Journal of Applied Electrochemistry **34**: 681–685, 2004.

Kinetics of the chemical dissolution of vanadium pentoxide in acidic bromide solutions

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Received 23 July 2003; accepted in revised form 12 February 2004

Key words: dissolution kinetics, redox flow cells, vanadium bromide redox cell, vanadium pentoxide dissolution

Abstract

A novel vanadium bromide redox flow battery employing a vanadium bromide electrolyte in both half-cells has been proposed. Preparation of the electrolyte for this redox cell requires the chemical dissolution of vanadium pentoxide powder in the acidic bromide supporting electrolyte. In this study, the kinetics of the chemical dissolution process were investigated and a second order surface controlled reaction is reported with rate equation given by: Rate $= 5 \times 10^{-4}$ (l mol^{-1} s^{-1}) [Br$^-$]^2 at 25 °C and an activation energy of 37.2 kJ mol^{-1}.

1. Introduction

The redox flow cell is an electrochemical system that allows energy to be stored in two solutions containing different redox couples with electrochemical potentials sufficiently separated from each other to provide an electromotive force to drive the oxidation–reduction reactions needed to charge and discharge the cell. Unlike conventional batteries, the redox flow cell stores energy in the solutions, so that the capacity of the system is determined by the size of the electrolyte tanks, while the system power is determined by the size of the cell stacks.

While the redox flow cell concept has been around for close to 30 years with several systems evaluated by various groups around the world, only the Vanadium Redox battery pioneered at UNSW [1–11] and the Regenesys systems developed by National Power in the UK [12–14] have reached commercial fruition. More recently, however, a novel redox flow cell that employs a vanadium bromide solution in both half-cells was proposed [15]. This system uses the V^{2+}/V^{3+} and Br^-/Br_3^- couples in the negative and positive half-cell electrolytes respectively, the electrolyte being produced by the chemical dissolution of vanadium pentoxide powder in acidic bromide solution.

In this paper, results from a kinetic study of the chemical dissolution process are described and the rate equation, rate constant and activation energy of the V_2O_5 dissolution process are reported.

2. Experimental

The kinetics of V_2O_5 chemical dissolution process in bromide solution were studied by measuring changes in vanadium ion concentration as a function of time under a range of conditions. A motor rotator and speed controller system were used to provide a constant stirring speed for the reactants in the reaction vessel. A glass propeller was connected to the motor rotator and this was immersed in the flask containing the reactants. The reaction vessel was submerged in a water bath that was maintained at a constant temperature by a temperature controller.

A fixed quantity of V_2O_5 powder (supplied by Kashima–Kita Electric Power Corporation, Japan) was added to the bromide solution and samples were taken every minute for the first 10 min, followed by 5 min sampling, until all of the V_2O_5 powder had dissolved The solution samples were taken by syringes which were fitted with micro filters to remove any undissolved oxide powder and stored in close sample tubes.

Using a Malvern particle analysis instrument, the specific surface area and average particle size of the V_2O_5 powder used in this study, were determined as 1.33 m^2 g^{-1} and 10.44 μm respectively.

Atomic absorption spectroscopy (Varian AA 20 Plus) with an acetylene/nitrous oxide flame was used to analyse the vanadium concentration as a function of time. Vanadium standards comprising 40, 80, 120, 160, and 200 ppm V were prepared using a 1000 ppm vanadium standard stock solution (Merck) and were used to prepare a calibration curve for the vanadium analysis.

3. Results and discussion

When V_2O_5 powder is added to a bromide containing solution, a redox reaction between the oxide powder and the bromide ions is expected to occur, this leading to the reduction of the V_2O_5 to the soluble V(IV) form, with the bromide ions undergoing oxidation to bromine. The chemical dissolution process can thus be described by the following reactions:

$$2Br^-_{(aq)} \Leftrightarrow Br_{2(g)} + 2e^-$$

$$V_2O_{5(s)} + 6H^+_{(aq)} + 2e^- \Leftrightarrow 2VO^{2+}_{(aq)} + 3H_2O_{(l)}$$

with the overall process given by:

$$V_2O_{5(s)} + 2Br^-_{(aq)} + 6H^+_{(aq)} \Leftrightarrow 2VO^{2+}_{(aq)} + 3H_2O_{(l)} + Br_{2(g)} \tag{1}$$

The initial rate equation for this reaction can be written as:

$$-r_{\mathrm{initial}} = kA[Br^-]_0^a\,[H^+]_0^b \tag{2}$$

where r_{initial} is the initial rate, k is the reaction rate constant, A is the total surface area of the V_2O_5 powder, $[Br^-]_0$ and $[H^+]_0$ are the initial bromide and hydrogen ion concentrations respectively and a and b are the reaction orders for the bromide and hydrogen ions. In the initial stages of the reaction, the surface area of the vanadium pentoxide is assumed to remain constant, therefore the initial rate equation becomes:

$$-r_{\mathrm{initial}} = k'[Br^-]_0^a\,[H^+]_0^b \tag{3}$$

where: k' = pseudo rate constant of the reaction.

3.1. *Reaction order with Respect to Br⁻*

In the determination of the reaction order with respect to Br^-, the concentration of H^+ was kept constant while varying the concentration of Br^-. The initial rate equation given by Equation 2 thus reduces to the form:

$$-r_{\mathrm{initial}} = k''[Br^-]_0^a \tag{4}$$

Using initial rate data for a number of different initial $[Br^-]$ concentrations, a plot of:

$$\log[r_{\mathrm{initial}}] \text{ vs } \log[Br^-]_0$$

should give a straight line of slope a, which is the reaction order with respect to Br^-.

A series of dissolution experiments was conducted using three solutions with initial Br^- concentration of 4.5, 5 and 5.5 M, each containing 3 M H^+. Each experiment was performed at 25 °C with a stirring speed of 400 rpm. The data obtained are presented in Figure 1 and show that the V_2O_5 dissolution rate increases with increased concentration of Br^-.

From the dissolution reaction given in Equation 1, the stoichiometric ratio between $[Br^-]$ and $[V_T]$ is one to one; therefore the concentration of Br^- at any time t can be calculated from:

$$[Br^-]_{t=t} = [Br^-]_0 - [V_T] \tag{5}$$

where $[V_T]$ is the total vanadium ion concentration in solution. Plots of the concentration of Br^- vs time for initial Br^- concentrations of 5.5, 5.0 and 4.5 M are presented in Figure 2. The initial rate of the reaction was calculated from the slope of the tangents at $t = 0$ for the different initial Br^- concentrations and the plot of log (initial rate) vs log $[Br^-]_0$ is shown in Figure 3.

From the slope of the straight line shown in Figure 3, the order of reaction with respect to Br^- was found to be 2.

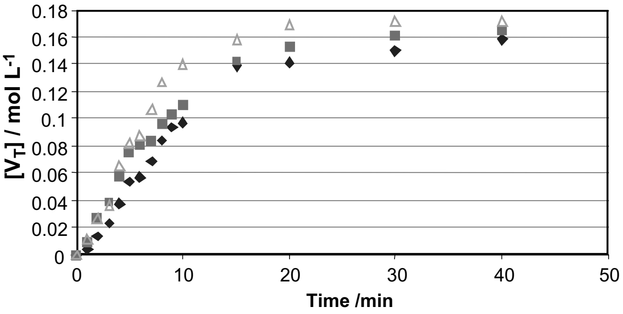

Fig. 1. Total vanadium concentration vs time in chemical dissolution of 15 g V_2O_5 in 3 M HBr and ◆ 1.5, ■ 2.0, △ 2.5 M NaBr with 400 rpm stirring speed at 25 °C.

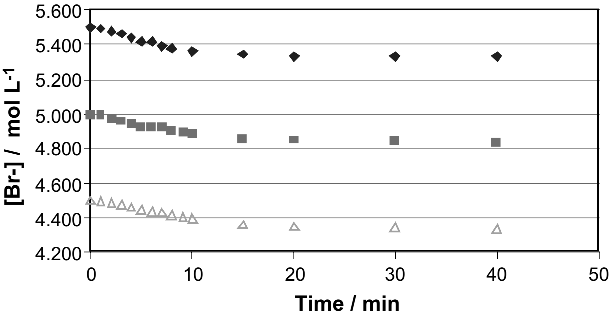

Fig. 2. $[Br^-]$ vs time in the chemical dissolution of 15 g V_2O_5 in 1 L of 3 M HBr containing △ 1.5, ■ 2.0, ◆ 2.5 M NaBr with 400 rpm stirring speed at 25 °C.

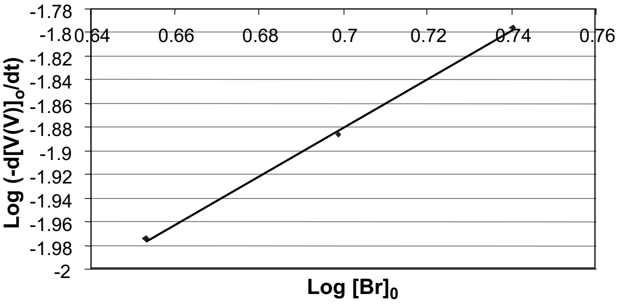

Fig. 3. Log (initial rate) vs log $[Br^-]_0$ in chemical dissolution of 15 g V_2O_5 in 1 l of 3 M HBr containing 1.5, 2.0 and 2.5 M NaBr with 400 rpm stirring speed at 25 °C.

3.2. *Reaction order with respect to H^+*

If the same initial Br^- concentration is used in the chemical dissolution with different initial H^+ concentration, at time 0, we can consider the concentration of Br^- to be constant. Therefore, the initial rate equation give by Equation 3 reduces to:

$$-r_{\text{initial}} = k''[H^+]_0^b \tag{6}$$

Thus, a plot of log (r_{initial}) vs log $[H^+]_0$ should give a straight line with a slope b being the reaction order with respect to H^+.

Four solutions with different initial $[H^+]$ were used in the determination of b. The four solutions were:

- 2.0 M NaBr + 2.5 M HBr,
- 1.5 M NaBr + 3.0 M HBr,
- 1.0 M NaBr + 3.5 M HBr, and
- 0.5 M NaBr + 4.0 M HBr.

The concentration of Br^- was thus kept constant at 4.5 M.

The same amount of V_2O_5 was added to each of the solution at 25 °C with a stirring speed of 400 rpm. The chemical dissolution data for each $[H^+]_0$ are presented in Figure 4. The result show that the higher the initial concentration of H^+, the higher the rate of the chemical dissolution of the vanadium pentoxide. From the dissolution Equation 1, the stoichiometric ratio between the H^+ and vanadium product is three to one. The concentration of H^+ at time t can therefore be calculated from:

$$[H^+]_{t=t} = [H^+]_0 - 3[V_T] \tag{7}$$

Plots of $[H^+]_{t=t}$ vs time for different initial H^+ concentrations of 4.0, 3.5, 3.0 and 2.5 M are given in Figure 5. The initial rate of the reaction was calculated for each of the different initial H^+ concentrations and the plot of log (initial rate) vs log $[H^+]_0$ is shown in Figure 6. The slope of the straight line in Figure 6 was found to have a value of 0.08, so the order of the reaction with respect to H^+ is 0.

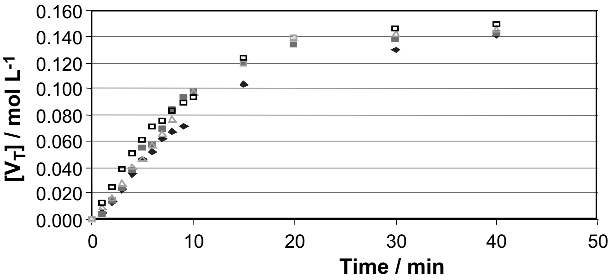

Fig. 4. Total vanadium concentration vs time in chemical dissolution of 15 g V_2O_5 in 1 l solution of $[Br^-]_0$ = 4.5 M and ◆ 2.5, ■ 3.0, △ 3.5 and 4.0 M $[H^+]_0$ with 400 rpm stirring speed at 25 °C.

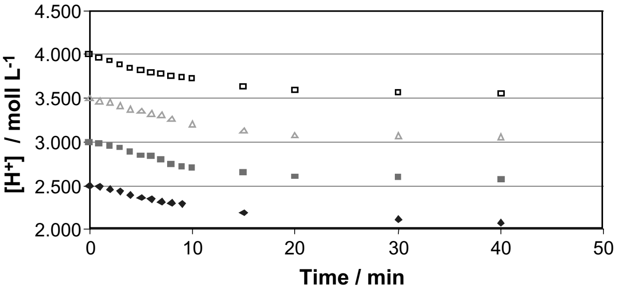

Fig. 5. $[H^+]$ vs time in the chemical dissolution of 15 g V_2O_5 in 1 l solution of $[Br^-]_0$ = 4.5 M and ◆ 2.5, ■ 3.0, △ 3.5 and □ 4.0 M $[H^+]_0$ with 400 rpm stirring speed at 25 °C.

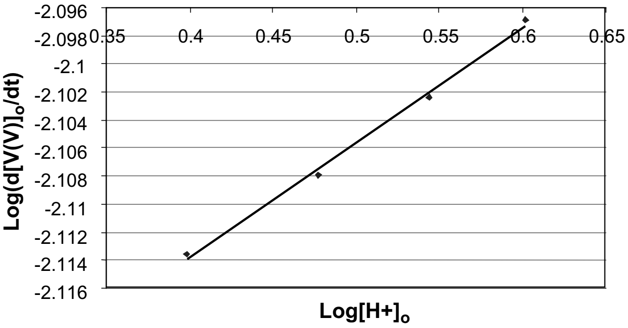

Fig. 6. Log (initial rates) vs log $[H^+]_0$ for chemical dissolution of 15 g V_2O_5 in 1 l solution of $[Br^-]_0$ = 4.5 M and 2.5, 3.0, 3.5 and 4.0 M of $[H^+]_0$ with 400 rpm stirring speed at 25 °C.

3.3. *Rate equation for dissolution of V_2O_5 in Br^- solution*

The reaction orders with respect to Br^- and H^+, as determined above are 2 and 0 respectively. The rate equation for the dissolution of vanadium pentoxide in bromine system can therefore be written as:

$$\text{Rate} = k[Br^-]^2 \tag{8}$$

where Rate is the dissolution rate at time t, k is the rate constant and $[Br^-]$ is the bromide concentration at time t. The integrated rate equation for the second order reaction can therefore be expressed by:

$$-\frac{1}{[Br^-]} = k \cdot t \tag{9}$$

a plot of $-1/[Br^-]$ vs time should thus give a straight line with slope k.

A typical plot of $-1/[Br^-]$ vs t is given in Figure 7. While a linear region is observed in the initial part of the plot, the remaining reaction does not fit the second order rate equation. This can be explained by the fact that the model assumes that the surface area of the vanadium pentoxide particles remains constant during the course of the reaction and this is not the case. Taking the slope obtained from the initial part of the plot corresponding to the first 10 min of the reaction, however, it is possible to assume that the surface area is constant. The value of k was thus obtained from the slope of the initial region for different initial concentrations of Br^- and the values are presented in Table 1.

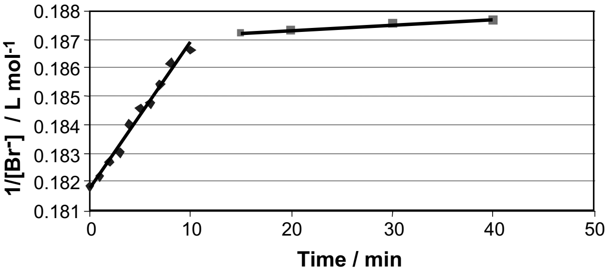

Fig. 7. Plot of $1/[Br^-]$ vs time for $[Br^-]_0$ = 5.5 M

The results in Table 1 show a k value of 0.0005 $l\,mol^{-1}\,s^{-1}$ for each of the initial concentrations of Br^-, confirming the validity of the second order reaction assumption. The overall rate equation for the chemical dissolution of vanadium pentoxide in Br^- solution can therefore be written as:

$$\mathrm{Rate} = 5 \times 10^{-4}(\mathrm{l\,mol^{-1}\,s^{-1}})[\mathrm{Br^-}]^2 \qquad (10)$$

3.4. *Effect of stirring speed on the chemical dissolution of V_2O_5 in Br^- solution*

The dissolution of the V_2O_5 in Br^- solution was investigated at different agitation intensities to observe the effect of stirring speed on the dissolution rate. The bromine solution used comprised of 3 M HBr + 2 M of NaBr and 15 g of $V_2O_{5(s)}$ was added to 1 l of the solution. The experiments were performed at 25 °C using stirring speeds of 250, 400, and 550 rpm. The total vanadium concentration, $[V_T]$ vs time plots for different stirring speeds are presented in Figure 8. The results show that the rate of the vanadium pentoxide dissolution reaction is the same at 400 and 550 rpm stirring speeds, so the reaction kinetics should be unaffected by stirring speed under the experimental conditions used above.

3.5. *Temperature dependence of chemical dissolution of V_2O_5 in Br^- solution*

In these experiments 15 g of $V_2O_{5(s)}$ was added to 1 l of a solution of 3 M HBr + 2 M of NaBr. The reaction vessel was placed in a water bath set at 25, 40 and 60 °C and the dissolution experiments were conducted using a stirring speed of 400 rpm. Plots of total vanadium concentrations vs time at different temperatures are presented in Figure 9.

Table 1. Values of k (rate constant) obtained from initial slope of $1/[Br^-]$ vs time plots for different $[Br^-]_0$ in 0–10 min time range at 25 °C.

$[Br^-]_0$/mol l^{-1}	k/l $mol^{-1}\,s^{-1}$
4.5	0.0005
5.0	0.0005
5.5	0.0005

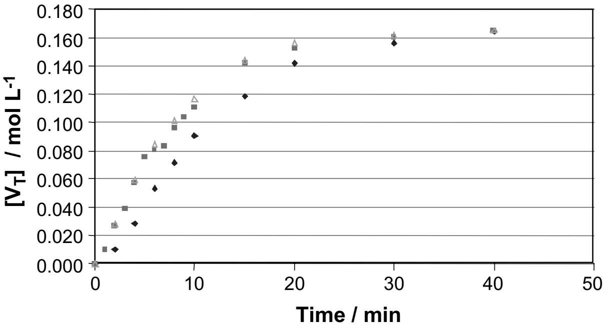

Fig. 8. Total vanadium concentration vs time plots for dissolution of 15 g V_2O_5 in 3 M HBr plus 2 M NaBr solution at different stirring speeds: ◆ 250, ■ 400 and △ 550 rpm.

Using the same method as described above, the values of the second order rate constant k were determined from the initial portion of each curve at the different temperatures and the values are presented in Table 2. Using the Arrhenius equation given by:

$$\ln k = \ln A - \frac{E_a}{RT} \qquad (11)$$

where: A = pre-exponential factor, E_a = activation energy. The value of the activation energy can be obtained from a plot of ln k vs 1/T. This plot gave a straight line with a slope of $-\frac{E_a}{R} = -4468.6$ K. The activation energy (E_a) for the dissolution reaction was thus calculated as 37.2 kJ mol^{-1}. The chemical dissolution of vanadium pentoxide in Br^- solution is thus

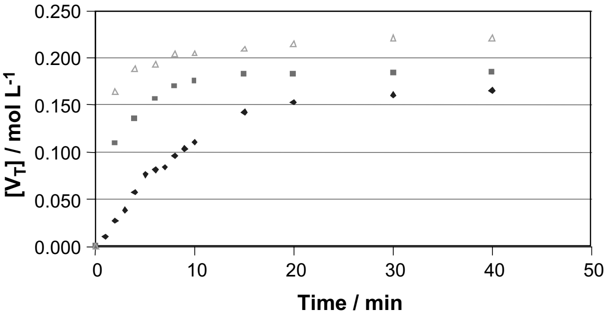

Fig. 9. Total vanadium concentration vs time plots for dissolution of 15 g V_2O_5 in 3 M HBr plus 2 M NaBr solution at different temperatures: ◆ 25, ■ 40 and △ 60 °C.

Table 2. Values of k obtained at different temperatures for 0–10 min of reaction.

Temp/K	$(1/T)/K^{-1}$	k/min^{-1}	k/s^{-1}	ln k
298	0.00336	5.00E–04	8.33E–06	−11.6952
313	0.00319	9.00E–04	1.50E–05	−11.1075
333	0.00300	2.40E–03	4.00E–05	−10.1266

confirmed as a second order surface reaction controlled process.

4. Conclusions

This study provides kinetic data for a new process for producing vanadium bromide electrolyte for the novel vanadium bromide redox flow cell, based on the chemical dissolution of vanadium pentoxide powder in acidic bromide solutions. The dissolution reaction involves the chemical reduction of the pentavalent vanadium compound by the bromide ions to produce a tetravalent vanadyl bromide solution.

The chemical dissolution of vanadium pentoxide in acidic bromide solution was found to follow a second order surface reaction controlled mechanism described at 25 °C by the rate equation:

$$\text{Rate} = 5 \times 10^{-4} (\text{l}\,\text{mol}^{-1}\,\text{s}^{-1}) [\text{Br}^-]^2$$

The activation energy of the reaction was calculated as 37.2 kJ mol^{-1}, the magnitude of which confirms that the reaction is not diffusion controlled at stirring speeds of 400 rpm or above.

Preliminary studies have shown that vanadium bromide solutions up to 4 M can be prepared and 3 M vanadium bromide solutions have already been evaluated in redox cell charge-discharge cycling tests with promising results. The vanadium bromide redox cell thus has the potential for almost twice the energy density of the original vanadium redox cell employing vanadium sulphate electrolytes, making it feasible for electric vehicle applications.

Acknowledgements

The authors are grateful to Mr Asem Mousa and Ms Katia Nasev for technical assistance in this project.

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