LIFETIME OF VANADIUM REDOX FLOW BATTERIES

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ABSTRACT

Flow batteries in general and the vanadium redox flow battery in particular exhibit potentially long lifetimes. This is mostly because that most of the energy is stored outside the electrochemical cells and the all vanadium-containing electrolytes do not decay from cross-contamination. However, shift in vanadium valency due to membrane leakage, membrane aging, increase in internal resistance, and parasitic side reactions will influence the battery capacity and require service action to rebalance the electrolyte. But unlike in conventional secondary batteries, the full capacity can be restored repeatedly. Service lifetime depends very much on the application, and thus it is advised to rather use the term “application service life” since the same battery will achieve different service lifetimes in different applications. This presentation will deal with lifetime considerations from the technical, application, practical, and economic point of view.

Keywords: vanadium redox flow battery, battery lifetime, application service life, decentralized energy storage for wind and solar energy, off-grid and grid-connected energy storage systems

INTRODUCTION

In conventional secondary battery systems, performance data include C-rate, cycle life, and calendar life with strong dependency on state of charge (SOC) and temperature [1]. In flow batteries, C-rate has no significance since most of the electrolyte is stored outside the electrochemical cells. Therefore, there is a need to reconsider definitions that are very suited for secondary batteries but might not be useful for flow batteries. In general, lifetime is determined by technical performance and limitations due to battery chemistry, as well as structural features due to battery layout and design. This paper deals with service life considerations from the technical, application, practical, and economic point of view.

EXPERIMENTAL

Service life predictions are difficult to derive since accelerated lifetime test procedures often divert from conditions under real applications. On the other hand, it is very cost- and time-consuming to perform service life tests under real conditions. From the customer’s point of view, end of service life is defined when the battery does not meet the application requirement in terms of power and capacity. In reality, batteries are somewhat oversized and applications may change over the years of use as well. The vanadium flow battery is best suited to accommodate for such changes.

For service life considerations, we have organized the battery in five major components: (1) the electrochemical cells and connectors, (2) the electrolytes contained in tanks, (3) pipes, pumps, and sensors, (4) power electronics, and (5) battery housing, including facility management such as air conditioning. In principle, each component can be replaced during maintenance, and economics will determine how long this may be sensible. In addition, there are technical limitations related to the battery chemistry that will have an impact on the lifetime of the electrochemical cells and the accessible capacity of the battery. While the electrochemical cells are subject to fail due to increase in internal resistance, the electrolyte capacity fade is due to an unbalanced vanadium concentration and shift in valency. Both failures can be corrected in situ by intermixing the electroytes and rebalancing. This is a fully reversible process and underlines the unique features of the vanadium flow battery.

In order to better understand the technical limitations of vanadium flow batteries, let us consider the open circuit voltage open current voltage (OCV) of the battery as a function of SOC at a given temperature (Figure 1).

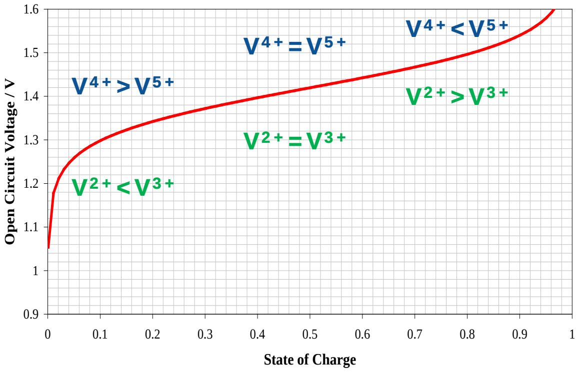

Fig. 1. OCV versus SOC at 298 K of a 1.6 M volt sulfate system in 2 M sulfuric acid.

The OCV relationship from Figure 1 was obtained experimentally using the so-called OCV cell of the commercial battery. The OCV was measured under flowing conditions and the incremented charge was registered and converted into an SOC value in percent. The OCV values were corrected for temperature.

The OCV versus SOC relationship shows an s-shaped characteristic, thus revealing for every voltage difference a distinct value for the SOC. This is very valuable since information on SOC can be provided online. According to the electrode reactions during charging and discharging, four valencies of vanadium are present.

At the positive electrode:

$$VO_2^+ + 2H^+ + e^- = VO^{2+} + H_2O$$

At the negative electrode:

$$V^{2+} = V^{3+} + e^-$$

Overall reaction:

$$VO_2^+ + 2H^+ + V^{2+} = VO^{2+} + H_2O + V^{3+}$$

In the negative electrolyte, V^{2+} and V^{3+} are present, while in the positive electrolyte V^{4+} and V^{5+} are present. During charging and discharging within one electrolyte the concentrations of vanadium in different valencies will vary; i.e., V^{2+} becomes dominant after the inflection point at 50% SOC, and in the negative electrolyte V^{5+} becomes dominant after the infection point. However, the concentrations of V^{2+} and V^{5+}, and V^{3+} and V^{4+} respectively, must be equal in order to obtain full capacity. In practical vanadium flow batteries the electrolytes become unbalanced during service life. The degree of unbalance depends strongly on the application. A shift to more V^{5+} is observed. Besides V^{5+} in solution, vanadium pentoxide (V_2O_5) can also precipitate in the positive tank and plumbing system. However, the amount is typically very small and negligible in terms of capacity loss. Despite that minor effect, (V_2O_5) can cause clogging of the electrochemical cells and cell failure. The reason for precipitation is increased temperature at high SOC. It is mostly the high SOC that limits the life of cells. Besides the V_2O_5 precipitation, oxidation of the graphite felt electrodes and bipolar sheet current collectors can occur and consume the carbon. Cell failure due to high internal resistance is the consequence. It would be best to avoid high oxidation states in the battery, i.e., when V^{5+} concentration exceeds 80%. The charging regime can be limited to that value of the expense of capacity. However, in unbalanced electrolytes, this value is difficult to handle.

Although a shift in valency will cause intermediate capacity loss, the vanadium is not lost and the full capacity can be recovered through rebalancing. The rebalancing process is done at the customer's site and is another major advantage of the vanadium flow battery.

Service life of the electrochemical cells is limited by the internal resistance, which tends to increase over time and is also strongly dependent on the application. However, the cells can be replaced easily during maintenance and the power can be fully restored at a moderate cost. The electrolyte volume disposed with the electrochemical cells is marginal in cost and will be replaced with the new cells.

RESULTS AND DISCUSSION

Service life cannot be separated from cost. As described in the introduction, in principle all components of the battery could be replaced many times. But in many cases this would not be economically sensible. The critical number will thus be the total cost of storage in relation to the delivered energy – which of course is strongly application-dependent. Expected lifetimes for the components, pumps, and pipes and sensors can operate from 1 to 5 years. Electrolytes and tanks are expected to be used economically up to 20 years, as well as major parts of the battery housing. Power electronics will be subject to replacement by newer instruments with higher-efficiency models after 5 years, but could also be used up to 10 years.

The issue of internal resistance and electrolyte running out of balance are closely interrelated, where the membrane plays an important role with respect to unbalance and aging in the first place. Membranes with high selectivity are advantageous over membranes with higher conductivity and reduced selectivity. Once the electrolyte runs out of balance, the cells will suffer from high oxidation corrosion, increased self-discharge, and cell resistance. Therefore, the lifetime of cells is still the big question mark. Since cell failure can have many reasons, more field experience is needed to make better predictions. An open question on long-term performance is also the influence of minor impurities in the electrolytes.

Online data acquisition and analysis are important requisites to learn more about performance under real conditions from the past and help extrapolate into the near future. One interesting number for forecasting service life is the sum of times during which the battery was in a high SOC. How high the SOC can be tolerated remains to be seen. On the other hand, limiting the SOC may solve the problem, especially with highly selective membranes. The disadvantage is the higher cost due to lesser utilization of the electrolytes. However, the electrolytes can be rebalanced in situ and recovered from one system and used in the next.

CONCLUSIONS

Service life of vanadium flow batteries is strongly dependent on the application. The electrochemical cell is the most critical component. Although the electrolytes do run out of balance during service, they can be rebalanced during maintenance. All other components can be replaced under cost considerations. Service life can be extended as long as sensible.

The cost of energy generation and storage in units/kilowatt hours delivered will differ from application to application. It contains all costs from investment through maintenance and is a useful number for comparison with other resources such as grid or fossil fuels.

REFERENCES

[1] D. Linden, “Secondary batteries service life,” *Handbook of Batteries Second Edition*, 1994, pp. 23.19-23.20.

BIOGRAPHICAL NOTE

Conference presenter: Martha Schreiber is co-founder and managing director of Cellstrom. She has over 25 years of experience in battery research and development, all dedicated to the design and implementation of electrochemical storage systems into mobile and stationary applications. She gained expertise in fundamental research at Stanford University and industrial experience at the Daimler Benz Company. Ms. Schreiber received a Diplom in Chemistry and a Ph.D. from the Technical University of Vienna, Austria, and a PhD from the Technical University, Delft, Netherlands.