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On the Determination of Coulombic Efficiency for Vanadium Redox Flow Batteries: Cutoff Voltage vs. State of Charge Limits

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One of the criteria for quantifying the performance of a vanadium redox flow battery (VRFB) is the coulombic efficiency (CE). Coulombic efficiency quantifies the efficiency of electron transfer within an electrochemical system. It is typically computed using the following formula [1]:

$$CE = \frac{\int_0^t I_d dt}{\int_0^t I_c dt}$$

where I_d is the discharging current and $I_c$is the charging current which are constant in most operations. In order to determine the charging and discharging times, it is a matter of convention to repeatedly charge and discharge a VRFB to pre-determined voltage limits and record the charging and discharging times for each cycle [1-2]. A major shortcoming of this technique is that it does not account for the capacity fade that plagues VRFBs during cyclic operation. Despite being designed to permit the passage of protons, the membranes used in these systems permit the unwanted transport of vanadium ions (crossover). The crossover of active species facilitates side reactions which in turn, diminish the system's capacity and operating voltage [3-4].

The consequence of not accounting for the decline in the capacity of the system can be illustrated with the following example: Let's assume that the VRFB is charged to 1.7 Volts (90% state of charge (SOC)). During the next cycle, 1.7 Volts will not correspond to a SOC of 90% but instead, an SOC less than 90%. This problem is compounded as the number of cycles keeps increasing and leads to an inconsistent basis for comparison.

To this end, the goal of this study is to utilize state of charge (SOC) limits to compute the coulombic efficiency and compare this with the conventional approach calculated based on the cut-off voltages. Unlike voltage limits, we claim that using SOC limits would provide for a more consistent basis for determining the coulombic efficiency. As a part of the study, the operation of a VRFB with a convection dominated membrane is simulated under symmetric and asymmetric current operation (i.e., different currents during charge and discharge). The simulations are performed using an in-house model developed as part of an earlier, comprehensive study [3]. The acquired data is used in conjunction with data on the system's SOC to correct for a decline in the system's SOC and compute the resulting coulombic efficiency.

Figures 1 and 2 compare the coulombic efficiencies obtained using voltage limits and SOC limits for two asymmetric current conditions. As shown by these figures, there is an obvious discrepancy between the values obtained by the two techniques and a reversal in the overall trend. This observed difference is indicative of the fact that one of the two techniques might yield results that are inconsistent with the physics that govern the operation of VRFBs. As a result, further investigation is necessary to verify the accuracy of these two techniques to define a more accurate approach for calculating the CE for these systems. Details of this investigation will be presented in this talk.

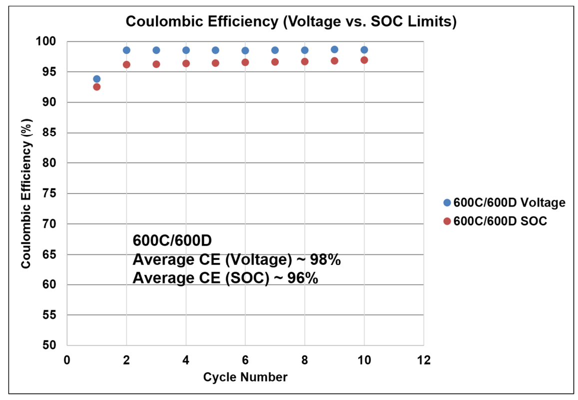

Figure 1. Coulombic efficiency over 10 cycles when operated at 600C/600D (charging at 600 A m^{-2} and discharging at 600 A m^{-2}) for the convection-dominated membrane.

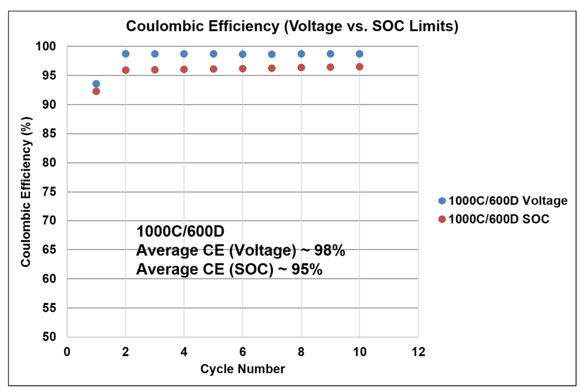

Figure 2. Coulombic efficiency over 10 cycles when operated at 1000C/600D (charging at 1000 A m^{-2} and discharging at 600 A m^{-2}) for the convection-dominated membrane.

References:

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