Communication—Observation of Arrhenius Behavior of Catholyte Stability in Vanadium Flow Batteries

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The stability of typical vanadium flow battery (VFB) catholytes with respect to precipitation of V_2O_5 was investigated at temperatures in the range 30–60 °C. In all cases a precipitate formed after an induction time, which decreased with increasing temperature and concentration of V^{V} and increased with concentration of sulfate. Arrhenius-type plots are shown for two typical solutions. These have excellent linearity and have similar slopes which yield an apparent activation energy of 1.79 eV (172 kJ mol^{-1}). The variation of induction time with temperature for various concentrations of V^{V} was simulated, and stability diagrams for additive-free VFB catholytes were generated.

Vanadium flow batteries (VFBs), also known as vanadium redox flow batteries (VRFBs), are currently the subject of much interest and recent research because they are attractive for a variety of large scale energy storage applications. An important advantage of a vanadium battery is that its energy storage capacity and its power capability can be scaled independently. VFBs have the additional advantage that cross-contamination due to transport through the membrane is effectively eliminated because the anolyte and catholyte differ only in the oxidation state of the vanadium. Also, since aqueous vanadium species are highly colored, the state-of-charge may be precisely monitored using ultraviolet-visible spectrophotometry.

The energy density of VFBs is limited by the solubility of V^{IV}, V^{III}, V^{V} and V^{V} in the electrolyte. In the anolyte, the solubility of V^{2+} and V^{3+} generally increases with temperature and decreases with increasing concentration of H_2SO_4 and this is also true for the solubility of the V^{IV} species, VO_2^{+}, in the catholyte. The predominant V^{V} species present in strongly acidic solutions such as typical VFB catholytes is the pervanadyl ion VO_2^{+}. The solubility of vanadium (V) oxide, V_2O_5, in this region of pH is ~0.1 mol dm^{-3} or less. Thus, at the concentrations typically encountered in VFB catholytes, V^{V} is expected to be thermodynamically unstable in solution with respect to precipitation as V_2O_5. However, precipitation is usually found to be very slow and, in practice, supersaturated solutions of V^{V} in sulfuric acid can persist for very long periods of time. The stability of these metastable solutions (VFB catholytes) decreases, as expected, as the concentration of V^{V} increases. This is reflected in a lowering of stability at a particular vanadium concentration as the state-of-charge (i.e. the fraction of vanadium present as V^{V}) of the catholyte increases.

Stability improves with increasing concentration of sulfate and in the presence of certain additives such as H_2PO_4.

Thus, there have been several studies of the stability of V^{V} in the catholyte of VFBs, and several mechanisms of precipitation have been proposed. However, there is an absence in the literature of detailed kinetic studies of the precipitation process and the variation with temperature has never been quantitatively analyzed. In this paper we report a quantitative study of the kinetics and demonstrate an Arrhenius-type dependence on temperature.

Experimental

Solutions of V^{IV} were prepared from VOSO_4 and H_2SO_4 (vanadyl (IV) sulfate hydrate 97% and sulfuric acid 98% obtained from Sigma Aldrich). Stock solutions of V^{V} (2.2 mol dm^{-3}) were prepared by electrochemical oxidation of the V^{IV} solution in a flow cell at room temperature (~20 °C) using carbon felt electrodes and a Nafion membrane. End-points were determined by monitoring the positive electrode potential (using 1.3 V vs Ag/AgCl at 10 mA cm^{-2} as end point) and verified by color changes in the electrolyte. These solutions were stored at ~4 °C and used to prepare series of other concentrations of V^{V} by dilution with known concentrations of H_2SO_4. Because samples were relatively small (~10 cm^3), volumes were measured by weighing and converting to volume by accurately measured densities.

Vanadium concentrations were determined volumetrically against standard 0.1 N KMnO_4 (Fisher Scientific) and H_2SO_4 concentrations were determined against standard 0.1 N KOH (Sigma-Aldrich). Water was distilled and deionized to a resistivity of >18 MΩ cm.

In a typical experiment, a 0.8-cm^3 sample of V^{IV} solution was placed in a small glass vial which was then immersed in a thermostatic water bath at a selected temperature; the solution temperature was within 0.1 K of the bath temperature in ~60 s. The water-bath reservoir was made of transparent glass and was fitted with a lamp, as shown schematically in Fig. 1, so that the solution in the vial was very clearly visible and the first signs of precipitation could be observed.

Results and Discussion

Solutions with V^{V} concentrations of 1.4–2.2 mol dm^{-3} and sulfate concentrations of 3.7–5.3 mol dm^{-3} were investigated at temperatures in the range 30–60 °C. In all cases a precipitate formed after some time, which was identified as V_2O_5 by X-ray diffraction. The time to precipitation, which we call the induction time, decreased with increasing temperature for a given solution; at any given temperature it decreased with increasing concentration of V^{V} and increased with increasing concentration of sulfate. This indicates that more concentrated V^{V} solutions are less stable with respect to precipitation, and that stability improves with increasing sulfate concentration, as previously reported.

Series of experiments were carried out in which the induction time τ for precipitation was measured as described above for a range of temperatures. Typical results are shown in Table 1 for two different electrolyte solutions. In Fig. 2, the logarithm of induction time is plotted against the inverse of temperature for each solution. It can be seen that, in each case, excellent linearity is obtained over the
temperature range investigated (30–60 °C). The slopes of the least-squares best-fit lines are very similar, with values of $2.074 \times 10^4$ K and $2.072 \times 10^4$ K for the 1.66 mol dm$^{-3}$ and 2.2 mol dm$^{-3}$ V$^V$ solutions, respectively. The corresponding intercepts have values of −53.889 and −55.417 respectively. The lower (more negative) value of the intercept for the higher concentration of V$^V$ reflects the shorter induction time at any given temperature, apparent from Fig. 2.

The plots in Fig. 3 are equivalent to Arrhenius plots and may be represented by the equation

$$\ln \tau = \ln A + m \frac{T}{J}$$  \hspace{1cm} [1]$$

where $\ln A$ and $m$ are the intercept and slope, respectively. The good linearity of the plots suggests that the process occurring during the induction period is kinetically controlled and that its activation energy is constant over this temperature range. From the average slope, $m = 2.073 \times 10^4$ K, of the graphs the apparent activation energy ($E^* = mk$ where $k$ is Boltzmann’s constant) is estimated to be 1.79 eV (172 kJ mol$^{-1}$).

**Table I. Induction time $\tau$ for precipitation for two electrolyte solutions over a range of temperatures. The $V^V$ concentrations were 1.66 mol dm$^{-3}$ and 2.2 mol dm$^{-3}$, respectively, and the total sulfate concentration was 4.4 mol dm$^{-3}$ in each case.**

<table>
<thead>
<tr>
<th>Temperature (°C)</th>
<th>2.2 mol dm$^{-3}$</th>
<th>1.66 mol dm$^{-3}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>30.0</td>
<td>430320</td>
<td></td>
</tr>
<tr>
<td>32.5</td>
<td>317880</td>
<td></td>
</tr>
<tr>
<td>35.0</td>
<td>108000</td>
<td></td>
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<tr>
<td>37.5</td>
<td>80040</td>
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<tr>
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<td>38580</td>
<td>204000</td>
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<td></td>
</tr>
<tr>
<td>60.0</td>
<td>5040</td>
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</tr>
</tbody>
</table>

From Equation 1 we generated a plot of induction time versus temperature for each of the two solutions represented in Fig. 2 using the respective values of $\ln A$ and $m$ (given above) from the best-fit lines. These plots are shown as solid lines in Fig. 3 for the temperature range 30–50 °C. By interpolation and extrapolation we generated similar plots at other concentrations of V$^V$. These are also shown in Fig. 3 as broken lines. Diagrams such as this can be used to quantify the stability of V$^V$ solutions of various compositions, as a function of temperature, using the induction time as a measure of stability: the longer the induction time, the more stable the solution. In practical VFBs, additives such as H$_3$PO$_4$ are used to stabilize the catholyte. Models of additive-free solutions, which generate stability diagrams...
such as that represented in Fig. 3, are useful as baselines against which to compare the effect of additives.

During the review process of this communication, we were made aware of another quantitative analysis of VV precipitation\(^\text{22}\) which addresses the kinetics of the precipitation itself rather than the induction process.

**Summary**

Typical VFB catholytes precipitate V\(_2\)O\(_5\) after an induction time, which decreases with increasing temperature and concentration of VV and increases with concentration of sulfate. Arrhenius-type plots for two typical solutions showed excellent linearity and had similar slopes. This suggests that the process occurring during the induction period is kinetically controlled with an apparent activation energy estimated as 1.79 eV (172 kJ mol\(^{-1}\)) from the Arrhenius slope. From the Arrhenius parameters, we can simulate the variation of induction time with temperature for various concentrations of VV. Plots generated in this way can serve as stability diagrams for VFB catholytes.

**References**


