increase in discharge power over FY13 objectives (4.9kW vs. 1kW) while operating at ~ 75% energy efficiency. In addition to using lower cost membrane materials, the stack employed a novel interdigitated design and lower pressure drop manifolds

to reduce the required pumping power for the system. With these improvements, the system cost for a commercial 1MW /4MWh redox flow battery system was projected to be < \$400/kWh.

IN FY 15, PNNL demonstrated a 5 kW/1 kWh scale prototype stack and system with 33% greater current density than FY 14 (320 mA/cm² vs 240 mA/cm²). The battery utilized the OE developed all-vanadium mixed acid electrolyte, a Nafion 212 membrane, a redesigned interdigitated design, and higher performance electrodes. Operating at 320 mA/cm², the stack exceeded target metrics by achieving an average power of 6.3 kW while maintaining a stack energy efficiency of ~75%. Including these improvements, the projected cost for a 1MW/4MWh redox flow battery system was projected to be \$315/kWh.

FY16 Quarter 1 Project Status Summary

The FY16 Q1 milestone was to “Evaluate performance of existing redox flow battery technology at 400 mA/cm² and determine efficiency/performance tradeoffs.” As discussed above, 20 cell stacks were assembled and the current density was progressively increased over the past 3 years from 160 mA/cm² to 320 mA/cm². The results of the stack efficiencies at a flow rate of 800 cc/min/cell and 50°C for FY 13, FY14, and FY15 is shown in Figure 2.

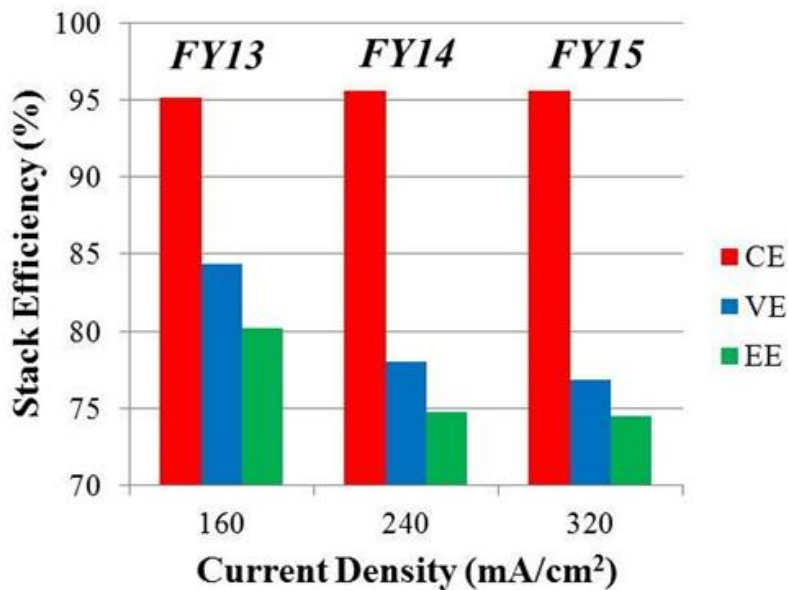


Figure 2. Stack efficiencies for 20 cell stack operated in FY13, FY14, and FY15 at 160, 240, and 320 mA/cm², respectively.

As shown in Figure 2, the stack energy efficiency was maintained at ~ 75% in FY 15 by utilizing a new interdigitated design and higher performance electrodes. Over the three year period, the stack energy efficiency showed a minimal decrease of 5% with a doubling of the current density. The average power of the stacks, however, was increased from 3.4 kW to 6.3 kW with a doubling of the current density, Figure 3.

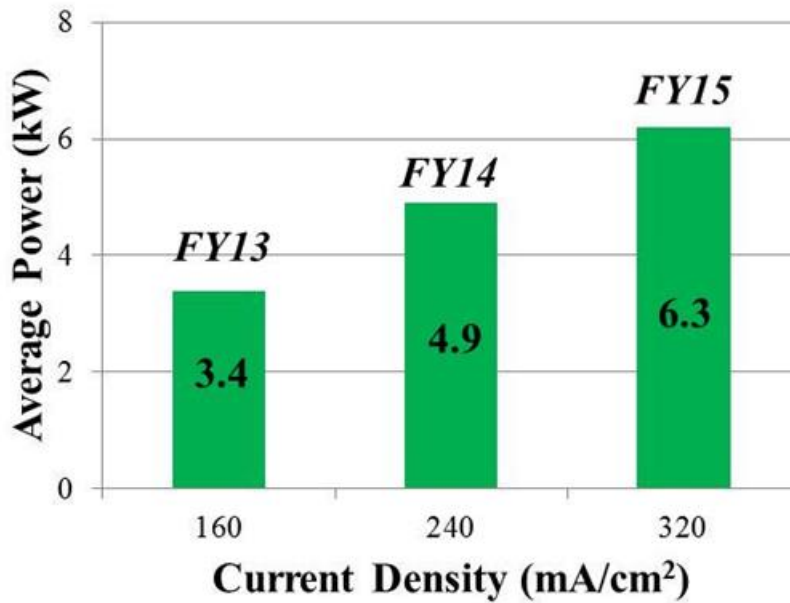


Figure 3. Average power for 20 cell stack operated in FY13, FY14, and FY15 at 160, 240, and 320 mA/cm², respectively.

The objective of Q1 was to test a single cell at 400 mA/cm² utilizing the FY15 design. The single cell was tested at 320 and 400 mA/cm² and 800 cc/min/cell, the results of the cell efficiencies are shown in Figure 4.

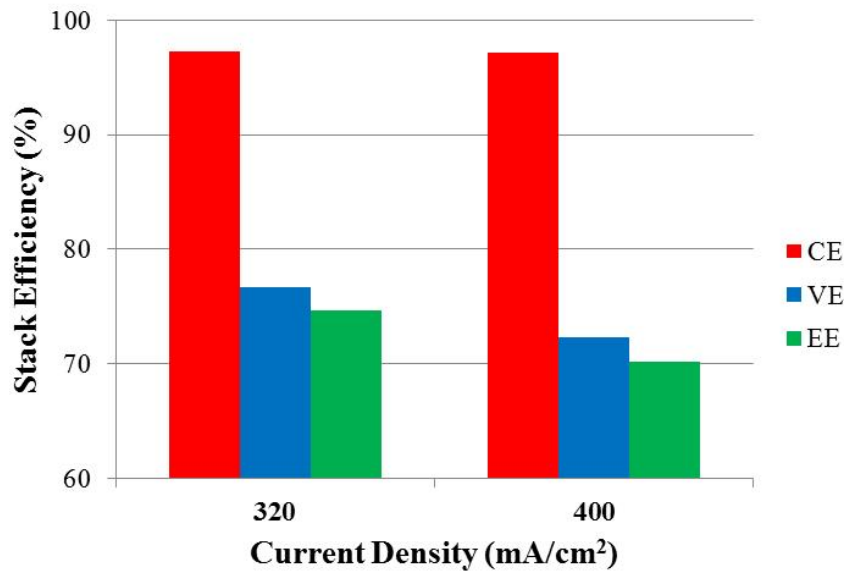


Figure 4. Stack efficiencies for the single cell operated at 320 and 400 mA/cm² at 35°C and 800 cc/min/cell.

As shown in Figure 4, a 4-5% reduction in overall stack energy efficiency was observed from increasing the current density from 320 to 400 mA/cm². The single cell operated at 320 mA/cm²

had a stack energy efficiency of ~ 75% whereas when the cell was operated at 400 mA/cm² the stack energy efficiency was decreased to ~70%.

Figure 5 compares the charge/discharge voltage curves for cells operated at 320 and 400 mA/cm² at a flow rate of 800 cc/min/cell. The voltage difference between the two current density plots is nearly identical over the entire operation range which indicates that the voltage drop is most likely dominated by ohmic losses in the cell. At the highest capacities, the voltages become non-linear which can be attributed to a mass transport overpotential which is controlled by the flow rate.

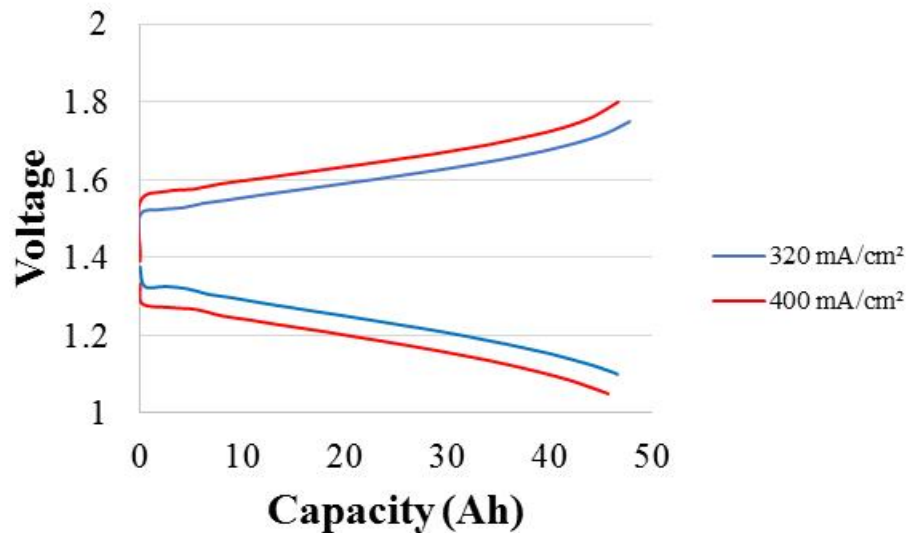


Figure 5. Charge and discharge performance of the single cell at 320 and 400 mA/cm² and a flow rate of 800 cc/min/cell.

Table 1 lists the discharge capacity, discharge temperature and pressure drops for the two different current densities studied in Figures 4 and 5. In general, the values listed in Table 1 are similar for both current densities and within targets for FY16.

	Discharge Capacity (Ah/L)	Discharge Temp (°C)	Pressure (psi) negative	Pressure (psi) positive
320 mA/cm ²	18	34	9.3	6.5
400 mA/cm ²	17.6	36	7.8	6.2

Table 1. Discharge capacity, discharge temperature and pressure drops for the single cell operated at 320 and 400 mA/cm² and at a flow rate of 800 cc/min/cell.

The single cell was cycled approximately 15 times at 320 and 400 mA/cm², and operated at ~35°C with a flow rate of 800 cc/min/cell. During cycling, the coulombic and energy efficiencies do not show any decay but are relatively stable during the charge-discharge cycling period. However, the discharge capacity fades as the flow battery is cycled, Figure 6. This

decay mechanism of the discharge capacity is reversible by remixing the electrolyte solutions or mitigated by engineering controls via a transfer techniques.

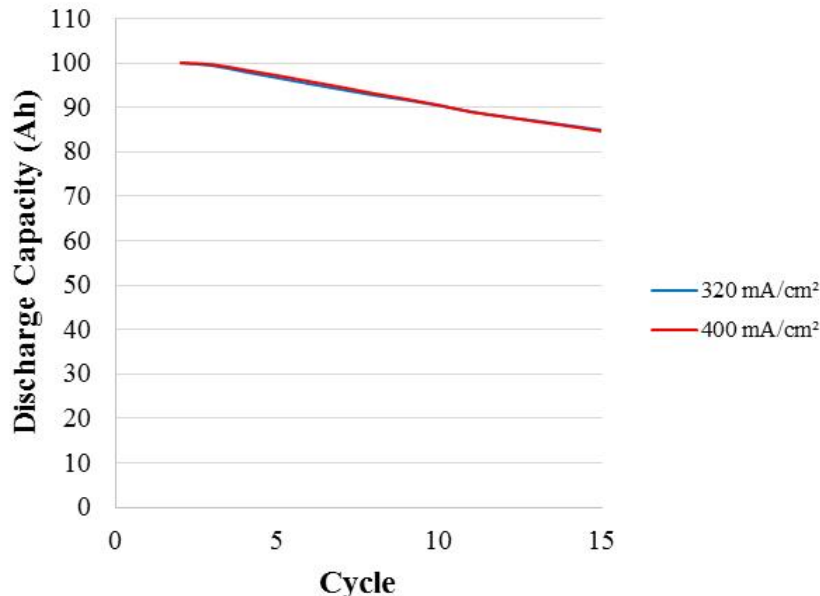


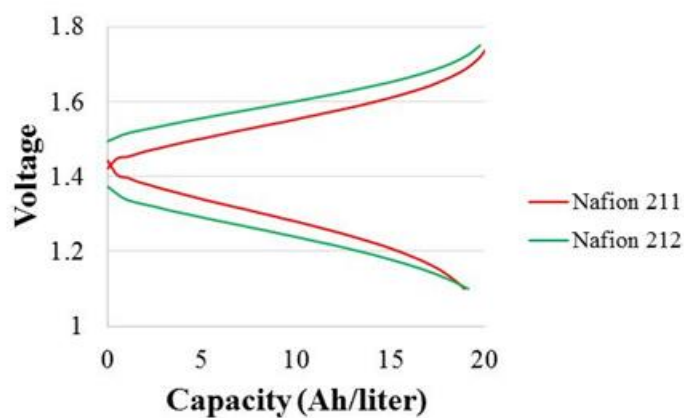
Figure 6. Discharge capacity as a function of cycling for the single cell at 35°C, 800 cc/min/cell, and 320 and 400 mA/cm².

Methods to further improve the stack energy efficiency will be further examined in FY16 at a current density of 400 mA/cm². Efforts will focus on improving the ohmic losses (i.e. bipolar plate, membrane) which appears to be the rate limiting step. The operating temperature and higher flow rates will also be examined to further improve the stack energy efficiency. These efforts will be reported in future reports in FY16.

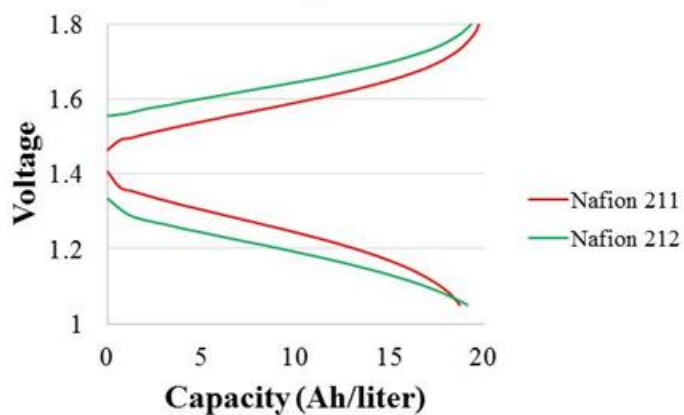
FY16 Quarter 2 Project Status Summary

The FY16 Q2 milestone was to “complete evaluation of experimental 3-cell stacks with component improvements to improve stack performance at higher current density.” For FY16, the current density target was increased from 320 mA/cm² to 400 mA/cm². Operating the stack at progressively higher current densities has been a focus over the past 3-4 years to reduce the stack cost. A higher current density, however, typically will reduce the stack and system energy efficiency. The primary goal of the stack development is to operate at a higher current density to reduce costs while maintaining a high stack energy efficiency. A thinner Nafion® membrane was investigated in Q2 as a function of current density (320 mA/cm² and 400 mA/cm²) and flow rate and compared to the design discussed in Q1.

Single cells with active areas of 780 cm² were fabricated in Q2 with Nafion® 211 and 212; the stack energy efficiency was measured as a function of current density and flow rate. As discussed earlier, Nafion® 211 is approximately half the thickness of the Nafion® 212; Nafion® 211 is ~ 1 mil thick and Nafion® 212 is ~ 2 mils thick. The charge/discharge voltage curves for both cells at 320 mA/cm² and 400 mA/cm² for a flow rate of 1200 cc/min/cell is shown in Figure 7.



a.



b.

Figure 7. Charge and discharge voltage performance for single cells with Nafion® 211 and 212 with flow rates of 1200 cc/min/cell and current densities of a.) 320 mA/cm² and b.) 400 mA/cm².

As shown in Figure 7, there is a difference in performance of the Nafion® membranes at both current densities. The voltage on charge and discharge is smaller for the Nafion® 211 membrane at a given capacity; more capacity can be attained at a given cut off voltage window. At the largest capacities (~ 20 Ah/l), however, the voltage on charge and discharge becomes similar. Both Nafion® membranes show nonlinear behavior at the highest capacities; suggesting that these losses are attributed to the electrode overpotentials.

Shown in Figures 8 and 9 are the coulombic, voltage, and energy efficiencies for the cells fabricated with Nafion® 211 and 212 as a function of flow rate at 320 mA/cm² and 400 mA/cm².

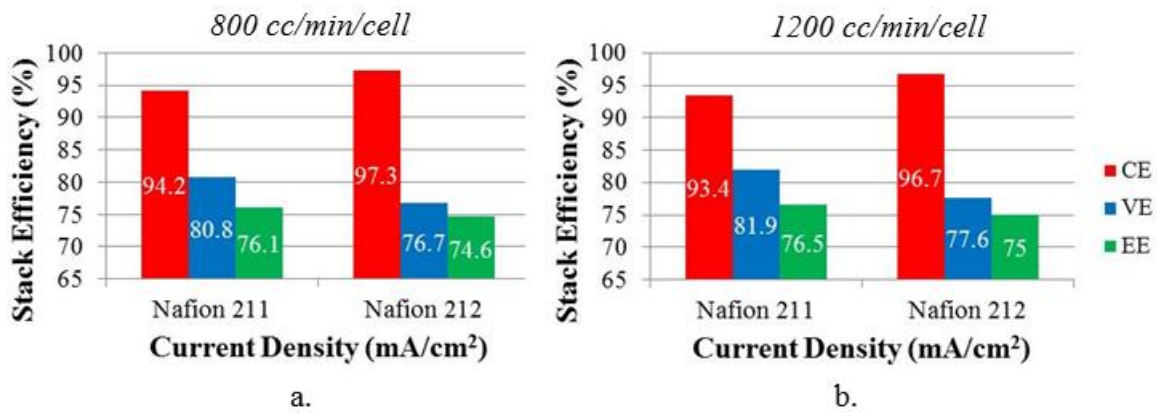


Figure 8. Coulombic, voltage, and energy efficiency for the Nafion® 211 and 212 membranes at 320 mA/cm² and flow rates of a) 800 cc/min/cell and b) 1200 cc/min/cell.

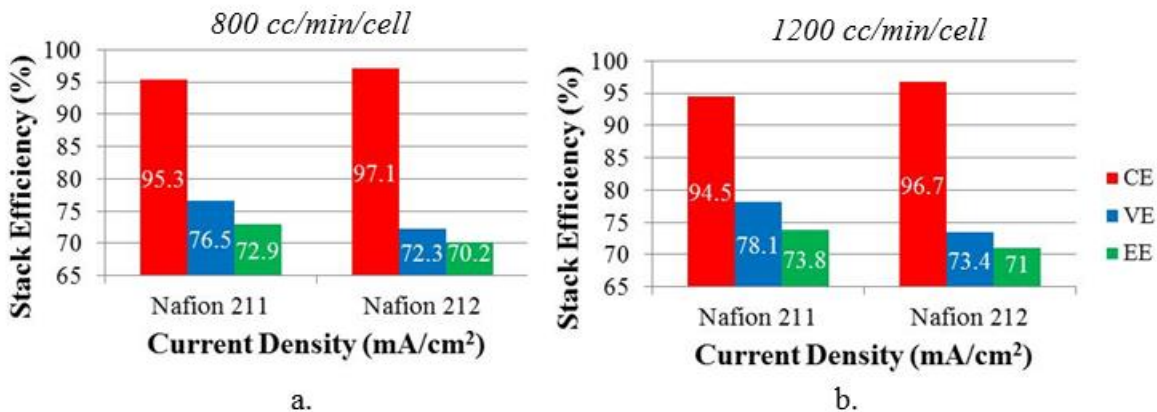


Figure 8. Coulombic, voltage, and energy efficiency for the Nafion® 211 and 212 membranes at 400 mA/cm² and flow rates of a) 800 cc/min/cell and b) 1200 cc/min/cell.

In all cases, the stack energy efficiencies were greater for the Nafion®211 membrane; in general a 2-3% increase was observed with greater increases at the highest current density. The coulombic efficiencies are dependent on the Nafion® membrane, the current density, and slightly dependent on flow rate. The decrease in coulombic efficiency with the thinnest Nafion® 211 membrane suggests slightly more cross over occurs with the thinner membrane. However, as the current density is increase the coulombic efficiency increases for the Nafion® 211 membrane most likely due to the decrease cycle time; the electrolyte spends less time in the stack and in contact with the membrane thereby reducing the amount of crossover at the highest current density. A slight decrease in coulombic efficiency is also observed with increasing flowrate; this decrease is very small and may be within experimental error of the measurements (~0.5-1%). The ohmic losses attributed to the thicker Nafion® 212 membrane decrease the voltage efficiency while an increase in flow rate tends to increase the voltage efficiency; these values dictate the overall stack energy efficiency. The stack energy efficiency for the cell fabricated with a Nafion® 211 membrane was ~73-74% when operated at 400 mA/cm² with flow rates of 800 cc/min/cell and 1200 cc/min/cell, respectively.

The experimental cell fabricated with a Nafion® 211 membrane was also tested at various current densities at 800 cc/min/cell; the stack energy efficiency and power for the cell are shown in Figures 9 and 10. The average discharge temperature of the electrolyte was ~35°C for all current densities and the pressure drop in the electrolyte circuit was typically less than 10 psi.

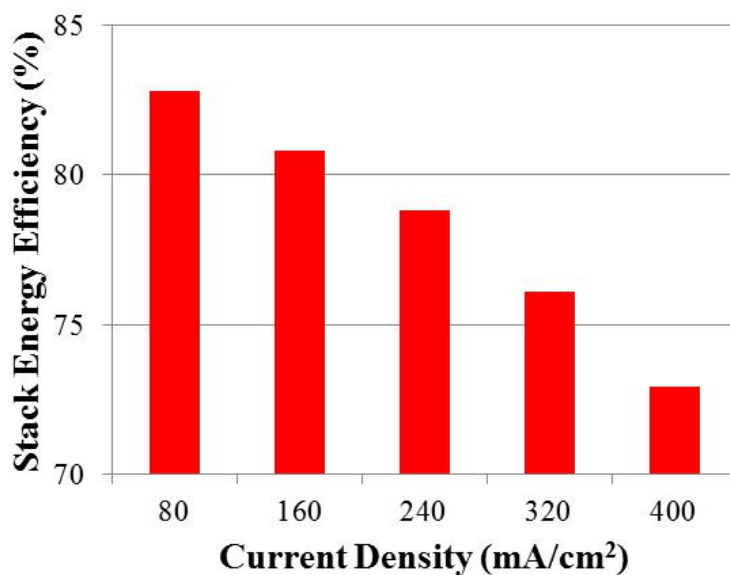


Figure 9. Stack energy efficiency as a function of current density for a cell fabricated with a Nafion® 211 membrane and a flow rate of 800 cc/min/cell.

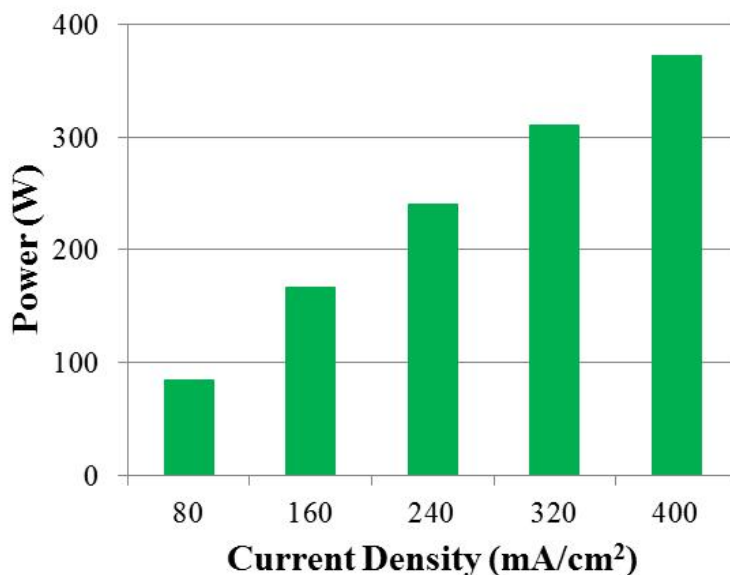


Figure 10. Power as a function of current density for a cell fabricated with a Nafion® 211 membrane and a flow rate of 800 cc/min/cell.

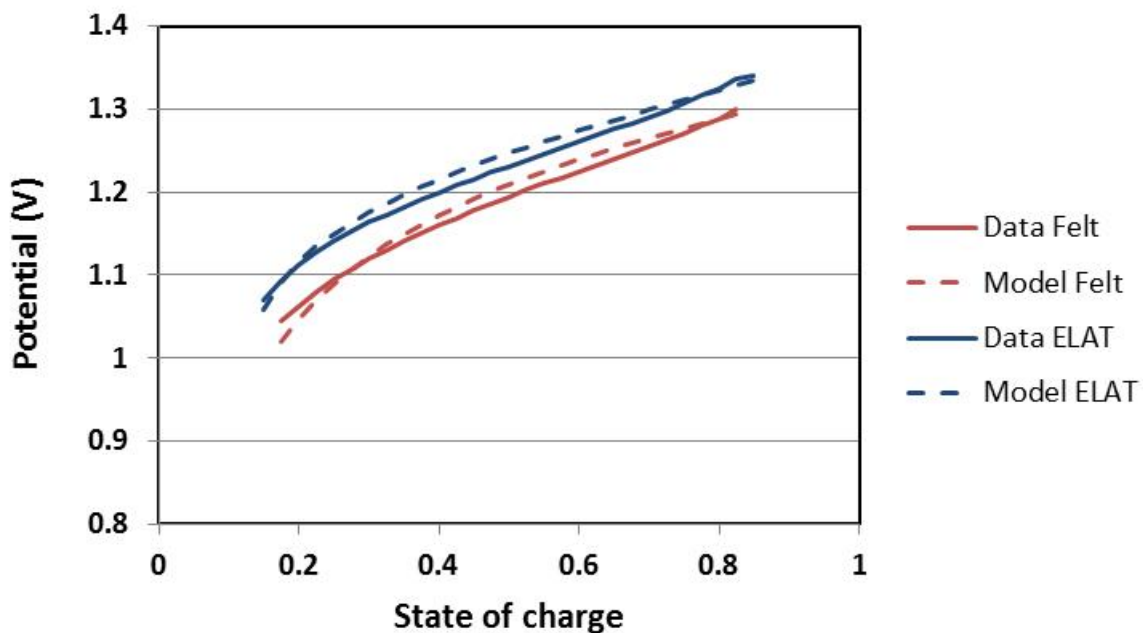
The advantage of using the Nafion® 211 membrane allows the stack to operate at a higher current density (400 mA/cm²) with a 3% increase in stack energy efficiency over the Nafion® 212. Quarter 3 will focus on cost performance at the higher current density and Q4 will focus

on fabricating and testing a kW scale stack operated at 400 mA/cm² and a high stack energy efficiency.

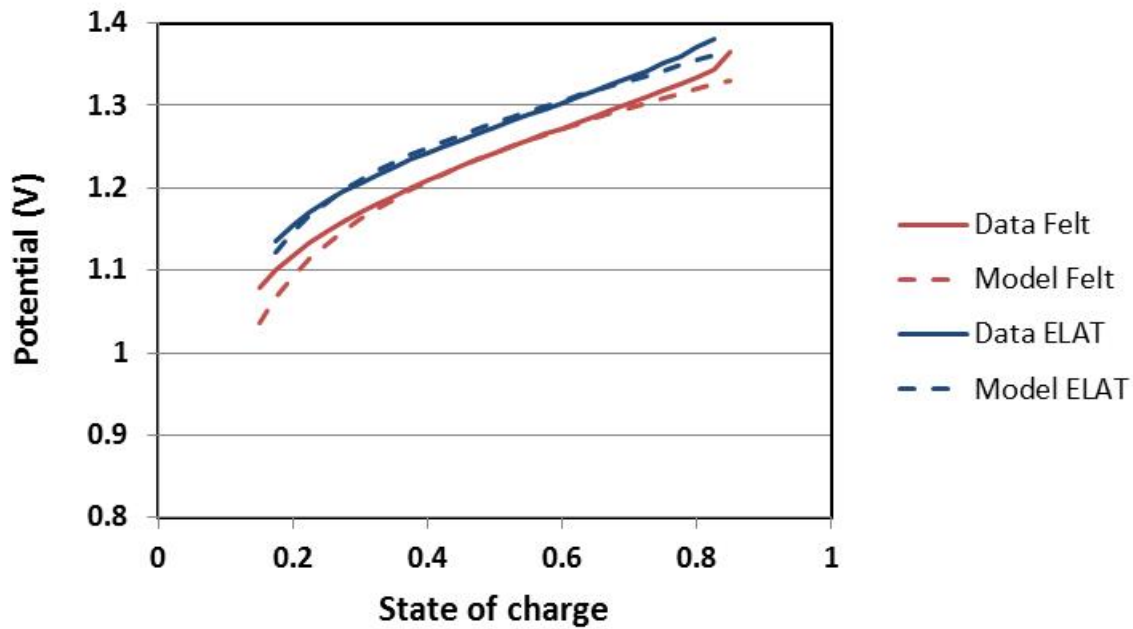
FY16 Quarter 3 Project Status Summary

A cost model was developed and validated in FY15 using a 20 cell stack operated between 160 and 320 mA/cm² and a flow rate between 400 to 1200 cc/min/cell. The model allows cell or stack data as input to estimate system cost for various power to energy ratios. Data obtained under various conditions can be interpolated to obtain the optimum operating conditions for various power to energy ratios. A bottom-up approach was used to develop the model that would predict redox flow battery performance without any empirical fitting factors. The active reaction zone for each electrode was computed at each SOC and power, with the current density and flow rate being modified at each SOC to provide the required power while optimizing efficiency.

Shown in Figure 11 is the predicted and experimental data for the 20 cell stack operated between 160 and 320 mA/cm² with a flow rate between 400 to 1200 cc/min/cell. Data shown in Figure 11 was selected with higher current densities and flow rate which have lower system costs.



a)



b)

Fig 11. Predicted and experimental data for the 20 cell stack operated at a) 320 mA/cm² and 1200 cc/min/cell and b) 240 mA/cm² and 800 cc/min/cell.

The model estimated a cost of \$305/kWh for the 20 cell stack operating at 320 mA/cm². A full description of the cost model developed for flow batteries is described in greater details in FY15 Quarter 3 Project Status Summary Report.

In FY16, the model was used to predict the flow battery performance at 400 mA/cm² and compare it to the experimental data. Single cells were fabricated with Nafion® 212 and Nafion® 211 and tested at 400 mA/cm² at various flow rates (400-1200 cc/min/cell). The stack energy efficiencies were ~ 73% and ~ 70% for the Nafion® 211 and 212 at 800 cc/min/cell, respectively, Figure 8. Slightly higher stack energy efficiencies (~1% increase) can be achieved by increasing the flow rate to 1200 cc/min/cell. The model was used to predict the cost associated with running the stack with Nafion®212 and 211 at 400 mA/cm² and 1200 cc/min/cell. The results are shown in Table 2.

Table 2. Parameters and results used in cost model

	Nafion®212	Nafion®211
Current Density (mA/cm2)	400	400
Flow Rate (cc/min/cell)	1200	1200
SOC range	81	81.2
\$/kWh	290	283
% Chemical costs	59	60

As described earlier, the Nafion®211 membrane improves the performance in comparison to Nafion®212. In addition, Nafion®211 is less expensive than Nafion®212 (1 mil versus 2 mil thick) which decrease the system costs as shown in Table 2.

Also shown in Table 2 is the percent of chemical costs to the overall system costs. In both cases described in Table 2, the chemical costs are approximately 60% of the total system costs. The primary chemical cost in the system is attributed to vanadium. As the stack performance has increased over the past 5-6 years, the cost of vanadium has become more prominent in driving the total system cost. Additions to the stack to improve performance (membranes with better performance and lower cost, interdigitated design for higher flow rates, and higher performing electrodes) have significantly dropped the costs of major components in the system. Figure 12 illustrates the cost associated with major components in the system as the current density is increased. The primary goal was to increase the operational current density while maintaining a high stack energy efficiency. As shown in Figure 12, this has driven the cost of many components down with the exception of chemical costs which is attributed to vanadium. The chemical costs are approximately 60% of the total system cost at 400 mA/cm².

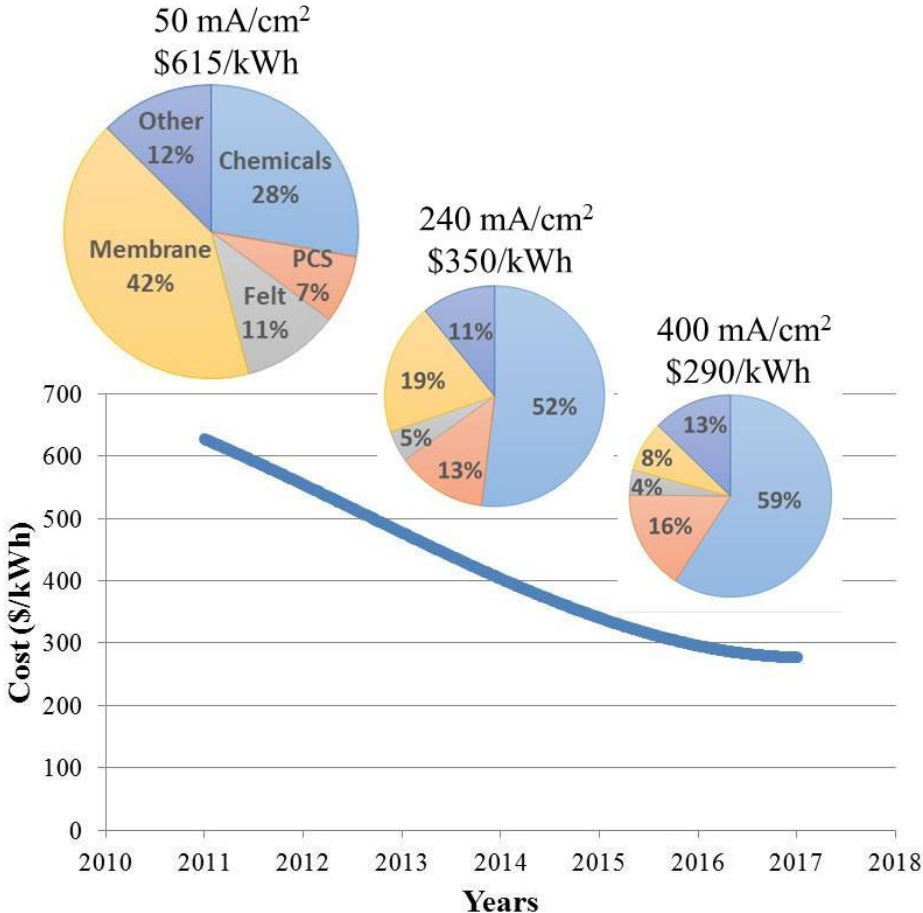


Figure 12. System cost for the all vanadium mixed acid redox flow battery

Quarter 4 will focus on fabricating and testing a kW scale stack operated at 400 mA/cm² with a high stack energy efficiency.

FY16 Quarter 4 Project Status Summary

The FY16 Q4 milestone was to “develop and demonstrate a kW scale redox flow battery system capable of meeting projected cost targets of <\$300/kWh for a projected 4-hour system. The increased current density target of 400 mA/cm² was achieved using a less resistant Nafion® NR-211 membrane, a monolithic bipolar plate design with an interdigitated flow pattern, and the mixed acid electrolyte.

During the fourth quarter, a 3-cell stack was assembled and operated at 400 mA/cm² to achieve the 1 kW target. A 20 cell stack was not fabricated in FY16 because the existing Arbin power supplies were not capable of supplying the required current and voltage needed for a 20 cell stack. The financial investment for a new Arbin power supply was not deemed necessary in FY16 because a 3-cell stack has historically scaled up very nicely to a 20-cell stack and FY16 is the last year for building the all vanadium redox flow battery operated at increasingly higher current density. Therefore, the performance of a 20-cell stack was extrapolated from the 3-cell performance in some instances, i.e. power.

As described earlier, the 3-cell stack was fabricated with cells with active areas of 780 cm². The stack was also fabricated using Nafion® NR-211 as the membrane, ELAT electrodes, the mixed acid electrolyte, and a monolithic bipolar plate with an interdigitated flow pattern. The flow rate was 800 cc/min/cell which was double the rate used in a standard flow through design.

The monolithic bipolar plate and flow frames used in FY16 are shown in Figure 13. The bipolar plate was a vinyl ester/graphite composite material that was pressed into a sheet and machined. The flow frames were also made of a vinyl ester loaded with glass fibers and processed similar to the bipolar plates.

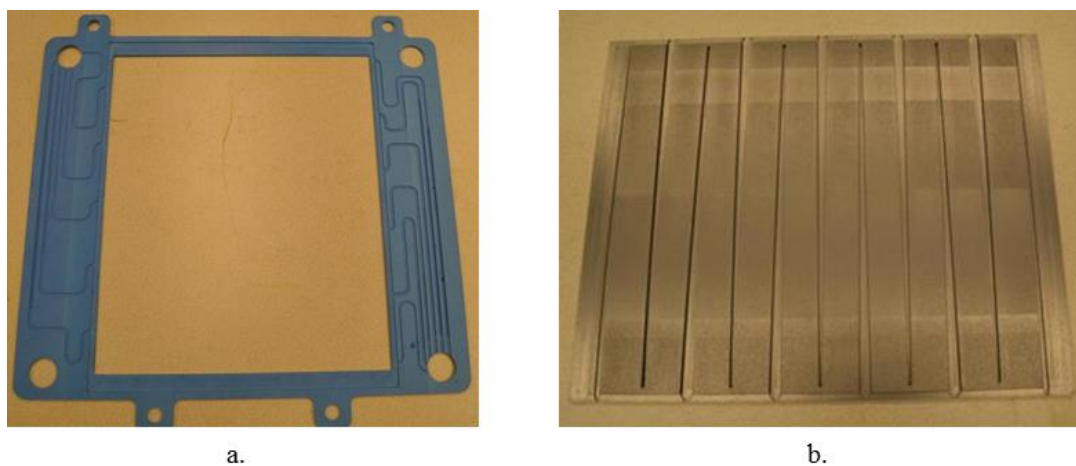


Figure 13. Stack components a) flow frame constructed with vinyl ester and glass fibers and b) bipolar plate constructed with vinyl ester and graphite.

An assembled flow frame with the bipolar plate is shown in Figure 14; a side view of the repeat unit is also illustrated. This material set was chosen because it can be scale up to large volume manufacturing with near net shape forming by hot pressing and would be a potential route to a low cost manufacturing.

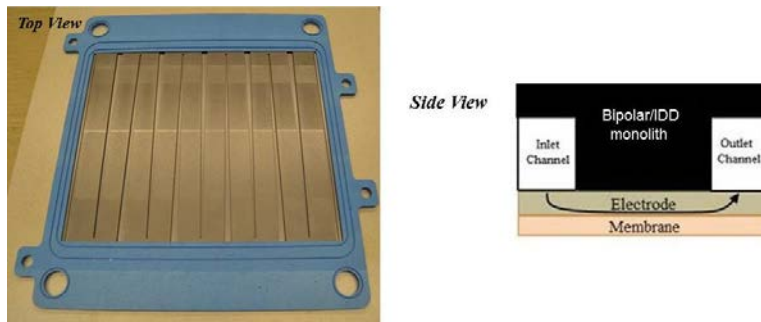


Figure 14. Assembled flow frame with bipolar plate and side view of repeat unit in flow battery stack.

As described in previous reports, the ability to operate the stack at higher flow rates enables higher current densities to be used which in turn can reduce system costs. This process is clearly shown in the costs analysis chart in Figure 12 (Q3 Project Status Summary). However, increasing the flow rate without increasing the back pressure is necessary to reduce the pumping power; this has been realized using an interdigitated flow design. Shown in Figure 15 is the pressure drop as a function of flow rate for the flow through design and the interdigitated flow design. The flow rate for the interdigitated design can be double and still maintain a back pressure approximately one half of the flow through design. This ensures the flow rate can be doubled without losing unnecessary losses associated with the back pressure in the flow circuit.

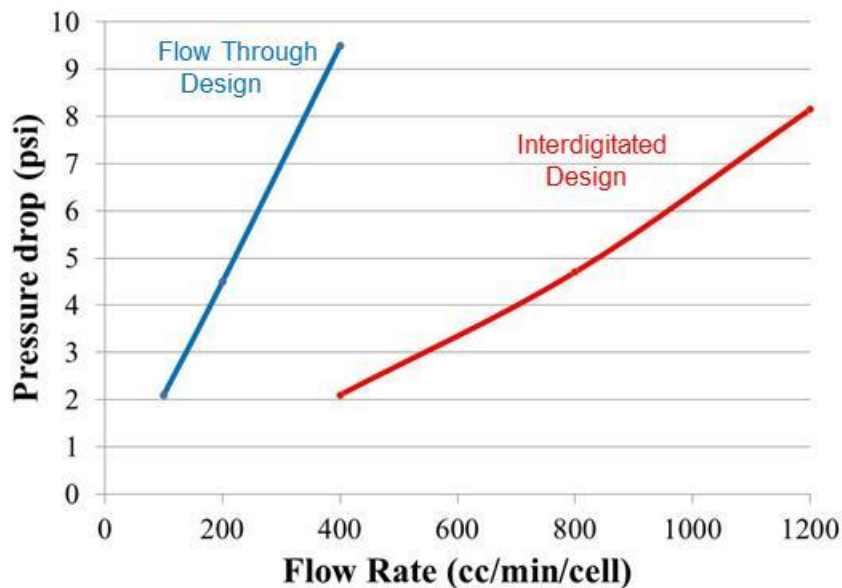


Figure 15. Pressure drop versus flow rate for the flow through and interdigitated flow designs.

During the fourth quarter of FY16, the 3-cell stack was operated at 160, 240, 320 and 400 mA/cm². The coulombic, voltage, and energy efficiency for the stack at the four current densities is shown in Figure 16. The coulombic efficiency was relatively constant at all the current densities studied, ~95-96%. The voltage efficiency and corresponding stack energy efficiency, however, was dependent on the current density. The higher current density resulted in greater losses (IR, overpotentials, etc.) which decrease the voltage efficiency. It should be

noted that the stack achieved the internal goal of ~75% stack energy efficiency. It is also observed in Figure 16 that if the stack was operated at a lower current densities (i.e. 160 mA/cm²); the stack would operate at a very high energy efficiency, ~85%.

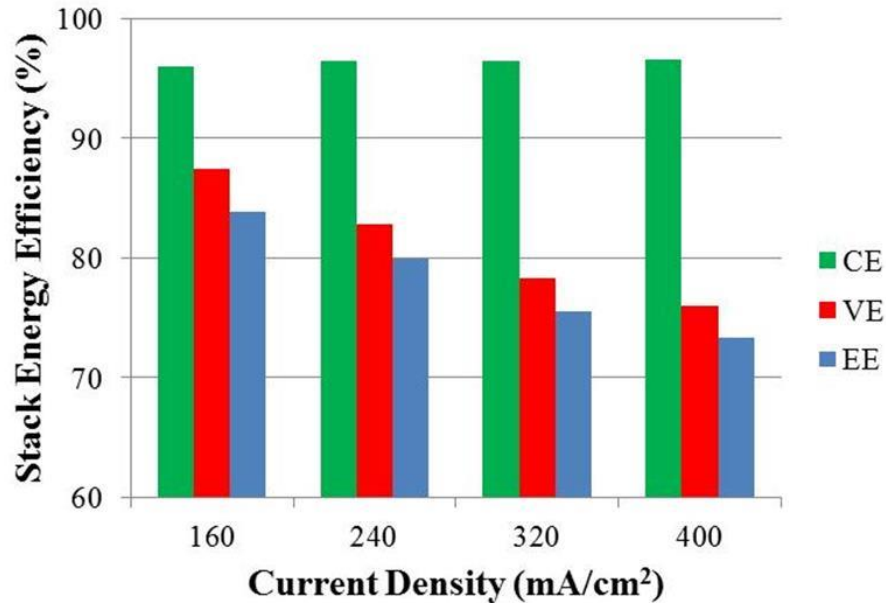


Figure 16. Coulombic, voltage, and stack energy efficiency for the 3-cell stack operated at various current densities.

The primary goal of this program over the past 4-5 years has been to increase the performance of the stack while reducing the cost. By increasing the current density, the number of cells and components within the stack has been reduced which reduces the overall system cost; this is illustrated in Figure 12. As described earlier, the goal was to increase the current density while maintaining a stack energy efficiency of ~75%. This goal has been achieved over the past four years as the current density has been increased from 160 to 400 mA/cm² in increments of 80 mA/cm². Each year new components or higher performing materials have been added to the stack to retain a stack energy efficiency of ~75%. Table 3 and Figure 17 illustrate the changes made to the stack in the past four years and the resultant stack energy efficiency as a function of current density.

Table 3. Component changes and results of stack energy efficiency over the past 4 years as a function of current density.

	Flow Design	Flow Rate (cc/min/cell)	Nafion Membrane	Electrode	Target Current Density (mA/cm ²)	Stack Energy Efficiency (%)			
						160 mA/cm ²	240 mA/cm ²	320 mA/cm ²	400 mA/cm ²
FY 13	Flow Thru	400	115	felt	160	71	67	58	53
FY 14	IDD - felt	800	212	felt	240	81	75	67	60
FY 15	IDD - laminated	800	212	ELAT	320	84	79	75	69
FY 16	IDD - monolith	800	211	ELAT	400	84	80	76	74

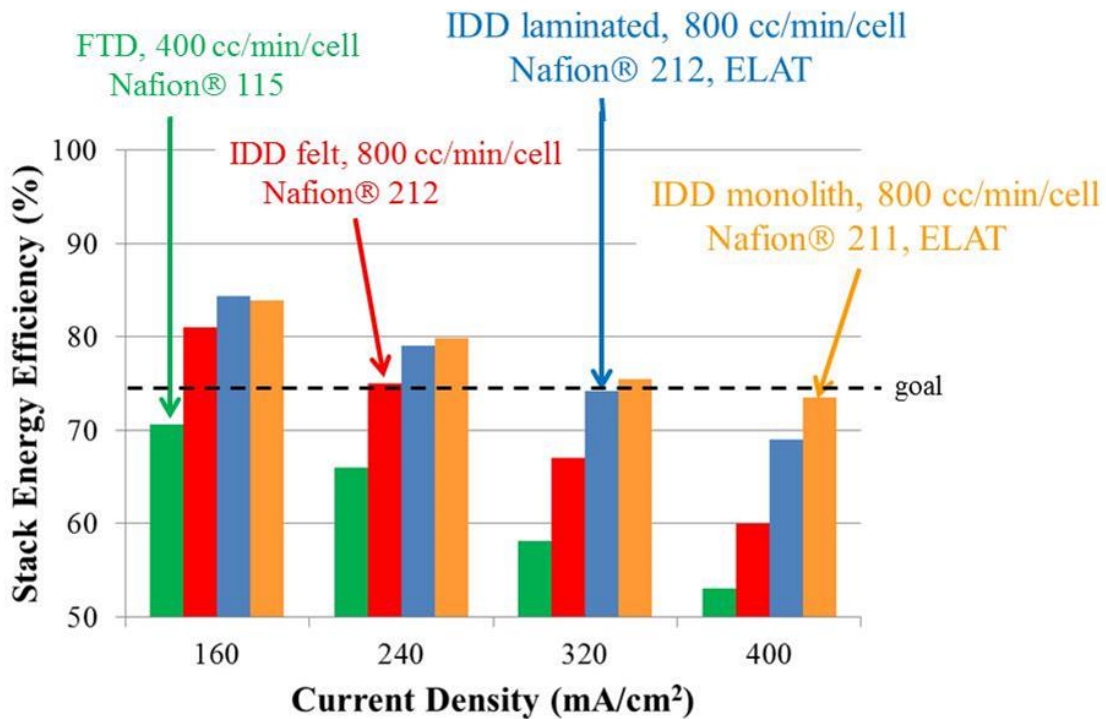


Figure 17. Stack Energy Efficiency as a function of current density for stacks fabricated over the past four years.

Lastly, the results of the 3-cell stack fabricated in FY 16 was used to extrapolate the power results for a 20-cell stack and compared to stacks fabricated in the past 3 years. The results are shown in Figure 18. In general, the results show a year over year increase in power while maintaining a relatively constant stack energy efficiency.

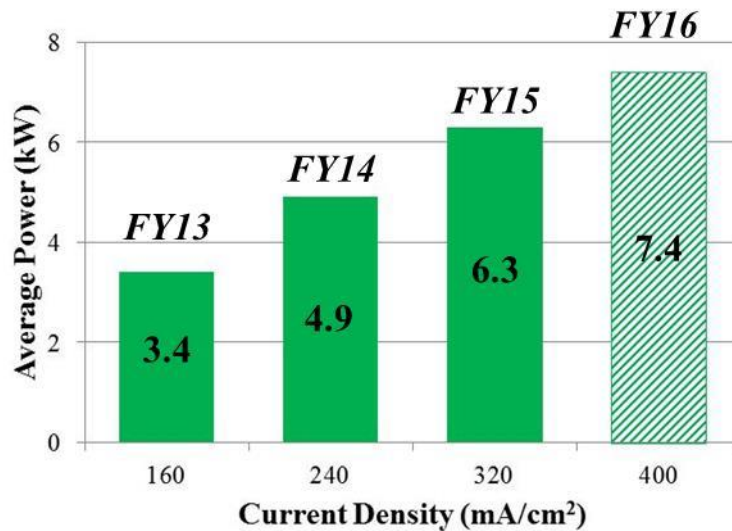


Figure 18. Average power for 20 cell stacks operated in FY13, FY14, FY15, and FY16 at 160, 240, 320, and 400 mA/cm², respectively.

Results over the past four years have shown that stacks can be fabricated at a lower cost and higher performance by enhancing specific components within the stack (i.e. flow design, membrane, electrodes, etc.) that directly influence the behavior at high current densities. The cost model proposed in the FY16 Quarter 3 Project Status Summary indicates that Vanadium is the primary driver in further reducing the cost of the Redox Flow Battery.

References

1. Z. Yang, J. Liu, S. Baskaran, C. H. Imhoff and J. D. Holladay, *JOM*, 2010, **62**, 14.
2. Z. Yang, J. Zhang, M. C. W. Kintner-Meyer, X. Lu, D. Choi, J. P. Lemmon and J. Liu, *Chem. Rev.*, 2011, 111, 3577.
3. C. Ponce de León, A. Frías-Ferrer, J. González-García, D. A. Szánto and F. C. Walsh, *J. Power Sources*, 2006, **160**, 716.
4. A. Price, S. Bartley, S. Male and G. Cooley, *Power Engineering Journal*, 1999, **13**, 122.
5. M. Skyllas-Kazacos, M. Rychcik, R. G. Robins, A. G. Fane and M. A. Green, *J. Electrochem. Soc.*, 1986, **133**, 1057.
6. *US Pat.*, 4 786 567, 1988.
7. E. Sum, M. Rychcik and M. Skyllas-Kazacos, *J. Power Sources*, 1985, **16**, 85.
8. E. Sum and M. Skyllas-Kazacos, *J. Power Sources*, 1985, **15**, 179.
9. *US Pat.*, 3 996 064, 1976.
10. S. Eckroad, *Technical Report*, EPRI-1014836, Electric Power Research Institute, Palo Alto, CA, USA, 2007.
11. L. Li, S. Kim, W. Wang, M. Vijayakumar, Z. Nie, B. Chen, J. Zhang, G. Xia, J. Hu, G. Graff, J. Liu and Z. Gary, *Adv. Energy Mater.*, 2011, **1**, 394.
12. S. Kim, M. Vijayakumar, W. Wang, J. Zhang, B. Chen, Z. Nie, Feng Chen, J. Hu, L. Li and Z. Gary, *Phys. Chem. Chem. Phys.*, 2011, **13**, 18186.

Distribution (Electronic)

<u>Name</u>	<u>Org.</u>	<u>Mail Stop</u>
Vincent Sprenkle	Pacific Northwest National Laboratory	
Imre Gyuk	DOE Office of Electricity Energy Storage Systems Program Manager U.S. Department of Energy 1000 Independence Avenue, SW Washington, DC 20585	