

A STEP-BY-STEP DESIGN METHODOLOGY FOR A BASE CASE VANADIUM REDOX-FLOW BATTERY

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The synthesis of chemical processes distinguishes chemical engineering process design from that of other engineering disciplines. In the work presented here, an approach usually applied to the synthesis of a traditional chemical production process is modified and used in the synthesis of an electro-chemical process for the storage of electrical energy. The intended use of this paper is for the development of case studies and homework problems for the chemical engineering curriculum, especially for the process design components of such a curriculum. It is intended to aid in the education of undergraduate students in the creation of process flow sheets and base cases for those processes with chemical reactions as a central element. The vanadium redox-flow battery (VRB) has some similarities to standard chemical processes usually studied in chemical engineering classes but offering a chance for the students to see these principles applied to a slightly different situation. As more chemical engineering graduates go to work in a wider variety of industries, they may need a wider experience during their education.

Redox-flow batteries represent one promising approach being considered by electric companies to store electric energy produced during periods of low demand (usually in the evenings) and use the energy during periods of high demand, usually during the day. The VRB was patented by research-

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ers at the University of New South Wales, Australia, where development has continued.^[1-4] Other recent reviews of flow batteries are also available.^[5-9] Because of the high capital costs for conventional electric energy generation systems, especially for hydroelectric and nuclear systems, it is more economical to operate such units as much as possible since the fuel costs are essentially zero, or a relatively small part of the total cost. Even for coal combustion systems, the capital costs have risen in recent years because of additional flue gas treatment. Economics usually still favor operating coal combustion systems as “base load” components that operate as much of the time as possible. Base load in this instance refers to the minimum amount of electrical power generated in order to meet the demand. To avoid installing high capital cost power (base load power) to meet peak energy needs, utility companies can use energy storage systems such as VRBs or make short-term use of gas-fired generators with high fuel costs but low capital costs. Despite the higher fuel costs, overall costs can be reduced by using the low-capital cost systems for short periods of high power demand.

The design methodology used here is adapted from one developed by Douglas, a step-by-step hierarchical process often used in chemical engineering classes proceeding through decision levels where more details are added to the flow sheet at each step or level of the design procedure.^[10] In addition, the capital costs of the battery system are evaluated at each level so that uneconomical designs are eliminated as early as possible and the syntheses efforts can be redirected to more promising directions as early in the design process as possible.

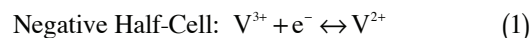
This paper focuses only on the capital costs of the battery system. The assignments to the students ended with an evaluation of the capital costs and did not include the operating costs. As noted earlier, the energy storage devices such as the VRB are attractive because their potential capital costs are lower than those of base load systems. The electric power industry has set targets for how low capital costs must become, and

development efforts are in progress to reach those goals.^[11] The goals of the student projects were to determine how close the current or foreseeable technology can come to the target for capital cost and to identify those components of the VRBs that are keeping the cost high and should be targeted for cost improvements. Only after the capital cost of VRBs can be reduced to values near the targets will it be useful to study operating costs in detail. VRBs are likely to be located on the sites of existing electric power plants. Flow batteries have few moving parts (such as pumps) and are usually suited for automated operations. Maintenance costs are expected to occur from corrosion and maintenance of electrolyte purity, but estimation of these costs is not reliably predicted by normal chemical engineering design practices taught in undergraduate courses and is expected to require pilot operating experience.

The design class was divided into six teams with three to four members per team. Each team considered a base case design and one or more variables/parameters to change. Parameters including membrane cost, efficiency, power capacity, and energy capacity were assigned to the groups. The capital costs for the VRBs were plotted vs. these parameters to show the difference that changing these parameters had on the capital costs. This provided a basis for direct comparison of the results from each team and allowed the entire class to consider and observe the effects of different parameters on the capital costs. Each change in a parameter represented a different operating condition or a different cost for a component of the battery.

BACKGROUND

A schematic of a vanadium redox battery system is shown in Figure 1. It may be called a system because it consists of tanks, pumps, and voltage conversion equipment as well as the actual battery cells. The battery cells consist of carbon felt electrodes and a cation exchange membrane (Nafion® 115), which divides the cell into two compartments. One compartment is filled with a solution of V(II) and V(III) ions while the other compartment is filled with a solution of V(IV) and V(V) ions. The vanadium ions are dissolved in sulfuric acid, usually 1 to 2 mol/liter. The electrochemical reactions occurring at each electrode while the battery is being charged are given in Eqs. (1) and (2). The reactions occurring while the battery is being discharged proceed in the opposite direction.



Each cell is assumed to produce 1.26 volts at zero current density, and in order to produce high voltages, the cells are stacked in series. As discussed later, inefficiencies reduce the effective voltage to values closer to one volt. Each electrode other than the end electrodes is “bipolar,” with one side acting as a cathode for the cell on one side and as an anode for the

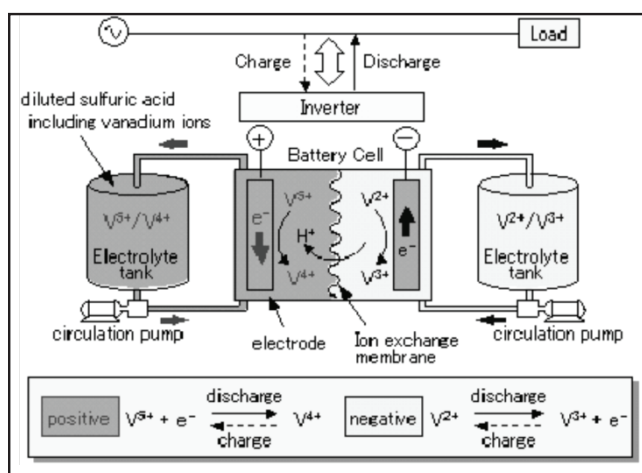


Figure 1. Schematic representation of a vanadium redox-flow battery.^[12]

cell on the other side. The unique feature of “flow” batteries is the liquid electrolyte, which can flow through the cell. As shown in Figure 1, there are two electrolyte solutions; both solutions flow through each cell on different sides of the membrane. The power produced by the battery is determined by the voltage produced (the number of cells in a stack), and the current produced is determined by the current density and the area of the carbon felt electrodes. Voltage can be lost from inefficiencies that may be affected by operating conditions. The total energy storage capacity is determined largely by the volume of the electrolyte solutions, the concentration of vanadium ions in those solutions, and the fraction of the vanadium ions used in any charge-discharge cycle. It is not practical to approach full utilization of all of the vanadium in the solutions. Again, any change in cell efficiencies that affects voltages produced has effects on stored energy recovered.

The decoupling of power and energy capacities in redox-flow batteries creates distinct advantages over other forms of energy storage. It allows for the power and energy capacities to be scaled independently in order to meet the unique needs of a particular utility. The power capacity required for the battery will determine the size of the cell stacks, the power conditioning system, the pumps, and the heat exchangers. The energy capacity required for the battery will determine the mass of vanadium electrolyte and the size of the storage tanks necessary. The capital costs therefore can be classified here in three areas:

1. Costs that scale in proportion to the power capacity;
2. Costs that scale in proportion to the energy capacity;
3. Costs that do not scale with size (the control system and balance of plant).

The step-by-step hierarchical method created by Douglas consists of several steps that include heuristics for the design of a chemical system. The first step consists of defining the process as continuous or batch, and the second step is an analysis of the raw materials, feed streams, and product streams. The subsequent steps are for analysis of the recycle system, the separation system, and the heat exchanger network. This method used by the students in the design study was adapted to the design of a VRB, keeping in mind the classification of the capital costs into the three areas already discussed:

- Level 1: Input information for the VRB;*
- Level 2: Input-output analysis;*
- Level 3: Power capacity considerations;*
- Level 4: Energy capacity considerations;*
- Level 5: Control system, and balance of plant;*
- Level 6: Total capital investment estimate.*

As with the procedure of Douglas, Levels 2, 3, 4, and 5 include a rudimentary economic (profitability) analysis that is guided by the analysis of previous levels. The profitability

analysis is based on the yearly profit produced by running the battery minus the capital expenses at every level annualized over the life of the components. This procedure, as with that of Douglas, allows for economical designs to be recognized quickly and uneconomical designs discarded so the process may begin again at the appropriate level. The procedure culminates in an estimate of total capital investment.

PROCESS SYNTHESIS HIERARCHY

Level 1: Input Information for the VRB

The first level of the adapted design methodology for a VRB is the definition of the design specifications for the VRB, as well as the costs for different component parts. To better illustrate the design method, the base case VRB used by the students is defined in Tables 1, 2, and 3. These

Stoichiometry	$V^{3+} + e^- \leftrightarrow V^{2+}$ $VO^{2+} + H_2O \leftrightarrow VO_2^+ + 2H^+ + e^-$
Operating Temperature	25 °C
Concentration of Vanadium	1 Molar
Concentration of H ₂ SO ₄	5 Molar
Power Capacity	1,000 kW
Energy Capacity	12,000 kW-hr
SOC Limits	0.20 ≤ SOC ≤ 0.80
Efficiency	0.91
Electrical Potential of a Cell	1.26 volts

Cycles per Year	328 (90% availability)
Cross Sectional Area of Cell	1 m ²
Current Density of Current Collector	40 mA/cm ²
Material of Construction: Tanks	PVC
Material of Construction: Heat Exchangers	High Ni Steel
Cells in a stack	100 cells/stack

Price of Output Power	\$0.45 per kW-hr
Cost of Input Power	\$0.045 per kW-hr
Vanadium Cost	\$25.13 per kg of V
Ion-exchange Membrane	\$500 per m ²
Current Collectors	\$51 per m ²
Carbon Felt	\$20 per m ²

design variables will be used as an example for calculations throughout this paper except where otherwise noted. The price of product electricity used in Table 3 is that needed to bound the spot prices of recent years as reported by the U.S. Federal Energy Regulatory Commission. This price represents

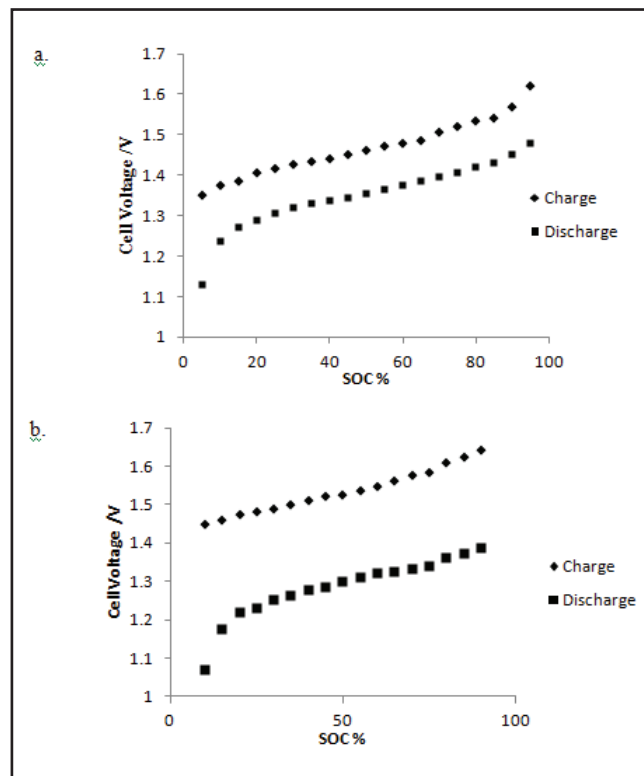


Figure 2. The cell voltage at different SOC's for (a) a current density of 40 mA/cm² and (b) a current density of 80 mA/cm².^[13]

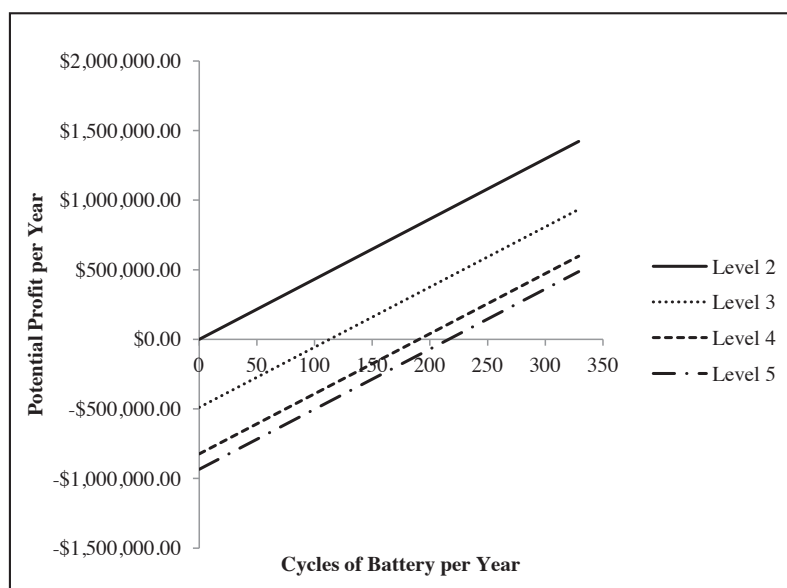


Figure 3. Economic potential for a vanadium redox-flow battery.

the upper bound of (peak) energy prices and is used here in a comparison mode to develop the base case process. After the base case is determined it would normally be subjected to optimization at near to actual market prices. The base case cost model is examined at near market prices in the final portion of this report.

To calculate the efficiencies for different current densities, data was taken from two graphs from a paper by You, et al. and plotted in Figure 2.^[13] These graphs show that the cell voltage while charging and discharging is dependent on the state of charge (SOC) of the VRB. 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. SOC is defined with Eqs. (3) and (4).

$$\text{SOC} \equiv \frac{C_{V2+}}{C_{V2+} + C_{V3+}} \text{ for the negative electrolyte, or} \quad (3)$$

$$\text{SOC} \equiv \frac{C_{V5+}}{C_{V5+} + C_{V4+}} \text{ for the positive electrolyte,} \quad (4)$$

Graph (a) of Figure 2 represents a current density of 40 mA/cm² while graph (b) of Figure 2 represents a current density of 80 mA/cm². 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 of that current density for a complete cycle. 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. The ratio of the discharged energy to the energy used to charge for the current densities of 40 mA/cm² and 80 mA/cm², as well as an assumed efficiency of 1 at 0 mA/cm², was used to calculate an equation of a line. The equation is $\eta_{\text{OA}} = 1 - 0.0021565x$, where x represents the current density in mA/cm².

Level 1 of the original Douglas procedure includes fundamental design information and whether the process is to be a batch or continuous process. The VRB is considered to be a semi-batch system. The electrochemical cells are converting the vanadium redox species much like a steady-state system, but the feed concentrations to the cells varies with time. This is much like a batch tank with a side stream of fluid circulating through a reactor. Thus, the work presented here is formulated in a way that is similar to that of Douglas, and Level 1 provides the basic information needed for design. The above input information is a matter of choice and does not necessarily represent an optimal design. The cost information used here is generally appropriate for

2011 U.S. dollars. The current densities and the charge and discharge efficiencies have been assumed to be equal for the example presented here.

Level 2: Input-Output Analysis

The costs of the energy required to charge the battery represents the majority of the cost of operating the battery, while the revenue stream resulting from operating the battery comes entirely from selling the energy discharged by the battery. By considering these costs and revenues, one can gauge the maximum economic potential of the VRB. This is much like a chemical process where the maximum economic potential is the difference between the product value and the raw material cost while neglecting any processing costs.

Eq. (5) may be used to calculate the economic potential for level 2. The cycles per year represent a full cycle, *i.e.*, the charging and discharging of the battery.

$$EP_2 = \left(E_D \times \frac{\$}{\text{kWh}_D} - E_C \times \frac{\$}{\text{kWh}_C} \right) \times \frac{\text{cycles}}{\text{year}} \quad (5)$$

E_C and E_D are defined by Eqs. (6) and (7).

$$E_C \equiv \frac{E_{sc}}{\xi_C} \quad (6)$$

$$E_D \equiv E_{sc} \times \xi_D \quad (7)$$

Example Calculation—Level 2 Economic Potential:

Using the base case design variables defined in Level 1, and Eqs. (3) – (5), the maximum economic potential can be calculated as follows:

$$E_C = \frac{12,000 \text{ kWh}}{0.91}$$

$$E_C = 13,187 \text{ kWh}$$

$$E_D = 12,000 \text{ kWh} \times 0.91$$

$$E_D = 10,920 \text{ kWh}$$

$$EP_2 = \left(10,920 \text{ kWh} \times \$0.45 \text{ kWh}^{-1} - 13,187 \text{ kWh} \times \$0.045 \text{ kWh}^{-1} \right) \times 328 \frac{\text{cycles}}{\text{year}}$$

$$EP_2 = \$1,417,155 \text{ yr}^{-1}$$

The economic potential for cycles of up to 350 per year are plotted in Figure 3 for Levels 2 through 5.

Level 3: Power Capacity Considerations

The next major costs of a VRB considered by the students are the power capacity considerations. The costs that scale

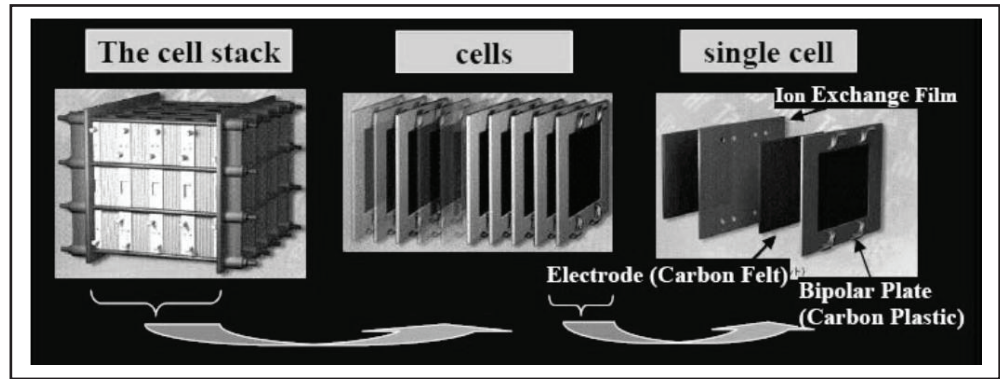


Figure 4. Cell stack construction.^[12]

with the power capacity of a VRB are the cells themselves, a power conditioning system (PCS) that converts electricity from AC to DC during charging and DC to AC during discharging while adjusting to the desired voltage, the pumps, and the heat exchangers.

The materials used to construct the cells consist of carbon felt electrodes, current collectors, and a membrane permeable to protons. A diagram of the cell construction is presented in Figure 4. As noted earlier, the electrical potential of a cell is dependent on the state of charge (SOC) of the vanadium ion solution being pumped through the cell.

Since the SOC is constantly changing during the charge and discharge process, the voltage—and therefore the power—of the VRB is constantly changing. The power rating of the VRB in the design methodology used by the students is the average power of the VRB over the charge/discharge cycle (or at 50% SOC). By using the average power for the design process, the correct energy capacity can be calculated without having to account for the changing voltage over the course of the cycle.

The number of stacks needed is dependent on the current density of the carbon felt electrodes and the number of stacks

in the VRB. The current through all the cells in a stack is constant and may be calculated by multiplying the current density of the carbon felt electrodes by their area, as in Eq. (8).

$$I_s = I_D \times A_C \quad (8)$$

In the model used by the students, the stacks were connected in parallel. In this manner, the electrical current produced by a stack is additive to the current produced by the other stacks. The electrical potential is

determined by the cell potential and the number of cells in a stack, both defined in Level 1 of this methodology. The power capacity of the battery is the electrical potential multiplied by the current capacity of the VRB. Since the power capacity of the battery is defined in Level 1, the number of stacks can be calculated with Eq. (9).

$$N_s = \frac{P}{V_s \times I_s \times \xi_c} \quad (9)$$

The power that is lost due to the inefficiencies of the battery is released through heat. The heat generation is based on a total energy balance around the charging or discharging battery and assumes that the only energy removed from this system is by the exit fluid stream. To estimate the heat generated by the VRB, Eq. (10) may be used for charging the battery and Eq. (11) for discharging the battery.

$$q = \frac{P}{\xi_c} \times (1 - \xi_c) \quad (10)$$

$$q = P \times (1 - \xi_d) \quad (11)$$

It is assumed that the heat generated is shared equally between both the cathode solution and the anode solution with the temperature change of the vanadium ion solutions dependent on the flow rate of the vanadium solution through the stack. To calculate the flow rate of the vanadium ion solutions, it is necessary to calculate the moles of vanadium ions oxidized per second then divide by the molarity of the vanadium ions in the solution, as in Eq. (12).

$$F_M = \frac{I_s \times N_c \times N_s}{F \times C_v} \quad (12)$$

Capital-related cost item	Fractions of fixed capital
Maintenance and repairs	0.06
Operating supplies	0.01
Overhead, etc.	0.03
Taxes and insurance	0.03
General	0.01
Total	0.14

F_M in Eq. (12) represents the minimum flow rate if all the vanadium ions in solution are oxidized while flowing through the cells. One of the sources of inefficiency in a flow battery is transport loss, which is associated with the complete conversion of all available vanadium ions flowing through the cell.^[14] Because of this, it was recommended to the students that a greater bulk flow of the vanadium ion solution be pumped through the cells than the minimum flow rate required. In the example presented here the minimum flow rate represents 10% of the greater bulk flow rate. The flow rates of both anode and cathode solutions used by the students were calculated with Eq. (13).

$$FA = \frac{F_M}{X_{v,p}} \quad (13)$$

With the flow rate, the change in temperature of the cathode or anode solution is calculated by Eq. (14).^[15]

$$\Delta T = \frac{q}{2 \times C_p \times F_A} \quad (14)$$

For estimation purposes, the heat capacity of the sulfuric acid solution is assumed. Because of the increased flow rate of the vanadium ion solution, the temperature rise of the vanadium ion solution may be such that heat exchangers are unnecessary. If the temperature rise during the pass of fluid through the stacks is less than 100 °C, the heat exchangers will not be considered in the analysis, however, some heat exchange may indeed be necessary and will need to be considered before final process design.

If the temperature of the vanadium ion solution necessitates the use of heat exchangers, Eq. (15) may be used to determine the size of the heat exchangers needed to bring the solution to room temperature.^[15]

$$A = \frac{q}{U \Delta T_m} \quad (15)$$

After determining the size of the heat exchangers, the size of the pumps required for the flow rate can be calculated if needed. The shaft power of the pumps can be calculated with Eqs. (16) and (17), for which F_A is in m³/s (in all other

Membrane Area (20 Stacks)	2000 m ²
Cost of Membrane	\$500 m ²
Total Cost of Membrane (20 Stacks)	\$1,000,000
Cost of Current Collectors	\$51 m ²
Total Cost of Current Collectors (20 Stacks)	\$103,020
Cost of Carbon Felt Electrodes	\$ 20 m ²
Total Cost of Carbon Felt Electrodes	\$80,800
Total Cost of Stacks (20 Stacks)	\$1,657,348
Annualized Cost of Stacks (20 Stacks)	\$501,754
Cost of Pumps (2)	\$86,112
Annualized Cost of Pumps (2)	\$26,070
Cost of Power Conditioning System	\$260 kW ⁻¹
Transformer Cost	\$36.58 kW ⁻¹
Cost of Breakers, Contacts, and Cabling	\$28.14 kW ⁻¹
Total PCS and Associated Items Cost	\$324,720
Annualized Cost of PCS and Associated Items	\$19,303
Total Annualized Cost of Level 3 Components	\$547,127

equations F_A is in liters/s).^[15]

$$W = \frac{F_A \times \Delta p}{\varepsilon_i} \quad (16)$$

$$\varepsilon_i = (1 - 0.12F_A^{-0.27})(1 - \mu^{0.8}) \quad (17)$$

The students were given an estimate of the cost of the Power Conversion System (PCS) to convert AC power to DC power and to convert the DC product from the battery back to AC power for returning to the electrical grid. The current cost of a PCS is estimated at \$260 per kW. The costs associated with the PCS are for the transformer, breakers, contacts, and cabling, which are estimated by EPRI.^[12]

To calculate the economic potential for Levels 3 and beyond, it is necessary to annualize the capital costs. The annualized capital costs include the annual expenses, the cost of capital, and equipment depreciation. The annual expenses used here are those that are directly proportional to fixed capital, as listed in Table 4.

The cost of capital considers the required return on investment for a given capital outlay. The required return on investment will vary by company but is assumed in this circumstance to be 10%. Annualized interest on invested capital expressed as a fraction of the initial capital investment is calculated with Eq. (18).^[16]

$$f_{RI} = \frac{n \left[\frac{i(1+i)^n}{(1+i)^n - 1} \right] - 1}{n} \quad (18)$$

The service life of the components, n in Eq. (18), is 10 years for the stacks and the pumps while the remaining components have a lifespan of 20 years.^[12] To simplify the calculation, straight line depreciation is used with fractional annual depreciation calculated as in Eq. (19).

$$f_D = \frac{1}{n} \quad (19)$$

The annualized cost of components may be calculated with Eq. (20)

$$AC = C_{\text{cost}} (0.14 + f_{RI} + f_D) \quad 20$$

The economic potential for Level 3 can then be calculated with Eq. (21).

$$EP_3 = EP_2 - AC_S - AC_{\text{HEX}} - AC_P - AC_{\text{PCS}} \quad (21)$$

Example Calculation of Level 3 Economic Potential

A summary of the components of the cell stack and their associated costs is given in Table 5. A stack consisting of 100 cells contains 101 current collectors (101 m²/stack, total for 20 stacks = 2020 m²), 202 carbon felt electrodes (202 m²/stack, total for 20 stacks = 4040 m²), and 100 membranes (100 m²/

stack, total for 20 stacks = 2000 m²). Added into the total costs for the stacks are manufacturing costs, shipping costs, and additional costs that were assumed to be 20%, 10%, and 10%, respectively, of the total capital costs of the components.^[12] The annualized costs of an equipment item are the annualized costs of the installed equipment items; an installation factor of 1.4 is used to modify the purchased costs of the stacks. Figure 3 shows that at Level 3 it is necessary to cycle the battery over 100 times a year in order to make a profit. The economic potential drops by over \$500,000 between Levels 2 and 3, which is significant. Examining the costs of components in Table 5 shows that the bulk of this drop in economic potential is due to the costs of cell ion exchange membranes.

LEVEL 4: ENERGY CAPACITY CONSIDERATIONS

The energy capacity of a VRB is determined by the mass of vanadium electrolytes in each solution. The stoichiometric equations listed in Level 1 show that one mole of vanadium ions will produce one mole of electrons when oxidized or reduced. Because of this, the students calculated the moles of vanadium ions needed by taking the moles of electrons oxidized by one cell in one second, multiplying by the charge time, multiplying by the number of cells in a stack, then multiplying by the number of stacks in the battery as in Eq. (22).

$$M_V = \frac{I_s \times \tau_c \times N_c \times N_s}{F} \quad (22)$$

This calculation will provide the moles of vanadium electrolytes needed for the cathode or the anode solutions and should be multiplied by two for the total amount needed. To calculate the amount of vanadium needed, however, changes in the SOC of the battery must be considered. As mentioned in Level 3, the electrical potential as a function of the SOC increases as the SOC increases. The VRB cannot be fully charged without using very high (infinite) voltages and cannot be fully discharged without a severe loss of voltage (efficiency) in the discharge. It is assumed that the base-case battery will operate between an SOC of 0.20 and 0.80, which means that M_V represents 60% of the total vanadium needed.

The tanks used to store the vanadium solution will vary in size with the volume of vanadium ion solution needed, and therefore with the energy capacity of the VRB. Because of the corrosive nature of sulfuric acid, the use of double-walled tanks should be considered. In the current example, the students used single-walled fiberglass tanks. The size of the tanks and amount of vanadium needed is estimated by Eqs. (23) and (24) (in the current example one liter of solution contains one mole of vanadium).

$$V_T = \frac{M_V}{M_U - M_L} \quad (23)$$

$$M_T = \frac{2 \times M_V}{(0.6)} \quad (24)$$

The economic potential for Level 4 is then calculated with Eq. (25).

$$EP_4 = EP_3 - AC_V - AC_T \quad (25)$$

This Level 4 methodology differs significantly from the method suggested by Douglas. He uses Level 4 for including the costs of separation systems in a chemical process. This is one place where a change was needed to the Douglas approach for the VRB.

Example Calculation for Level 4 Economic Potential

A summary of the components' associated costs with Level 4 considerations is presented in Table 6. To account for the costs of preparing the solution, the capital cost of the vanadium was multiplied by 1.1. To annualize the costs it was assumed that the tanks, vanadium, and sulfuric acid could be used throughout the lifespan of the battery. A reasonable estimate for this lifespan of 20 years was used by the students.^[12] The drop in economic potential between Levels 3 and 4 is more than \$400,000, and Figure 3 shows that it is necessary to have over 200 cycles per year in order to make a profit. $EP^4 = \$870,027 \text{ yr}^{-1} - \$393,519 \text{ yr}^{-1} - \$68,217 \text{ yr}^{-1}$
 $EP^4 = \$408,292 \text{ yr}^{-1}$

LEVEL 5: BALANCE OF PLANT

The last of the major costs of a VRB are associated with the balance of plant costs. These costs may also be associated with the power and energy capacity of the VRB, but are included in another level for simplicity.

The balance of plant costs are based on the EPRI calculations and include the costs for construction (not already

accounted for), costs for the control system, and building and site preparation costs.^[12] Building and site preparation costs are estimated on average to be around \$900 per square meter of the facility in 2007. Accounting for an inflation rate of 3%, the cost in 2011 was \$1,012 per square meter. An estimate for the size of the facility is 500 m²/MW^[12] Adjusting for inflation, the control system is estimated at \$22,509 and the remaining costs are \$56/kW.

$$EP_5 = EP_4 - AC_{BP} \quad (26)$$

Level 5 is not comparable to any level of the Douglas model. It is used to essentially capture all the remaining capital costs elements that are not functions of power or energy.

Example of Level 5 Annualized Capital Costs Estimation:

$$EP_5 = \$408,292 \text{ yr}^{-1} - \$150,487 \text{ yr}^{-1}$$

$$EP_5 = \$257,804 \text{ yr}^{-1}$$

Level 6: Capital Investment Estimate

The last step makes use of the information gathered in the earlier steps to create a capital investment estimate table.

TABLE 6
Level 4 Capital Costs

Concentration of Vanadium	1 mol/L
Volume of Solution	596,984 L
Cost of Vanadium	\$25.13 kg ⁻¹
Total Cost of Vanadium Solution	\$1,528,470
Annualized Cost of Vanadium Solution	\$393,519
Tank Size	656,680 L
Total Cost of Tanks	\$264,960
Annualized Cost of Tanks	\$68,217

TABLE 7
Capital Cost Estimate

Equipment ID	Number	Capacity	Purchased Cost	Installation and Material Factor	Capital Investment
Cell Stacks (100 cells per stack)	V-101	20 stacks	\$1,183,120	1.4*	\$1,657,348
Vanadium Solution	S-101	596,984 liters	\$1,528,470		\$1,528,470
Tanks	T-101	656,680 liters, Fiberglass	\$88,320	3	\$264,960
Heat Exchanger	C-101	na	0	4	0
Pumps	P-101	7.9 Watts	\$11,482	7.5	\$86,112
PCS System and Associated Costs	E-101	1,000 kVA	\$324,720	1	\$324,720
Balance of Plant Costs			\$584,509	1	\$584,509
Total Cost			\$3,720,621		\$4,446,119

* for manufacturing costs, shipping costs, and additional costs

A table from the example is presented in Table 7. This methodology has covered only the capital costs of a VRB; the operating costs were not included in the student assignments. While a complete summary of the total costs of operating a VRB would include the operating costs, the intent of this design methodology was to include only the capital costs.

FUTURE POSSIBLE COST REDUCTIONS

Table 7 shows that the cost of the cell stacks and the cost of vanadium were identified as major contributors to capital cost. In this section the possibility of cost reduction for these two variables is explored. The reduced cost of \$35/m² for ion exchanged membranes reflects one author's expected reduction in manufacturing cost caused by increased demand for membranes and improved manufacturing.¹⁹ The reduced cost of vanadium at half of the value in Table 3 may be more optimistic, but it is based on the observed volatility of vanadium prices in recent years as reported by the U.S. Geological Survey. The economic potential in the following analysis is based on a more realistic market value of electricity.

The capital cost elements of the base case model reported in Tables 1, 2, and 3 are only changed by the reduction of ion exchange membrane costs in the results shown in Table

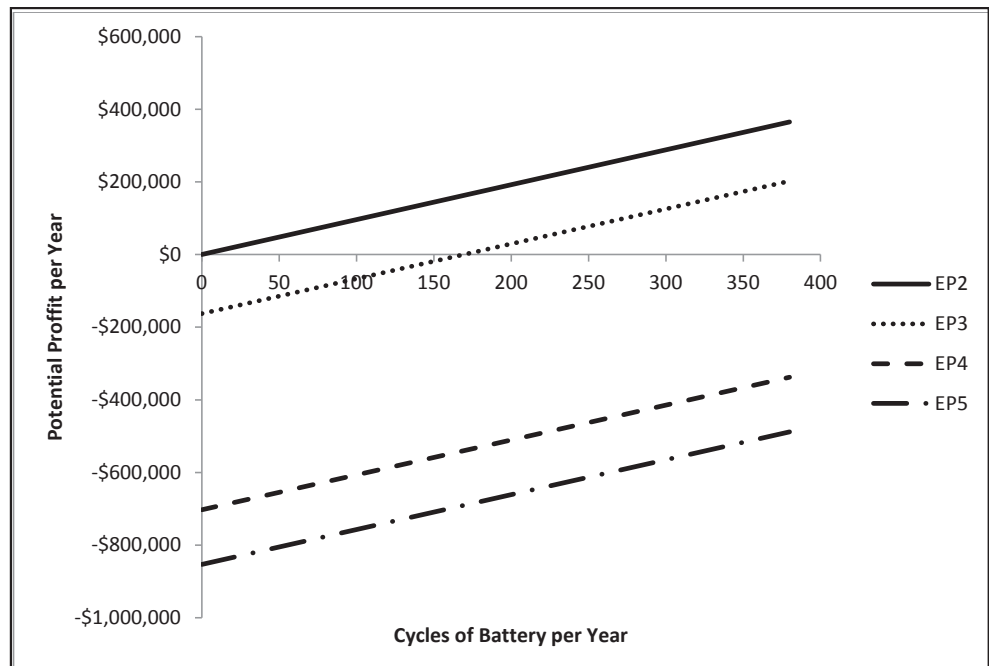


Figure 5. Economic potential for a vanadium redox-flow battery at reduced membrane cost conditions.

8. The capital costs per MWh are reduced to \$262. The economic potential of the reduced cost system shown in Figure 5 is based on the price of product electricity of \$0.10/kWh and a purchased cost of \$0.01/kWh and shows that the cost of Level 4 and 5 are always negative, indicating no opportunity for profit at the conditions of the study.

The capital costs elements of the base case model reported in Tables 1, 2, and 3 are changed by both the reduction of ion exchange membrane costs and reduced vanadium costs in the results shown in Table 9 (next page). The capital costs per MWh are reduced to \$198. The economic potential of the

TABLE 8
Capital Cost Estimates at Reduced Ion Exchange Membrane Cost

Equipment ID	Number	Capacity	Purchased Cost	Installation and Material Factor	Capital Investment
Cell Stacks (100 cells per stack)	V-101	22 stacks	\$276,709	1.4*	\$387,393
Vanadium Solution	S-101	650,820 liters	\$1,666,307	1	\$1,666,307
Tanks	T-101	656,680 liters, Fiberglass	\$88,320	3	\$264,960
Heat Exchanger	C-101	na	0	4	0
Pumps	P-101	20 Watts	\$11,482	7.5	\$86,112
PCS System and Associated Costs	E-101	1,000 kVA	\$324,720	1	\$324,720
Balance of Plant Costs			\$584,509	1	\$584,509
Total Cost			\$2,952,047		\$3,314,001

* for manufacturing costs

TABLE 9
Capital Cost Estimates at Reduced Ion Exchange Membrane Cost and Reduced Vanadium Costs

Equipment ID	Number	Capacity	Purchased Cost	Installation and Material Factor	Capital Investment
Cell Stacks (100 cells per stack)	V-101	22 stacks	\$276,709	1.4*	\$387,393
Vanadium Solution	S-101	650.820 liters	\$828,843		\$828,843
Tanks	T-101	656,680 liters, Fiberglass	\$88,320	3	\$264,960
Heat Exchanger	C-101	na	0	4	0
Pumps	P-101	20 Watts	\$11,530	7.5	\$86,476
PCS System and Associated Costs	E-101	1,000 kVA	\$324,720	1	\$324,720
Balance of Plant Costs			\$584,509	1	\$584,509
Total Cost			\$2,114,631		\$2,476,901

* for manufacturing costs

reduced cost system shown in Figure 6 is based on the price of product electricity of \$0.10/kWh and purchased cost of \$0.01/kWh and shows that the improved cost of Levels 4 and 5 is still always negative, introducing no opportunity for profit at the conditions of the study.

The results shown here indicate that reduced costs for ion exchange membranes and vanadium do not appear to be sufficient to make the system profitable at the conditions of this study. Additional cost reductions will be necessary. Such cost reductions may be found in activities such as increasing the range of SOC values for system operation and improving the cell current density and efficiency as well as other general cost reductions.

GENERAL OBSERVATIONS

Our current CBE process design classes consist of two senior classes (CBE 480 and 488 or 490). CBE 488 is the honors version of CBE 490 and typically has industrial sponsorship. CBE 480 covers fundamental chemical process design: process creation and definition, flow sheet development, design and costing of equipment, optimization, economic analysis, and reporting; the textbook is by Ulrich and Vasudevan^[15] with supplemental information on flow sheet creation by Douglas.^[10] CBE 488/490 are both traditional capstone design projects with the primary deliverables being oral and written design

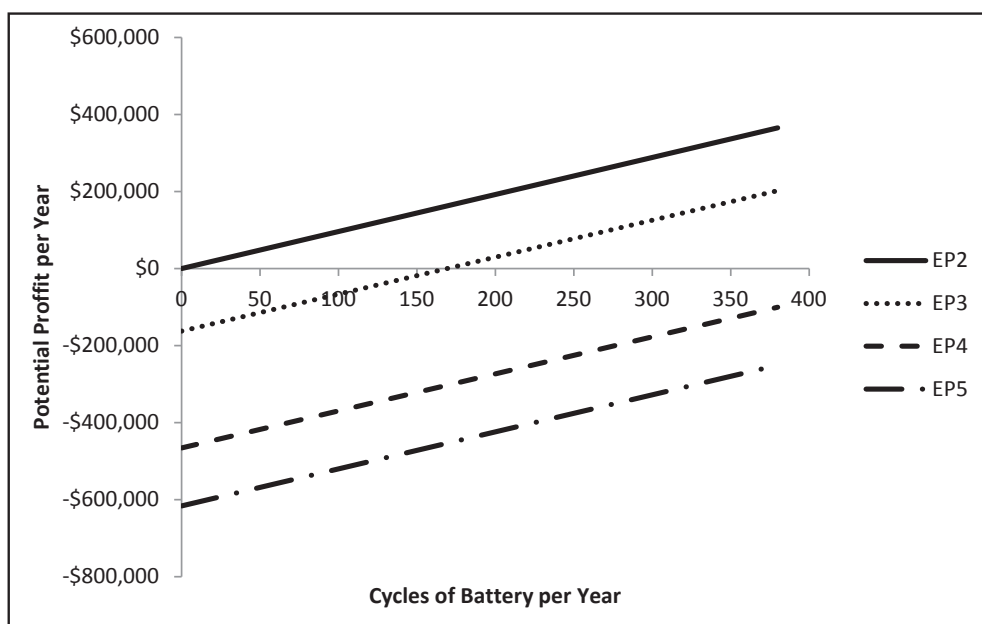


Figure 6. Economic potential for a vanadium redox-flow battery at reduced membrane cost conditions and reduced vanadium cost.

reports. Both CBE 480 and CBE 488 or 490 are required 3-semester-hour classes. The case study presented here was the primary focus of CBE 488 and a shortened version used as a homework problem in CBE 480. Different CBE 488 teams had different design variables, such as current density, in addition to studying a common base case on which to report.

The development of the case study presented here was sponsored by EPRI. One of the co-authors of this study, Haresh Kamath, was a primary author of an authoritative study of all-vanadium redox-flow batteries (EPRI - 1014836).^[12] Kamath was instrumental in the study reported here as well as the design of the problem statement for the students, discussion and explanation of system details, and review of the

final presentations and reports. Several students stayed for continued discussion with Kamath and other EPRI personnel after the final presentation; all students approved the transmission of their final report to EPRI. One of the authors of this paper and an expert on electrochemical technology, Thomas Zawodzinski, gave lectures on electrochemistry and electrical storage batteries in CBE 480. The roles of EPRI, Kamath, and Zawodzinski added authenticity to the project.

The students had a unique opportunity to do process design work on an electrochemical process; they were also exposed to experts in the field. They were surprised at the scale of existing and planned electro-chemical storage facilities and the relationship between mass and energy balances that is facilitated by the flow of electrical energy. The students also learned that the economics of electrochemical processes may be analyzed similarly to chemical processes. In general, the students appeared to receive the project very well as indicated with an overall student evaluation of CBE 488 as 4.6/5.0. If used again, the future studies may focus on different battery chemistries. The study may also be shortened for use in a Mass and Energy Balance class or a Green Engineering class.

CONCLUSIONS

Working through the six levels of this design procedure allowed the students to modify the chemical engineering design procedures that are the standard for a chemical engineering education. Applying these traditional procedures to a nontraditional system gave valuable experience needed to a field that is no longer restricted to the petroleum or chemical industries. In addition to the experience of applying chemical design principles to a different type of system, the students also received insight into the electric utility industry.

The potential profit at Level 2 and above is shown in Figure 3 for the original study conditions. The figure shows the annual profits (the y-axis) at each level for an increasing number of charge/discharge cycles per year (the x-axis). The students concluded that capital costs were such that it would be difficult to construct and operate a VRB at a profit and because of this, there is no need to look into the details of the operating costs until the capital costs can be lowered. The two largest contributions to the capital costs found by the students were the cost of the permeable membrane and the cost of the vanadium electrolyte. Any future developments will need to decrease these costs to make the investment in a VRB more attractive. The potential profit from a VRB was also found to be strongly affected by the cost of peak power electricity. Since the students assumed a ten-fold difference between the cost of base-load power to feed the battery and peak load power produced by the battery, further reductions in the cost of base-load power would have limited effects. The cost analysis presented here does appear to be sufficient evidence that further process improvements may indeed make the VRB a commercially viable technology.

NOMENCLATURE

Term	Description	Units
A	Surface area of heat exchanger	m ²
A _C	Electrode area	m ²
AC _{BP}	Annualized cost of balance of plant costs	\$/yr
AC _{HEX}	Annualized cost of heat exchangers	\$/yr
AC _p	Annualized cost of pumps	\$/yr
AC _{PCS}	Annualized cost of power conditioning system	\$/yr
AC _S	Annualized cost of stacks	\$/yr
AC _T	Annualized cost of storage tanks	\$/yr
AC _V	Annualized cost of vanadium	\$/yr
C _{cost}	Capital cost of a component	\$
C _p	Heat capacity of vanadium ion solution	J/(°C 1)
C _{V2}	Concentration of V (II) ions	mol/l
C _{V3+}	Concentration of V (III) ions	mol/l
C _{V4+}	Concentration of V (IV) ions	mol/l
C _{V5+}	Concentration of V (V) ions	mol/l
ε _i	Intrinsic efficiency of pump	
ξ _C	Charging efficiency	
ξ _D	Discharging efficiency	
E _C	Energy used to charge the battery	kW-hr
E _D	Energy discharged from the battery	kW-hr
E _{SC}	Energy capacity of the battery	kW-hr
EP ₂	Economic potential for Level 2	\$/yr
EP ₃	Economic potential for Level 3	\$/yr
EP ₄	Economic potential for Level 4	\$/yr
EP ₅	Economic potential for Level 5	\$/yr
f _D	Depreciation factor	
f _{RI}	Return on investment factor	
F	Faraday's constant	C/mol
F _A	Actual flow rate of vanadium ion solution	l/s
F _M	Minimum flow rate of vanadium ion solution	l/s
I _D	Current density of electrodes	amp/m ²
I _S	Current through a stack	amp
M _L	Concentration of V (II) at lower charging limit of 0.20	mol/l
M _T	Total concentration of vanadium	mol/l
M _U	Concentration of V (V) at upper charging limit of 0.80	mol/l

M_V	Total amount of vanadium needed for battery	mol
N_C	Number of cells in a stack	
N_S	Number of stacks in the battery	
η_{oA}	Overall efficiency of battery	
Δp	Pressure drop	Pa
P	Power capacity of battery	W
q	Heat	W
SOC	State of charge of battery	
τ_C	Time to charge or discharge battery	hr
ΔT	Temperature change of vanadium through stack	$^{\circ}\text{C}$
ΔT_{LM}	Log mean temperature difference	
U	Heat transfer coefficient	$\text{W}/(\text{m}^2 \text{ } ^{\circ}\text{C})$
μ	Viscosity of vanadium solution	$\text{Pa}\cdot\text{s}$
V_S	Potential of a stack	V
V_T	Volume of tank	l
$X_{V,P}$	Fraction of vanadium ions converted per pass	

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