Inquiry: The University of Arkansas Undergraduate Research Journal

Volume 18   Article 6

Spring 2015

A New Design Method for Vanadium Redox Batteries in Renewable Energy Systems

Casey Gibson
Unversity of Arkansas, Fayetteville

Karla G. Morrissey Unversity of Arkansas, Fayetteville

Follow this and additional works at: http://scholarworks.uark.edu/inquiry

Part of the Power and Energy Commons, and the Sustainability Commons

A New Design Method for Vanadium Redox Batteries in Renewable Energy Systems

By: Casey Gibson
Department of Biological Engineering

and

Karla G. Morrissey
Department of Chemical Engineering

Faculty Mentor: Roy McCann Ph.D.
Department of Electrical Engineering

Abstract

This study investigated the behavior of vanadium redox flow batteries (VRFBs), which are batteries capable of easily switching between charging and discharging modes, making them a suitable option for storing intermittent sources of alternative energies (solar, wind, etc). Since different sizes of the battery provide varying voltages, optimal parameters for a particular home are key for implementation. These parameters, specifically the cell and tank volumes of the battery that are capable of providing consistent on-load voltage, were determined using data from a 13 kW solar array and a medium-sized house. Charge/discharge current values were used to run a mathematical model that provided on-load voltage over time graphs based on parameter input values. Using this model, the optimal parameter values were found to be 11.5 L for the cell volume and 103.7 L for the tank volume, which maintenained the on-load voltage well above 0.80 V (10% of cell standard emf).

Introduction

Since their invention in the 1980s, vanadium redox flow batteries have shown beneficial properties, such as high energy efficiencies, long life cycles, and controllable energy capacities that are crucial for the ongoing effort to store intermittent energy sources such as wind and solar energy (Xie, 2011). Redox flow batteries are rechargeable and contain two separate tanks of liquid electrolyte material separated by an ion-exchange membrane (Rychcik & Skyllas-Kazacos, 1988). On either side, there are tanks of negatively and positively charged chemical substances that undergo redox (reduction-oxidation) reactions, in which electrons are transferred between substances. The oxidation number of a substance denotes the charge, and by finding the oxidation numbers of elements before and after reactions, it can be determined whether electrons were lost or gained, and the flow of electrons through the battery cell generates electricity.

Specifically, vanadium redox batteries were studied for this project. On the positive side of the battery, vanadium is found in the states: VO_2^+/VO^{2+}, while it is found as V^{2+}/V^{3+} at the negative electrode (Xie, 2011). While the battery is charging, VO^{2+} is oxidized (loses electrons) to become VO_2^+, and V^{3+}

is reduced (gains electrons) to become V^{2+}, shown by equations (1) and (2) below. The opposite reactions occur while the battery is discharging

(1)   Positive Electrode:

$$VO^{2+} + H_2O - e^- \rightarrow VO_2^+ + 2\,H^+$$
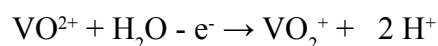
(2)   Negative Electrode:

$$V^{3+} + e^- \rightarrow V^{2+}$$
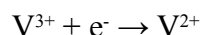
This particular type of flow battery can easily be upsized or downsized based on demand, simply by increasing or decreasing the size of the battery or the amount of vanadium electrolyte material (U.S. Patent No. 6,764,789, 2004). Additionally, this battery is very stable because of its ability to quickly respond to changes in battery load; essentially, it bridges the gap between energy supply and demand (Xie, 2011). As a result, vanadium redox batteries are promising for use with inconsistent energy sources such as solar panels. To illustrate, the battery will store energy while the sun is out, but it will discharge when the sun is obscured or during nighttime. However, because of the delicacy of designing an optimal ion-transport membrane found in the cells, these batteries have not been commercialized (Chen, Hickner, Agar, & Kumber, 2013). In the

meantime, more research is needed on mathematically characterizing the behavior of VRFBs. Mathematical models allow for further understanding of the VRFBs and how to best implement them in electrical systems.

Over the last few decades, renewable energy from solar, wind, hydroelectric, and other sources have been researched and employed throughout the world, yet energy demands are not being met and instead are rapidly increasing, expecting to double by 2050 (Yang et al., 2010). As copious advances continue to be made in renewable energy technologies, some researchers are investigating how to store this energy for later consumption. Energy generated from natural sources such as wind and the sun are highly susceptible to local weather patterns, creating periods of large energy generation and almost zero generation, such as nighttime in terms of solar energy (Shwartz, 2013). Renewable energy is therefore not only unreliable during certain periods, but also limited in conditions when more energy is being produced than is being consumed.

Consequently, this problem has called for a deep investigation towards technology that can store excess energy, particularly in the form of electrochemical storage in batteries which can be used during peak hours when energy generation cannot meet the demand (Resch, 2013). These batteries include lead-acid, lithium-ion, sodium-sulfur, and particularly vanadium redox flow batteries. Vanadium redox flow batteries are relatively newer than the others, therefore still require much research. However, they show promising qualities in that they are less reactive and prone to combustion than sodium-sulfur batteries, and they withstand frequent charge/discharge cycles better than lead-acid batteries.

While VRFBs could potentially increase the use of renewable energy, incorporating alternative energy sources with storage batteries has some disadvantages. For example, there are concerns about increased emissions due to power plant cycling to compensate for fluctuations in renewable energy sources. These fossil fuel plants are designed carefully to minimize emissions under constant power conditions. Also, generators might exhibit premature failure of components because of exposure to the thermal and pressure-related stresses of cycling. However, a study conducted by the National Renewable Energy Laboratory demonstrated that the negative cycling effects were negligible in comparison to the reductions

of CO_2, NO_x, and SO_2 emissions resulting from the use of alternative energy (NREL, 2013). In fact, net carbon emissions were reduced by one third.

Thus, a primary step in designing an electric power grid using vanadium redox batteries is to develop mathematical models based on the reaction kinetics and efficiency in real-time, particularly in residential settings. These models can be used to predict their efficiency and reliability when incorporated into the electric power grid. As a result, in the near future it could be possible to make homes more autonomous from the public electric grids with personal solar panels connected to vanadium redox batteries (Resch, 2013). By mathematically optimizing variables like tank volume and battery cell size, vanadium electric grids can be tailored to meet the specific energy demands of a consumer while reducing reliance on the electric power grid. Quantified validation of the potential success of vanadium redox batteries in renewable energy systems will make actual implementation closer to reality.

Characterization of Generation and Electrical Load

The first objective was to use power generation data from an installed PV system (solar panels installed at the Fayetteville Public Library) and power consumption data from a household to determine x_3, or the charge/discharge current of the battery. SolrenView, a data website from the company, Solectria, was used to find the power generated in kilowatts for a particular day (August 2, 2013) chosen specifically because of its greatly varying measurements of energy generated throughout the day (SolrenView, 2013). Note, this graph (Figure 1) shows the power generated scaled up by a factor of 3.5 so that the power generated by the solar panels roughly equaled the power consumed by the household. The household data was collected from the Southwestern Electric Power Company (SWEPCO), which used a General Electric "Smartmeter" to record the average power being consumed at one minute intervals (SWEPCO, 2013). These values are graphed in Figure 1.

As shown in Figure 1, the energy generated by the solar panels varies significantly throughout the day, generating zero power until 7 am, and then reaching peaks of power generation around mid-
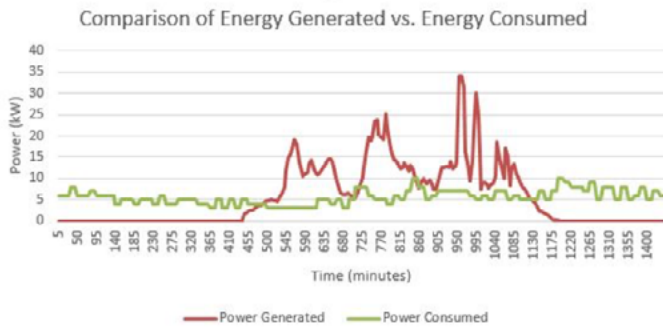
Figure 1. Power Generated on August 2, 2013 from 13 kW Installed Photovoltaic Array

morning, mid-afternoon, and early evening. The data from the family household gave insight into the peak energy usage hours for a typical family and how these hours differ from times of optimal solar power generation. For example, solar energy was most available in the afternoon, but electricity usage peaked in the evening. The variable, x_3, was found by taking the average power generated, P_{Gen}, by the PV system at five minute increments, subtracting the average power consumed, P_{Con}, by the household, and dividing by the standard voltage for house outlets, 120 V. The charge/discharge current (Figure 2) for an overall two-day cycle was found using equation (3).

(3) $$x_3 = \frac{P_{Gen} - P_{Con}}{120V}$$

Analysis and Modelling of VRFB

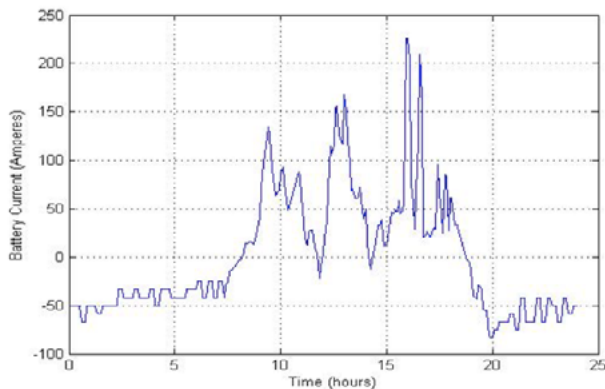The next objective was to characterize the behavior of the VRFB using a mathematical model.

Figure 2. Charge/Discharge Current over 24-hour Cycle

Table 1.

Defined Variables, Parameters, and Constants

x_1	Concentration of V^{2+} in cell
x_2	Concentration of V^{2+} in tank
x_3	Charging/ discharging current
x_4	No-load voltage
x_5	On-load voltage
μ_1	Volume of cell
μ_2	Volume of tank
μ_3	Maximal concentration of vanadium
μ_4	Load resistance
μ_5	Impedance of battery
E_e^0	Standard electromotive force based on the concentration of hydrogen ion
W_0	Flow rate

The mathematical model was developed using the following four equations (Minghua & Hikihara, 2008). Table 1 lists the variables, parameters, and constants included in the equations used to derive the mathematical model.

(4) $$\frac{d^2 x_1}{dt^2} + W_0 \left(\frac{1}{\mu_1} + \frac{1}{\mu_2} \right) \frac{dx_1}{dt} + \frac{1}{\mu_1 F} \frac{dx_3}{dt} + \frac{W_0}{\mu_1 \mu_2} \frac{x_3}{F} = 0$$

(5) $$\frac{dx_2}{dt} + \frac{1}{\mu_2} \left\{ \mu_2 \frac{dx_1}{dt} + \frac{x_3}{F} \right\} = 0$$

(6) $$x_4 = E_e^0 + \frac{2RT}{F} \ln \frac{x_1}{\mu_3 - x_1}$$

(7) $$x_5 = x_4 - x_3 (\mu_4 + \mu_5)$$

Equation (4) shows the relationship between the design parameters, μ_1, μ_2, and W_o, and x_3, which is the concentration of V^{2+} in the cell at a constant flow rate. The forcing equation is depicted by the last two terms that contain x_3. Equation (5) relates the concentration of V^{2+} in the tank to the concentration in the cell and the charging/discharging current. The no-load voltage, x_4, given by equation (6) gives the voltage of the battery when there is no energy demand. Equation (7) accounts for the load resistance and impedance of the battery when there is energy demand to give the on-load voltage, x_5. A mathematical model was developed using MATLAB, shown in Figure 3, incorporating equations (4), (6), and (7) and the values calculated
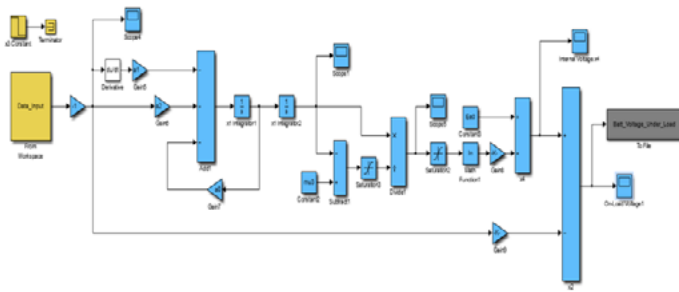
30

3

Figure 3. MATLAB On-load Voltage Simulator

for x_3 to find x_5, or the on-load voltage.

The charge/discharge current found from the first objective was used to run the simulator and derive a graph of the on-load voltage over time depending on the different values used for cell and tank volumes at a constant flow rate.

Verification of the Model

To verify the model (third objective), the simulator was set at the experimental values of the design parameters, μ_1 and μ_2, and this graph was compared to the experimental results shown in Figure 4. The parameters for the model were set as follows: 0.100 L for the cell volume, 0.900 L for the tank volume, and a constant 3.5/12 L/min for the flow rate. These values equaled the cell and tank volumes used for the experiment with the small-scale VRFB, totaling 0.987 L for cell and tank volumes. After running the mathematical model, the theoretical on-load voltage graph set at the experimental parameter values was produced. Figure 4 and 5 were then compared to find the validity of the model.

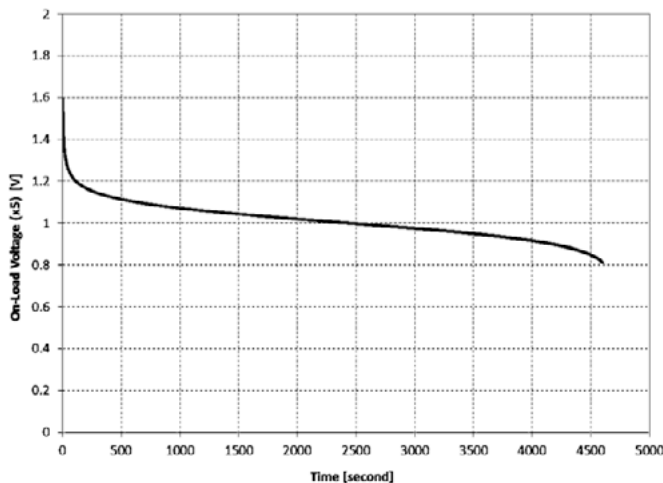These results shown in Figure 4 for the on-

Figure 4. Experimental On-load Voltage of VRFB

load voltage were provided by Listenbee, Jeong, and McCann (2014) using the small-scale VRFB. Our graph of the on-load voltage, using our mathematical model set at these experimental parameters, is shown in Figure 5 below.

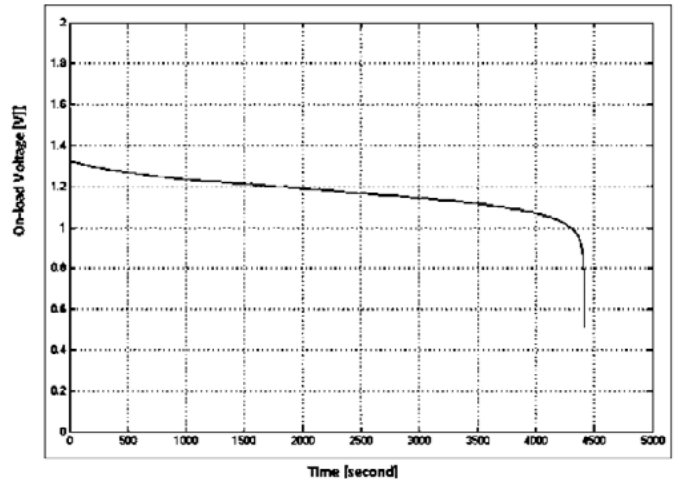Comparing Figures 4 and 5, the relative shapes

Figure 5. On-load Voltage of VRFB Generated by Mathematical Model

of the curves with respect to time and the change in on-load voltage matched, validating the mathematical model based on the experimental data gathered from the partner institution. The load resistance and impedance, μ_4 and μ_5, of the actual battery were unknown due to difficulty in quantifying these parameters by the ASU researchers. However, for the model to be valid, these parameters were essential, as the level of resistance depends on the cell volume. Also, load resistance and battery impedance affects the efficiency of the VRFB. Therefore, μ_4 and μ_5 were adjusted until the graph (Figure 5) closely matched the experimental graph (Figure 4). The resulting values for μ_4 and μ_5 that validated the model were 5.5 mΩ for μ_4 and 0.55 mΩ for μ_5.

Design Method for VRFB

Once validated, the model was used to complete the fourth objective: determine the optimal design parameters to suit the energy needs of the household. Optimal was defined as the values of μ_1 and μ_2 that kept the on-load voltage from going below 0.80 V. This value was determined by analyzing equation (6), showing the no-load voltage that contains a natural log function of the vanadium ion concentration. If

the ion concentration decreased to a low value, the value of the equation (voltage) droped off rapidly as demonstrated in Figure 4. Since inverters can only handle a certain range of voltage changes, these inverters cannot compensate for large voltage drops. Thus, the house would either not have electricity, or would have to rely on a traditional, nonrenewable electric grid to compensate for a large voltage drop within the battery. When the ion concentration was at 10% of the cell standard, the voltage of the battery was roughly 0.80 V.

With this value determining the required minimum on-load voltage, the cell and tank volumes were manipulated to determine how the values affected the on-load voltage. As μ_1 and μ_2 were increased, the on-load voltage graph was vertically transformed towards increasing voltage. Figure 6 shows this trend with the cell volume set at 100 L and the tank volume set at 900 L.
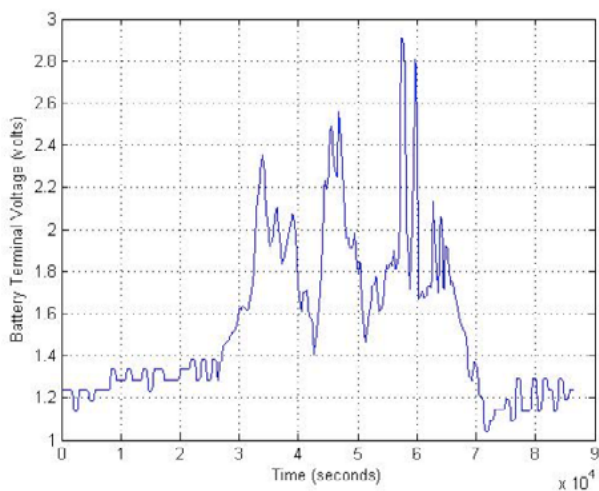

Figure 6. On-load Voltage vs. Time with 100 L Cell

Likewise, as μ_1 and μ_2 were decreased, the graph was vertically shifted towards decreasing voltage. This trend is shown in Figure 7 with the cell and tank volumes set at 5.0 L and 45 L, respectively.

Since the size of the cell has a large impact on the overall cost of a VRFB due to the expensive ion-exchange membrane, the value for μ_1 was picked based on the smallest value that it could be set to while keeping the resultant on-load voltage above 0.80 V throughout the entire 24-hour cycle. According to the graphs, any volume below 11.5 L resulted in a voltage drop of below 0.5 V, as shown in Figure 7. Therefore, the resulting value for the volume of the cell was
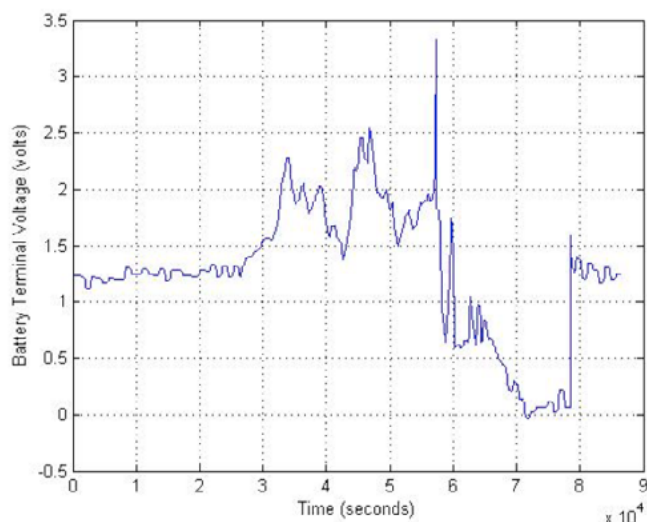

Figure 7. On-load Voltage vs. Time with 5 L cell

11.5 L. The tank volume, set at a 9:1 ratio to the cell, was found to be 103.7 L. As shown in Figure 8, these values kept the on-load voltage above 1.0 V for the entire 24-hour period. These values, equaling a total volume of 115.2 L, are practical for implementation into an actual residential setting.
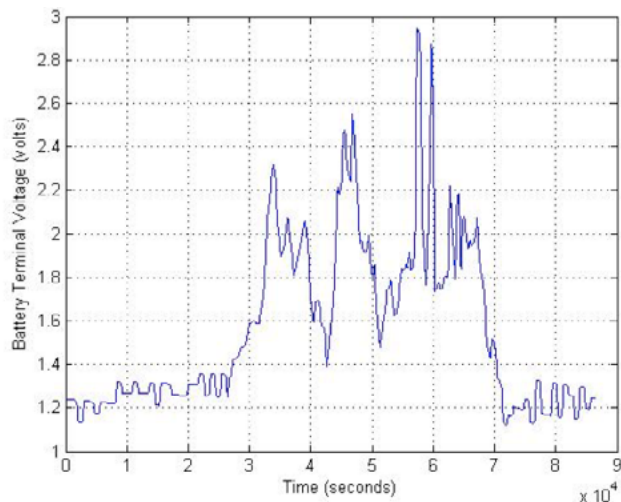
Conclusions and Future Work

Figure 8. On-Load Voltage of VRFB with Optimal Parameters

Energy storage could be a solution to the problem of bridging the gap between energy demand and energy supply from intermittent sources of energy. Simulating the results of integrating energy storage technology, such as VRFBs, into various settings could help increase the use of renewable energy and make going "off-grid" a more feasible option. Beginning with data gathered from a PV array system and an actual home, this data was used to run

a mathematical model that simulated the behavior of a VRFB. This model produced graphs of the available on-load voltage over time. By analyzing these graphs, the minimum cell and tank volumes that would avoid significant voltage drops were determined.

Although the values for cell and tank volumes were relatively small, larger cell volumes correlated to smaller resistances due to the inverse relationship between cell surface area and resistance. Smaller resistances result in higher efficiencies, so there is a tradeoff between size and efficiency. Larger batteries are more efficient but more expensive as well. While the cell and tank volumes largely depend on the electrical load, which varies per scenario, the volumes could always be increased above the minimum total volume needed to increase the battery's efficiency, depending on how much a consumer or company is willing to spend.

Since the experimental data for the on-load voltage matched our theoretical data, the model was validated. Using this validated model, future researchers could characterize the scaled up or scaled down behavior of vanadium redox batteries of any size. Also, by using a different current input, the model could predict the behavior of VRFBs in numerous settings, such as a hospital, university, or factory, which have widely varying energy loads. The next step in future research would be to actually construct a battery based on the parameters from the model and implement its technology into a home with alternative energy sources.

References

Chen, D., Hickner, M. A., Agar, E., & Kumber, E. C. (2013). Optimized anion exchange membranes for vanadium redox flow batteries. *ACS Applied Matterials Interfaces*, *5*(15), 7559-7566. doi:10.1021/am401858r**.**

Listenbee, R., Jeong, K., & McCann, R. (2014, July). *Integrated computational and experimental framework on advanced flow battery for renewable power plant applications*. Proceedings of the ASME 2014 8th International Conference on Energy Sustainability.

Minghua, L. & Hikihara, T. (2008, July). A coupled dynamical model of redox flow battery based on chemical reaction, fluid flow, and electrical circuit. *IEICE Transactions on Fundamentals of Electronics, Communications, and Computer Sciences*, *E91A*(7), 1741-1747. Retrieved October 10, 2013.

National Renewable Energy Labroatory. (2013). The western wing and solar integration sudy phase 2 (Report No. DE-AC36-08GO28308). Retrieved from http://www.nrel.gov/docs/fy13osti/55588.pdf

Resch, R. (2013, September 25). Solar power and energy storage: Pairing technologies vital to our future. *RenewableEnergyWorld.com*. Retrieved October 1, 2013, from www.renewableenergyworld.com/rea/news/article/2013/09/solar-power-and-energy-storage-pairing-technologies-vital-to-our-future.

Rychcik, M., & Skyllas-Kazacos, M. (1988). Characteristics of a new all-vanadium redox flow battery. *Journal of Power Sources*, *22*(1), 59-67.

Sekiguchi, S., Furusato, K., Miyabayashi, M., Satou, K., Tanimoto, T., & Naitou, S. (2004). *U.S. Patent No. 6,764,789*. Washington, DC: U.S. Patent and Trademark Office.

Shwartz, M. (2013, September 9). Stanford scientists calculate the energy required to store wind and solar power on the grid. *Stanford News*. Retrieved October 1, 2013, from http://news.stanford.edu/news/2013/september/curtail-energy-storage-090913.html.

SolrenView. (2013). ARTP enterprise center. Retrieved from http://solrenview.com.

SWEPCO (2013, September). [Mobley, MC] Monthly household usage.

Xie, X. (2011, November 25). Vanadium Redox-Flow Battery. *stanford.edu*. Retrieved October 1, 2013, from http://large.stanford.edu/courses/2011/ph240/xie2.

Yang, Z., Zhang, J., Kintner-Meyer, M. C. W., Lu, X., Choi, D., Lemmon, J. P., & Liu, J. (2010). Electrochemical energy storage for green grid. *Chemical Reviews*, *111*(5), 3577-3613.