

Capital Cost Sensitivity Analysis of an All-Vanadium Redox-Flow Battery

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Interest in the development of redox-flow batteries (RFBs) for large-scale grid storage is growing, and considerable investments have been made into the research and development of RFBs over the past few decades. Unfortunately, practical implementation has been hampered by various cost and performance issues typical of an immature state of development. One critical factor for the competitiveness of this technology is the installed cost. In this work, we incorporate recent developments in all-vanadium RFBs research and present an analysis of the associated cost factors. The major components of a RFB that affect installed cost are identified and used as variables to create a capital cost function. The function is then used to calculate the rate of change of the capital costs with respect to the major components. The capital costs are also calculated for a range of component values and plotted. Key findings include a high sensitivity of system capital cost to purity of vanadium and substantial fractions of the cost associated with perfluorosulfonic acid membranes currently used for proton transport.

Introduction

Redox flow batteries (RFBs) are being developed for use in large-scale electrical grid storage. There are a number of potential benefits that could be provided by large-scale electrical grid storage RFBs. RFBs could be used to store energy during periods of low demand and supply power during periods of peak demand, forgoing the need for additional expensive investments in generating capacity to meet peak demand. Also electrical energy generated from renewable resources such as wind or solar could be stored in a RFB for use when supplies of renewable power are limited. RFBs could help stabilize transmission lines, act as an uninterruptable power supply for sensitive equipment, and improve service reliability for customers (1). But in spite of research and development over the past few decades, practical implementation is hampered by various cost and performance issues typical of an immature state of development of the technology.

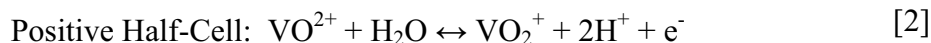
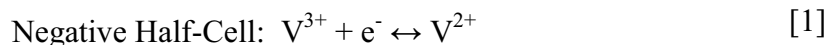
One critical factor for competitiveness of this technology is its installed (capital) cost. ARPA-e targets capital costs of \$100/kWh installed, an aggressive target for lowering the capital costs. Analysis is needed to consider if it is even feasible to meet this kind of target with current technology and to evaluate the changes that are most

likely to result in large reductions in capital cost. Thus, economic analyses can provide focus to research activities. For example, the trade-off in cost between factors primarily associated with energy density (redox couples, achievable concentrations of electrolyte solutions) and electrical power density (electrochemical converter performance) will provide insight into appropriate priorities for different deployment scenarios.

In this work, we present an analysis of the cost factors associated with vanadium redox flow batteries (VRBs), which are widely viewed as a possible target technology. We previously analyzed VRB systems using chemical process engineering design strategies (2,3). The major variables affecting the capital costs are identified.

Background

A VRB is a system utilizing a redox reaction to both charge and discharge the battery by means of a flow of the reactants through the electrochemical cells, see Figure 1. Each cell is divided into half-cells by means of a membrane permeable to protons, while the cell itself contains electrodes that collect or provide electrons for the redox reaction. The cells are arranged in stacks and connected in series to increase the electrical potential of the VRB, while stacks are connected in parallel to increase the current capability of the VRB. The redox reaction for the VRB is provided by two solutions of vanadium ions pumped through the cell stacks from storage tanks external to the stack. The tanks store the solutions and, thus, the energy supply for the stack. The solution pumped through the negative half-cells contains V^{2+} and V^{3+} ions and the solution pumped through the positive half-cell contains V^{4+} and V^{5+} ions. Vanadium is dissolved in sulfuric acid to a typical concentration of 1 molar. The redox reactions occurring in the half cells while the battery is being charged are:



During discharge, the reactions are simply the reverse of these reactions.

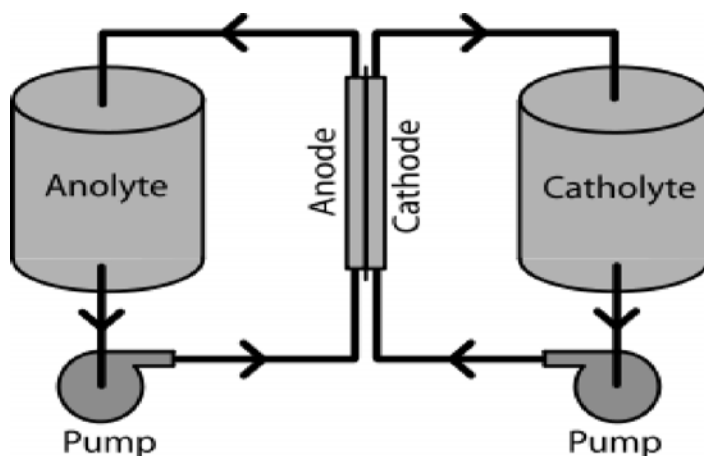


Figure 1. Schematic representation of a vanadium redox –flow battery (4).

The approach presented here for evaluating the sensitivity of the overall costs of a VRB to the selected design variables is taken, in part, from a paper by Moore, et al. in which a hierarchical method is used in the design process (5). The core of this method is the categorization of the capital costs into identifiable areas that are examined in a step by step procedure, with each step building upon the previous step. The categories presented for analysis of the capital costs are:

1. Costs that scale in proportion to the power capacity;
2. Costs that scale in proportion the energy capacity;
3. Costs that do not scale with size.

The first two categories constitute the greater portion of the capital costs of the battery, and will be the areas in which the cost sensitivity analysis will focus.

The electrical power capacity is determined by the design of the cell stacks. The amount of electric current produced by a cell is dependent on the current density of the cell and the active electrode area. The cells in a stack are assumed to be identical, however, and the cost model presented here does not allow for any change in current through a stack. The desired voltage is achieved by selecting the appropriate number of cells in a stack. The electrical potential of a stack is increased when the cells in a stack are connected in series. Each cell adds to the electrical potential of the stack by the value of the added cells electrical potential. The desired total current is achieved by changing the area of the cells in a stack or by connecting additional cell stacks in parallel.

The electrical power of the VRB is dependent on the overall number of cells in the battery. The current capacity of a cell, and thus the current capacity of a stack, is calculated by multiplying the current density of the electrode by the active electrode area. The current capacity of the VRB is calculated by multiplying the current capacity of a cell by the number of stacks, and the electrical potential of the battery is calculated by multiplying the electrical potential of one cell by the number of cells in a stack. The electrical power is then the product of the current capacity and the electrical potential.

The energy capacity of the VRB is determined by the concentration of vanadium and the volume of the process solutions. For a fixed concentration of vanadium, the greater the volume of the solutions the more energy can be stored by the battery. Larger volumes will be required for battery designs that require a higher electrical energy capacity, or a longer cycle time at a given power. An important consideration associated with the energy capacity of the VRB is the state of charge (SOC). The SOC defines the concentrations of the reactants and the products at any given point in time and represents the amount of energy the VRB is storing relative to its full capacity (6). The SOC of the VRB is considered because the electrical potential of the battery is dependent on the SOC. This is illustrated by Figure 2, which shows the relationship of the electrical potential to the SOC (7). While the graph of the cell potential in Figure 2 approaches the boundaries asymptotically; the middle of the graph is approximately linear. It is therefore advantageous to set the limits of the SOC for the VRB within this middle region, where the dramatic drop off or increase in electrical potential can be avoided. In addition, narrowing the limits of the SOC provides a smaller range of fluctuation in the power of

the VRB. Any change in the SOC during a pass of solution through the cell stack will result in reduced efficiencies since the conducting electrodes will produce only the lower voltage from the exit conditions. To minimize the inefficiencies, the solution flow rates were maintained sufficiently high so that only incremental changes in the SOC occurred during a single pass through the stack. Thus, the SOC corresponds to a gradual change in the composition in the solution tanks with time as the vanadium ions are oxidized or reduced.

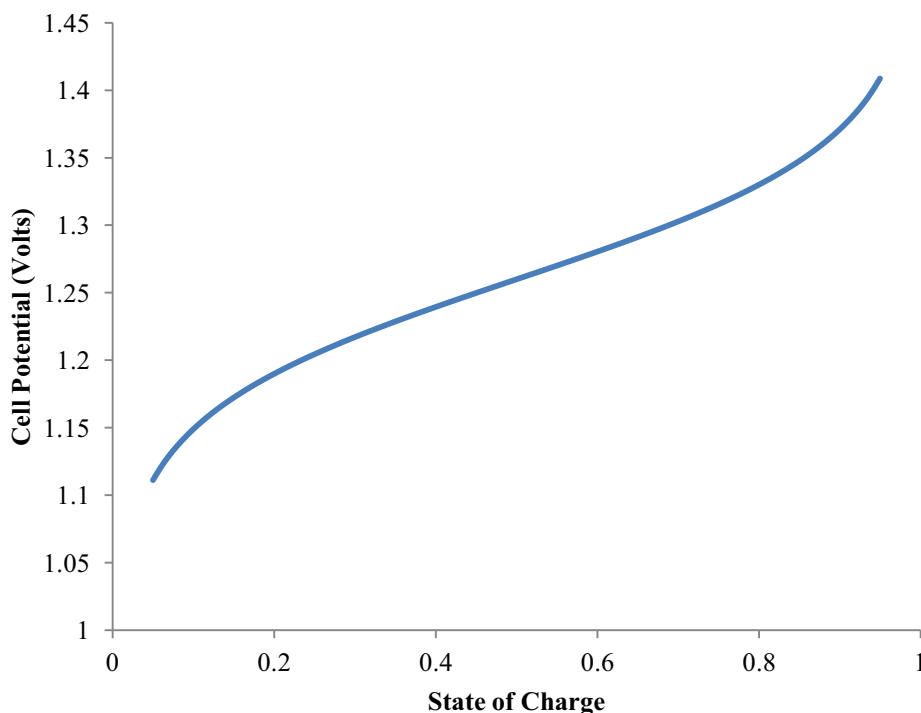


Figure 2. The effect of SOC on cell electrical potential (8).

Method

The sensitivity analysis begins by defining a base case VRB. In this paper, the base case is based upon the following conditions:

A. Reaction Related Information

- a. Stoichiometry (See Equations 1 and 2 above)
- b. Temperature: Near room temperature (25°C)
- c. Concentration of vanadium: 1 M
- d. Concentration of H₂SO₄: 5 M
- e. Electrical power capacity : 1,000 kW
- f. Energy capacity: 12,000 kW-hr
- g. Cycle time (for charge or discharge): 12 hr

- h. State of charge considerations: Minimum = 0.20, Maximum = 0.80
 - i. Average Potential of cell: 1.26 Volts (9)
 - j. DC to DC efficiency: 0.91
- B. Design Details
- a. Size (cross sectional area) of cell: 1 m²
 - b. Cell stack size: 100 cells
 - c. Design current density of cell: 40 mA/cm²
 - d. Materials of construction for tanks and heat exchangers: PVC and high Ni steel
 - e. Temperature adjustment in flow from cell stack: 15 °C
- C. Cost Information
- a. Industrial Grade Vanadium cost: \$21.13/kg of V (10)
 - b. Cell Construction Materials (11)
 - i. Ion-exchange membrane: \$500/m²
 - ii. Electrodes: \$51/m²
 - iii. Carbon felt: \$20/m²
 - c. Costs are in 2011 U.S. dollars

The capital cost of this base case is about \$4.5 million, or about \$380 per kWh. The costs of the components as a percentage of total capital costs can be seen in Figure 3. From the above base case variables a mathematical model was derived using the costs of different components of a VRB. The components are categorized according to their relationship to the electrical power capacity and energy capacity of the VRB. The variables chosen that are associated with the electrical power capacity of the VRB are the membrane cost and the current density. The variables chosen that are associated with the energy capacity of the VRB are the cycle time, the cost of the vanadium electrolyte, and the limits for the state of charge. The mathematical model derived is represented as a function of the components that affect the overall capital costs, taken as variables, in equation 3:

$$\begin{aligned}
 f(x) = & 3016.9 \times \frac{\tau_c (hr) \times P (W) \times C_v (\$/g)}{(0.8 - S_{CL}) \times \eta_{OA}} + 0.794 \\
 & \times \frac{P (W) \times (5151 + 202 \times C_M (\$/m^2) + 100 \times C_M (\$/m^2))}{I_D (mA/cm^2) \times \eta_{OA}^2} \\
 & + 355707.36 \times \left(\frac{\tau_c (hr)}{12}\right)^{0.6} \\
 & + 830.72 \times \frac{P (W)}{\eta_{OA}} + 22509 \\
 & + 1227.6 \times \left(\frac{P (W)}{\eta_{OA}}\right)^{0.6} + 15268.4 \times \left(\frac{P (W)}{\eta_{OA}}\right)^{0.22}
 \end{aligned} \tag{3}$$

See Table 1 for variable definitions. With this function the relative sensitivity index can be defined by equation 4:

$$\text{Relative sensitivity index} = \text{abs}\left(\frac{df}{dx}\Big|_{BCP} \times \frac{x_0}{f_0}\right) \quad [4]$$

where BCP is the base case point, x is the cost component variable, f is the capital cost function, x_0 is the component variable at the base case, and f_0 is the overall capital cost at the base case. The relative sensitivity index is then a measure of the rate of change of the capital costs for a particular component variable at the base case values. Since the absolute value of the equation is taken, the higher the result the greater the variable's influence on overall capital costs.

Table 1. Nomenclature

Variable	Description	Units
τ_c	Time necessary to fully charge or discharge the VRB.	hr
P	Power capacity of the VRB.	W
C_V	Cost of the vanadium ions.	\$/g
S_{CL}	Lower limit of the SOC.	
η_{OA}	Overall efficiency of the VRB (DC to DC).	
C_M	Cost of the membrane.	\$/m ²
I_D	Current density.	mA/cm ²

The relative sensitivity is useful, but it is limited to measuring the effect of the variables at their base case value. If the relationship between the variables value and the capital costs is not linear, then the variables effect on overall capital costs cannot be adequately measured in this way. To understand the effects of changing variable values of a certain range, another method was used. Starting with the base case values, the variables are selected individually and given a range of values. The capital costs of the VRB are then calculated for each of these values, and divided by the energy capacity of the VRB to attain the value for capital cost per kilowatt hour for comparison to the ARPA-e goal of \$100/kwh. The costs for the tanks, pumps, and heat exchanges were taken from a textbook by Ulrich (12).

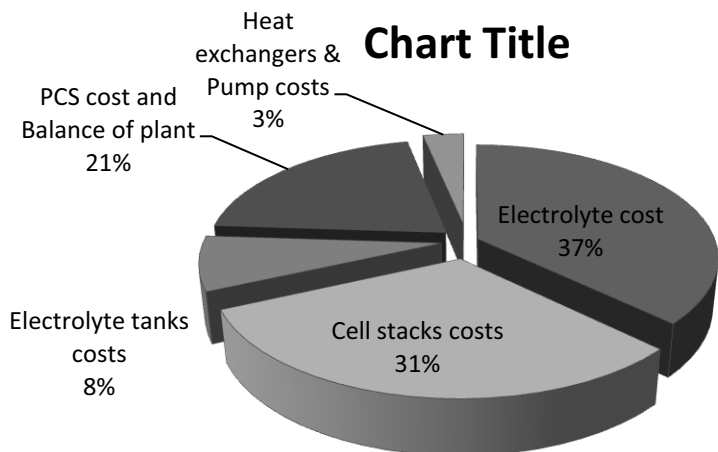


Figure 3. The Capital Costs of the Base Case VRB

The cost for the permeable membranes represents the majority of the costs for the cell stacks of a VRB. In the base case scenario, it alone represents about one-fourth of the total capital costs for the VRB. To test the sensitivity of the system cost to the membrane cost, the total capital costs for the VRB was calculated for membrane costs ranging from $\$100/\text{m}^2$ to the base case cost of $\$500/\text{m}^2$.

The current density of the electrodes has a significant effect on the number of stacks required. When the size of the cell is constant, the added current capacity increases the current through the stack, requiring fewer stacks in order to meet the electrical power requirement. The total capital costs were calculated for a range of current densities of $20 \text{ mA}/\text{cm}^2$ to $100 \text{ mA}/\text{cm}^2$. The increase in current density of the electrodes increases the over potential during charging and lowers the potential during discharge, and thus lowers the efficiency of the VRB. To calculate the efficiencies for different current densities data was taken from two graphs from a paper by You (13). The graphs from the paper can be seen in Figure 4. These graphs show that the cell voltage while charging and discharging is dependent on the SOC of the VRB. Graph (a) represents a current density of $40 \text{ mA}/\text{cm}^2$ while graph (b) represents a current density of $80 \text{ mA}/\text{cm}^2$. The area beneath the charging curves represents the amount of energy used to charge the VRB and the area beneath the discharging curves represents the amount of energy discharged from the VRB. The ratio of the discharged energy to the charging energy can then be used as the efficiency for that current density. An assumption was made that the relationship between current density and efficiency was linear. The linear dependence of efficiencies with current density was determined from the data at $40 \text{ mA}/\text{cm}^2$ and at $80 \text{ mA}/\text{cm}^2$ and an assumed efficiency of 1 at $0 \text{ mA}/\text{cm}^2$. This equation was calculated to be:

$$\eta_{OA} = 1 - 0.0021565x \quad [5]$$

where x represents the current density in mA/cm^2 .

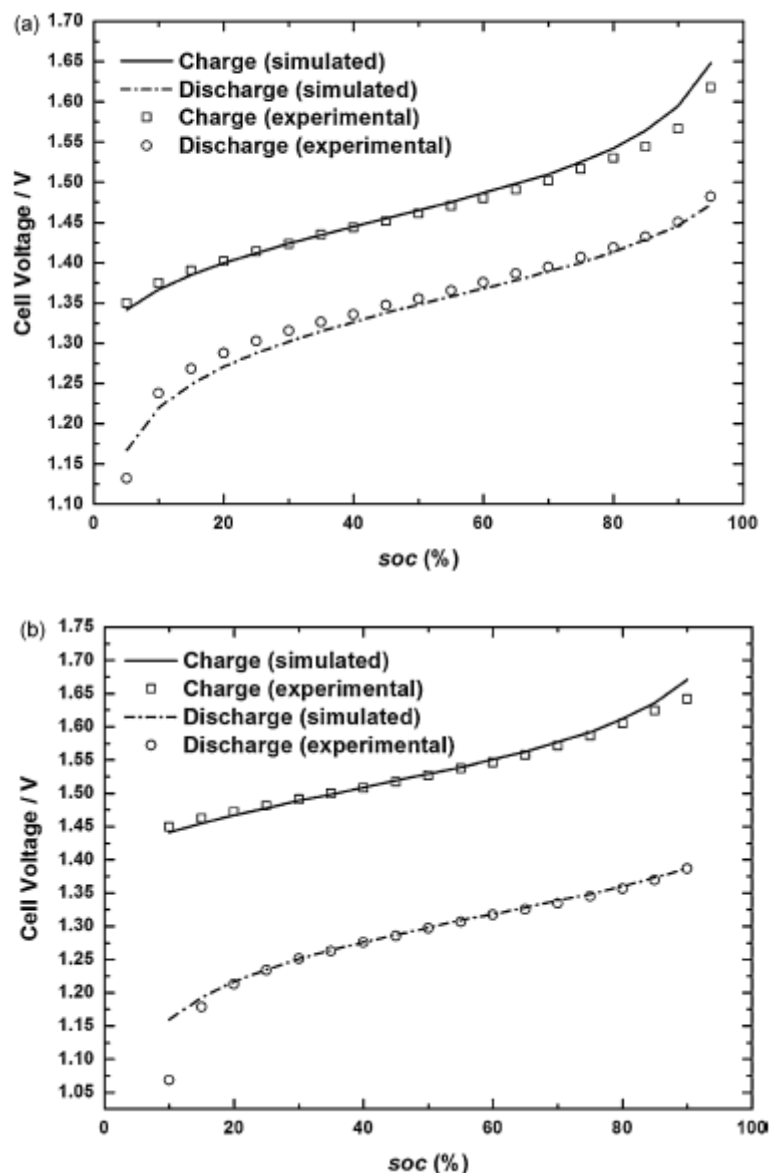


Figure 4. The cell voltage at different SOC for (a) a current density of 40 mA/cm² and (b) a current density of 80 mA/cm (13)

The cycle time determines the amount of energy the VRB must store, the longer the cycle time the greater the mass of vanadium electrolyte required to store the energy. The sensitivity of the overall capital costs to the cycle time is examined by holding the electrical power of the VRB at the base case value and changing the charge and discharge time for values between from 4 hours to 12 hours (total cycle time from 8 hours to 24 hours).

The major cost associated with the energy storage capacity of the VRB is the cost of the vanadium electrolyte, which at the base case value represents about 40% of the capital costs of the entire battery (13). The base case, however, assumes industrial grade vanadium while most research into VRB has been done in the laboratory with a higher grade of vanadium. The higher grade of vanadium is significantly more expensive. If deployment of VRBs increases the demand for higher grade vanadium, the cost for higher grade vanadium could fall, possibly to prices somewhere between the current cost for low grade and current costs for higher grade vanadium. To examine the effects of this on the capital costs of a VRB the costs of the vanadium was varied from the industrial base case value of \$0.021 per gram to the laboratory grade value of \$2.10 per gram.

As the SOC range becomes narrower, there is a need for a greater capacity of the vanadium electrolyte since less vanadium is utilized during each cycle. To examine the effect of this on the total capital costs of the VRB, the upper SOC limit is held at 0.8 while the lower SOC limit ranges from 0.2 to 0.7. For this study, the electric current density was a parameter of interest; so in all cases, the battery was charged and discharged at a constant current density.

The energy capacity of a VRB is a product of the power capacity and the cycle time. It is the amount of power (in kW) applied over a certain period of time (hours), and is measured in kilowatt-hours. If the energy capacity of a VRB is held constant, an increase in the power will provide for a decrease in the cycle time for the battery, while an increase in the cycle time will provide for a decrease in the power. The increase in power capacity requires the addition of stacks of cells, increasing the capital costs associated with the power capacity. The cycle time influences the amount of vanadium electrolyte required, as well as the size of the tanks, which affects the capitals costs as well. To see the effects on the capital costs when power capacity increases and the cycle time decreases, the energy capacity is held constant while the power ranges from 1000 kW to 3000 kW and the charge/discharge time ranges from 12 hours to 4 hours (a total cycle time of 24 to 8 hours).

Results

The values of the relative sensitivity index are given in Table 2. When the power capacity is fixed, the cycle time has, by far, the largest affect on capital cost with the price of vanadium having the next greatest affect. The cost of increasing the cycle time is a function of the cost of the vanadium; the longer the cycle time, the more vanadium electrolyte is necessary. This emphasizes the effect that the price of the vanadium electrolytes have on the capital costs. When the energy capacity is fixed, the power capacity and the cycle time have large and equal effect on the capital costs.

Table 2. Summary of Sensitivity Indexes

		Relative Sensitivity Index
Fixed Power Capacity Variables	Current Density	0.3092
	Cycle Time	0.6101
	Membrane Cost	0.2612
	Electrode Cost	0.021
	Vanadium Cost	0.3337
	Lower SOC Limit	0.1112
Fixed Energy Capacity Variables	Power Capacity	0.4881
	Cycle Time	0.4881

The sensitivity of the capital cost per kWh to various variables is presented below with accompanying graphs. In each case the remaining variables are held constant so that the effects of the intended variables on the overall capital costs is illustrated more clearly.

The sensitivity of the capital cost per kilowatt-hour to the costs of the membrane can be seen in Figure 4. The sensitivity of the capital costs to the membrane costs does not change as the membrane costs increase, but the capital costs do rise. With the present day costs (used as the base case cost) the capital cost per kilowatt-hour is about \$391, which trends down to \$284 per kilowatt when the membrane price is \$40 per square meter, a DOE target for fuel cells.

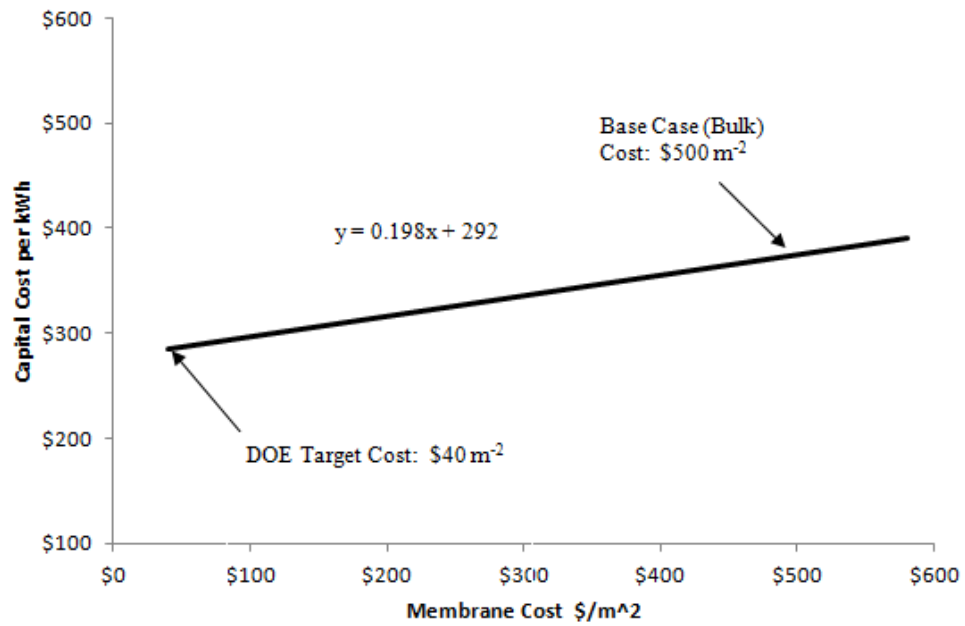


Figure 5. The effect of membrane cost on capital costs

The sensitivity of the capital costs per kilowatt-hour to the current density can be seen in Figure 5 for a family of curves representing different membrane costs. At lower current densities and higher membrane costs the capital costs are quite sensitive to the current density. As the membrane cost is lowered, however, current density has less of an effect on the capital costs. For all the membrane costs, the capital costs become less sensitive to the current density as the current density is increased. This result can be explained by the cost of the materials related to the energy capacity of the VRB, which are \$185 per kWh and do not change. As the costs related to the power capacity decrease, their contribution to the capital costs per kilowatt-hour becomes less and less significant, until the majority of the overall cost is related to the costs for the components associated with the energy capacity.

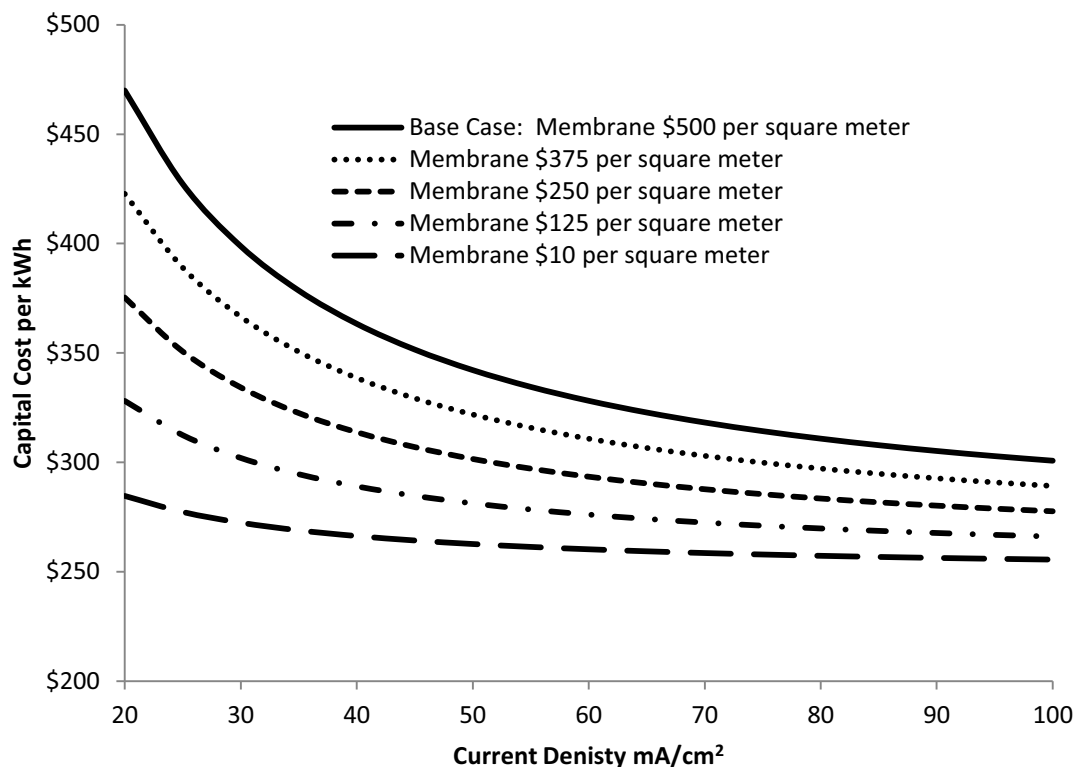


Figure 6. The effect of current density on capital costs

The sensitivity of capital costs to current density for different electrode prices can be seen in Figure 6 for a family of curves representing different electrode prices. The increase in current density once again shows diminishing returns when approaching 100 mA/cm². The electrode price does not affect the sensitivity of the capital costs to the current density, as the lines show the same level of curvature for each electrode price.

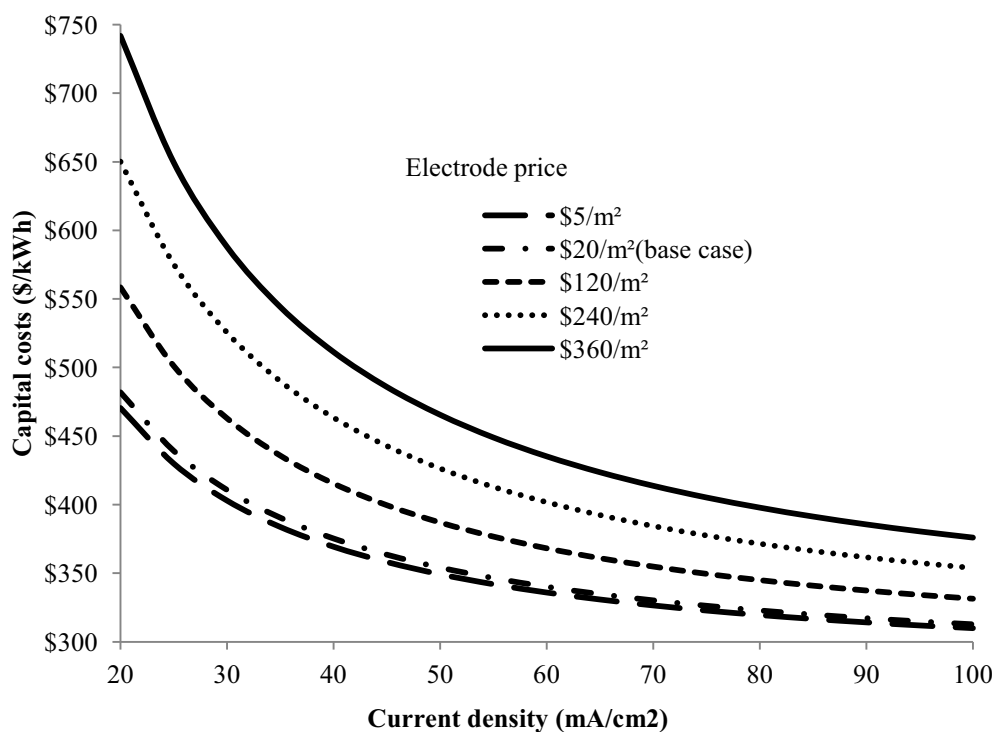


Figure 7. The effect of current density on capital costs for different electrode costs

The sensitivity of the capital costs per kWh to the cycle time can be seen in Figure 7. When the power capacity is constant at 1 MW, increasing the cycle time lowers the capital costs per kWh. The total capital costs will increase because of the larger tanks required and greater volume of vanadium electrolyte, however, the increase in the energy capacity of the VRB more than offsets this expense and lowers the capital costs per kWh.

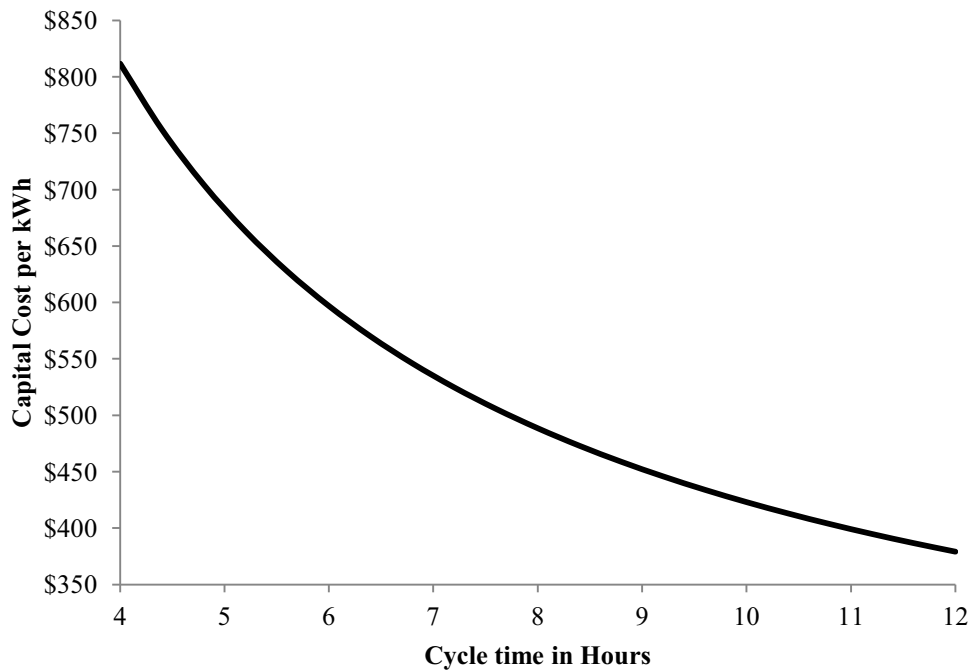


Figure 8. The Effect of Cycle Time on Capital Cost per Kilowatt-Hour for a 1 MW VRB

The sensitivity of the capital cost per kWh to the cost of vanadium can be seen in the semi-log graph in Figure 8. The capital cost per kWh showed the greatest range when increasing the cost of the vanadium from the cost of industrial grade vanadium at \$0.021 per gram to laboratory grade vanadium at \$2.10 a gram. There is a 100 fold increase in the cost of the vanadium electrolytes that increases the capital costs per kilowatt-hour from around \$300 to around \$12,000. The differences in the price can be explained by the purity of the vanadium, with the laboratory grade vanadium being of much higher purity. It is then important for a VRB to be able to use the lowest purity of vanadium as possible, so that the price of the vanadium can be kept at a minimum.

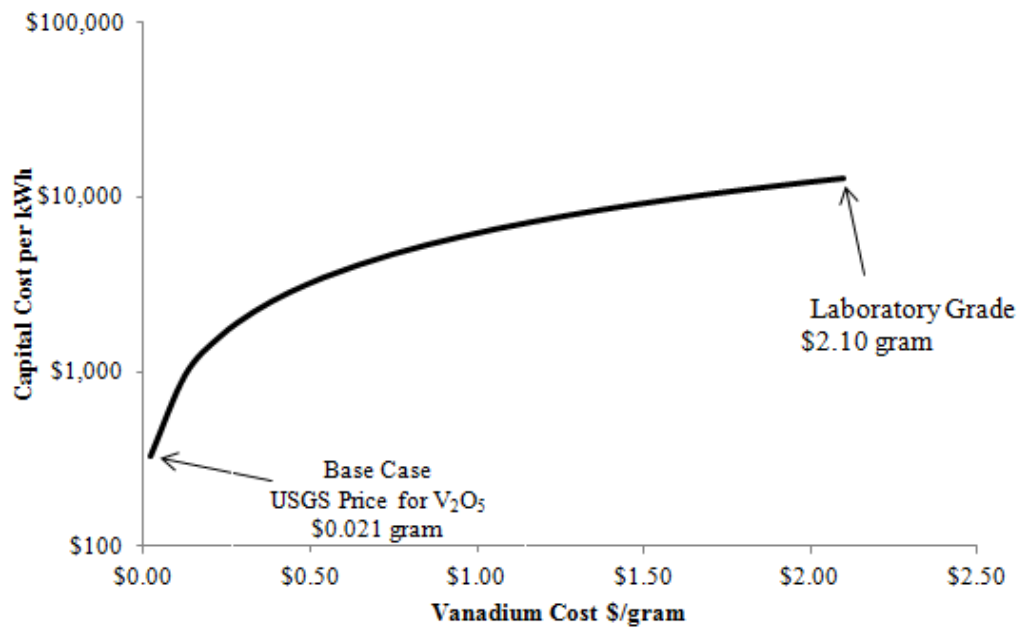


Figure 9. The Effect of Vanadium Electrolyte Cost on a VRB

The increase in the capital costs per kilowatt hour as the SOC limits are narrowed can be seen in Figure 9. As the SOC limits are narrowed by raising the lower limit toward a static upper limit of 0.80, the capital costs per kilowatt hour increases. This increase becomes more dramatic the narrower the SOC range, in this case the higher value for the lower limit. This increase is due to the fact that as the lower limit of the SOC approaches the upper limit of 0.80, the difference in the volume of vanadium solution needed to store the energy at those limits becomes greater and greater. For example, when the lower SOC limit is raised from 0.2 to 0.225, the volume of vanadium electrolyte solution needed increases by 4.3%, however when the SOC limit is raised from 0.3 to 0.325, the volume of vanadium electrolyte solution needed increases by 5.2%.

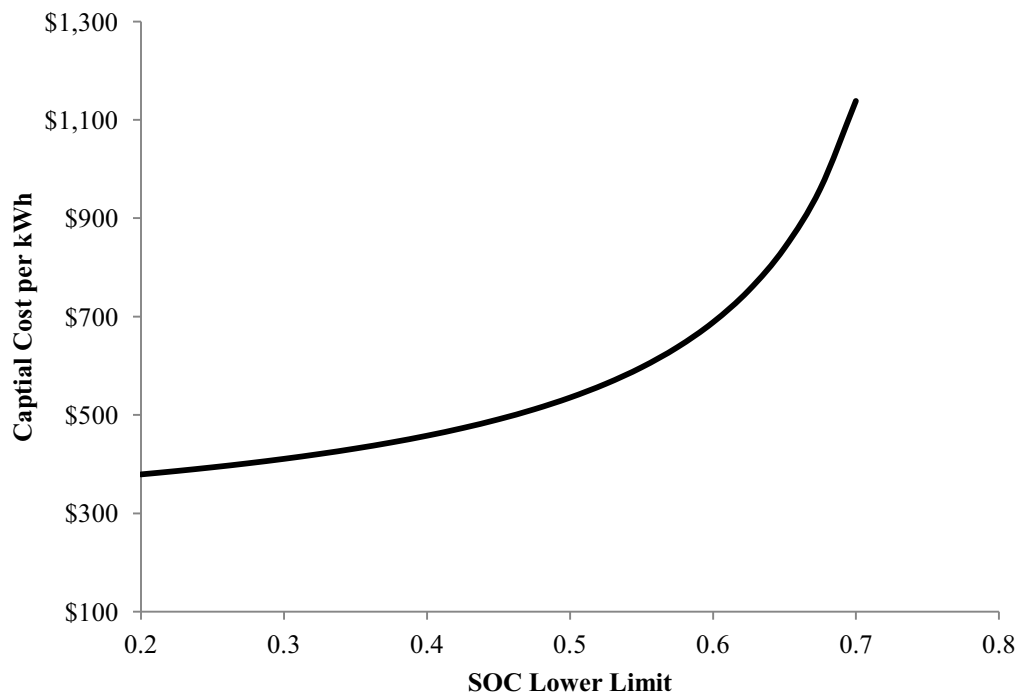


Figure 10. The Effect of SOC Limits on Capital Costs per Kilowatt-Hour

The graphs on Figure 10 show the capital costs per kilowatt-hour of a VRB when the energy capacity is held constant at 12 MWh, and the power capacity is raised while the cycle time is decreased. The higher power capacity translates into greater capital costs for the VRB.

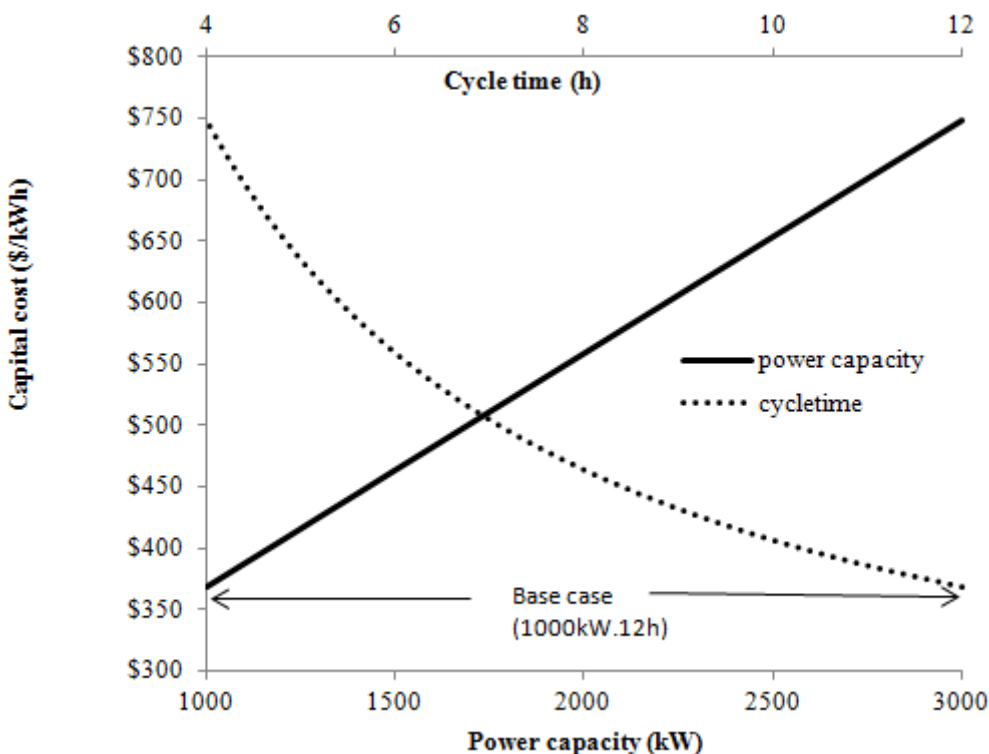


Figure 11. The Effect of Cycle Time and Power Capacity on Capital Costs per Kilowatt-Hour for a 12 MWh VRB

Conclusion

The relative sensitivity index for a fixed power capacity shows the importance of the costs of the vanadium to the overall capital costs. In addition, the capital costs per kilowatt-hour showed the greatest range when the vanadium costs were varied from the cost of industrial grade vanadium to the costs of laboratory grade vanadium. Note that a relatively large change in vanadium costs was considered in this analysis. Of course, the large change makes the cost of vanadium appear to be an especially important parameter. The large change in vanadium cost was used because it was apparent that the use of high purity vanadium at current prices (approximately \$2,100 per kg) would be prohibitively expensive. It is clear that using vanadium costs near that of the lowest grade vanadium will be necessary to keep the capital costs of the VRB down. Vanadium costs like those for the laboratory grade vanadium would be almost 120 times greater than the ARPA-e

goal. Better definition of vanadium purity requirements, less expensive sources of vanadium, and lower costs for reaching the required purity appear to be important needs for the VRB to meet or approach the ARPA-e goal.

When the energy capacity is held constant and the power capacity and cycle time are manipulated, the increased costs of the components related to the power capacity far out weigh the savings in the cost for the vanadium electrolyte and the tanks due to the lowered cycle time. This shows that there is a greater economic feasibility for VRB designs with a lower power capacity and longer cycle time for a set energy capacity.

The capital costs per kilowatt-hour are sensitive to the SOC limits, and the trade off between the greater fluctuation in the power of the discharge and narrower SOC limits must be carefully weighed against this when designing a VRB. If it is necessary to have a narrower range of power while discharging, the rise in the capital costs of the VRB will be steep. However, VRB uses where the power discharge is allowed a greater range will make the VRB far more affordable.

The increase in current density showed diminishing returns because of the costs of the components associated with the energy capacity. While the increase in the current density had a significant effect on the costs of the components associated with the power capacity, increasing the current density will have to be coupled with ways to decrease the costs of the components associated with the energy capacity to have a greater effect.

Since varying only one variable at a time was inadequate to reach the ARPA-e goal of \$100 per kWh for any of the variables, a more holistic approach must be taken in which multiple variables will be needed to reach the goal. Since some of the parameters reflect the different needs of individual electrical utility companies, it may be easier to meet or approach the cost goals for some applications than for others.

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