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 flow 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 very slow and, in practice, supersaturated solutions of vanadium(VII) in sulfuric acid can persist for very long periods of time. The stability of these catholytes is the pervanadyl ion $\text{VO}_2^+$, in the catholyte. The predominant $\text{V}^\text{V}$ species present in strongly acidic solutions such as typical VFB electrolytes is the pervanadyl ion $\text{VO}_2^+$. The solubility of vanadium (V) oxide, $\text{V}_2\text{O}_5$, in this region of $p\text{H}$ is around 0.1 mol dm$^{-3}$ or less. Thus, at the concentrations typically encountered in VFB catholytes, $\text{V}^\text{V}$ is expected to be thermodynamically unstable in solution with respect to precipitation as $\text{V}_2\text{O}_5$. However, precipitation is usually found to be very slow and, in practice, supersaturated solutions of $\text{V}^\text{V}$ 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 $\text{V}^\text{V}$ 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 $\text{V}^\text{V}$) of the catholyte increases. Stability improves with increasing concentration of sulfate and in the presence of certain additives such as $\text{H}_2\text{PO}_4$. Thus, there have been several studies of the stability of $\text{V}^\text{V}$ 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 $\text{V}^\text{IV}$ were prepared from $\text{VOSO}_4$ and $\text{H}_2\text{SO}_4$ (vanadyl (IV) sulfate hydrate 97% and sulfuric acid 98% obtained from Sigma Aldrich). Stock solutions of $\text{V}^\text{V}$ (2.2 mol dm$^{-3}$) were prepared by electrochemical oxidation of the $\text{V}^\text{IV}$ 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 $\text{V}^\text{V}$ by dilution with known concentrations of $\text{H}_2\text{SO}_4$. Because samples were relatively small (∼10 cm$^3$), volumes were measured by weighing and converting to volume by accurately measured densities.

Results and Discussion

Solutions with $\text{V}^\text{V}$ 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 $\text{V}_2\text{O}_5$ by X-ray diffraction. The time to precipitation, which we call the induction time, decreased with increasing concentration of $\text{V}^\text{V}$ and increased with increasing temperature for a given solution; at any given temperature it decreased with increasing concentration of $\text{V}^\text{V}$ and increased with increasing concentration of sulfate. This indicates that more concentrated $\text{V}^\text{V}$ 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 $\tau$ for precipitation was measured as described above for a range of temperatures. Typical results are shown in Table I 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 30–60°C. In all cases a precipitate formed after some time, which was identified as $\text{V}_2\text{O}_5$ by X-ray diffraction. The time to precipitation, which we call the induction time, decreased with increasing concentration of $\text{V}^\text{V}$ and increased with increasing temperature for a given solution; at any given temperature it decreased with increasing concentration of $\text{V}^\text{V}$ and increased with increasing concentration of sulfate. This indicates that more concentrated $\text{V}^\text{V}$ 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 $\tau$ for precipitation was measured as described above for a range of temperatures. Typical results are shown in Table I 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 30–60°C.
Test solution
Glass vial
Thermometer
Thermostatic water bath
Lamp

Figure 1. Schematic illustration of apparatus used for precisely measuring the induction time for precipitation of VFB catholyte samples at constant temperature.

temperature range investigated (30–60°C). The slopes of the least-squares best-fit lines are very similar, with values of 2.074 × 10^4 K and 2.072 × 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 plots²⁰,²¹ and may be represented by the equation

\[ \ln \tau = \ln A + \frac{m}{T} \]  

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 (\( E^a = mk \) where \( k \) is Boltzmann’s constant) is estimated to be 1.79 eV (172 kJ mol⁻¹).

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 H₃PO₄ are used to stabilize the catholyte. Models of additive-free solutions, which generate stability diagrams

| Temperature (°C) | 2.2 mol dm⁻³ | 1.66 mol dm⁻³ |
|-----------------|--------------|--------------|
| 30.0            | 430320       |              |
| 32.5            | 317880       |              |
| 35.0            | 108000       |              |
| 37.5            | 80040        |              |
| 40.0            | 38580        | 204000       |
| 42.5            | 31140        | 178200       |
| 45.0            | 14700        | 86880        |
| 47.0            | 9720         | 40440        |
| 50.0            | 7860         | 30000        |
| 55.0            | 9060         |              |
| 60.0            | 5040         |              |

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.

Figure 2. Logarithm of induction time plotted against the inverse of temperature for electrolyte solutions with V^V concentrations of (a) 1.66 mol dm⁻³ and (b) 2.2 mol dm⁻³. In each case, the total sulfate concentration was 4.4 mol dm⁻³.

Figure 3. Plots of induction time versus temperature for seven different concentrations of V^V (as indicated) at a total sulfate concentration of 4.4 mol dm⁻³ in each case. The solid lines were generated from Equation 1 using values of \( \ln A \) and \( m \) from the best-fit lines in Fig. 2. The broken lines were generated by interpolation and extrapolation, assuming a linear variation of \( \ln \tau \) with inverse of temperature (K⁻¹).
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 V\textsuperscript{V} precipitation\textsuperscript{22} which addresses the kinetics of the precipitation itself rather than the induction process.

**Summary**

Typical VFB catholytes precipitate V\textsubscript{2}O\textsubscript{5} after an induction time, which decreases with increasing temperature and concentration of V\textsuperscript{V} 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\textsuperscript{-1}) from the Arrhenius slope. From the Arrhenius parameters, we can simulate the variation of induction time with temperature for various concentrations of V\textsuperscript{V}. Plots generated in this way can serve as stability diagrams for VFB catholytes.

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