Chemically regenerative redox fuel cells
II. Regeneration reaction studies

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The kinetics of the reduction of TiO^{2+} with H_2 has been studied using a platinum catalyst in hydrochloric acid medium. The kinetic results were used to design the performance of a chemically regenerative redox fuel cell with the Ti^{3+}/TiO^{2+} redox couple as anode system. Also the results from another chemically regenerative redox fuel cell with the $Fe(EDTA)^{2-}/Fe(EDTA)^{-}$ redox couple as anode system are presented. In both redox cells the VO_2^+/VO^{2+} redox couple was used as cathode system.

1. Introduction

The principles of the chemically regenerative fuel cell have been described by Kummer and Oei [1, 2]. We have recently shown [3] that inexpensive membranes can be used successfully in the redox fuel cell. The chemical regeneration is an essential point in the redox fuel cell. In order to select the proper redox systems for use in the chemically regenerative redox fuel cell it is necessary to obtain data for the regeneration rates of promising redox couples. This involves measurement of the oxidation rate with oxygen of the reduced redox couple used at the cathode and the reduction rate with hydrogen of the oxidized redox system used at the anode. Suitable cathodic couples are those whose redox potentials are near that of oxygen, and suitable anodic couples are those whose redox potentials are near that of the fuel (e.g. hydrogen). In addition the exchange currents for both couples should be high.

In the present work we have used the VO_2^+/VO^{2+} couple as cathode system. The regeneration of this cathode system has earlier been found to work well with oxygen using a NO_3^-/NO catalyst [2]. We have therefore adopted the same catalyst for regeneration of the VO_2^+/VO^{2+} system in our experiments. As anode systems we have investigated further in detail the Ti^{3+}/TiO^{2+} and the $Fe(EDTA)^{2-}/Fe(EDTA)^{-}$ redox couples. The normal potential of the Ti^{3+}/TiO^{2+} system in acid solution is $= 0.1$ V [4] which means that it should be possible to regenerate Ti^{3+} from TiO^{2+} with hydrogen. We have therefore studied the kinetics of the reduction of TiO^{2+} with hydrogen in order to elucidate the mechanism and determine the activation energy of the reaction.

2. Regeneration experiments

2.1. *Kinetics of the TiO^{2+} reduction with H_2*

The reaction vessel for studying the reduction of

TiO^{2+} was a 250 ml reaction flask containing $TiCl_4$ dissolved in 10% hydrochloric acid and connected with a reflux condenser. As catalyst we used 2% Pt on alumina (3 mm pellets) commercially obtained from Johnson Matthey Chemicals. An amount of 0.25 g catalyst, corresponding to 5 mg Pt, was used in every experiment. The solution was heated to the desired temperature and flushed with hydrogen under vigorous stirring. The reaction was followed spectrophotometrically by measuring the absorbance of formed Ti(III) at 500 nm. From a knowledge of the molar absorption coefficient of Ti(III) in hydrochloric acid ($\varepsilon = 9.6\,M^{-1}\,cm^{-1}$) it was possible to determine the concentration of Ti(III). Measurements were performed at 50, 60 and 70° C respectively. It was found that for every temperature the Ti(III) concentration increased linearly with time. A rate constant (k') for a zero-order reaction was determined for different initial titanium (IV) concentrations and at the different temperatures. Thus

$$d[Ti(III)]/dt = k' \qquad (1)$$

These rate constants were found to vary approximately linearly with the initial concentration of titanium (IV) (Fig. 1). This means that the reaction follows a first-order relation. Thus

$$-d[Ti(IV)]/dt = k''[Ti(IV)] = k' \qquad (2)$$

The rate constant (k'') could thus be determined at every temperature. It is reasonable to suppose that the rate constant (k'') is dependent on the hydrogen concentration in the solution. Thus

$$k'' = k[H_2] \qquad (3)$$

From literature data [5] on the solubility of hydrogen in water at atmospheric pressure we can obtain the H_2-concentration and thereafter the rate constant (k) from Equation 3. The results of the estimation of rate constants are presented in Table 1. The rate constants were then used to determine the activation energy of

Table 1. Rate constants for the reduction of TiO^{2+} with hydrogen

| Temperature °C	k'' min^{-1} g_{Pt}^{-1}	Solubility of H_2 in water [5] $\times 10^3$ M	k M^{-1} min^{-1} g_{Pt}^{-1}
50	0.270 ± 0.010	0.84	320 ± 15
60	0.288 ± 0.010	0.78	370 ± 15
70	0.278 ± 0.010	0.65	428 ± 15

the reaction according to the Arrhenius equation:

$$k = ae^{-E/RT} \qquad (4)$$

The ln k against $1/T$ plot is shown in Fig. 2. The obtained value of the activation energy was $13\,kJ\,mol^{-1}$. This low value indicates that the rate determining step for reduction of TiO^{2+} with hydrogen is the diffusion of hydrogen towards the catalyst surface. This means that with a suitable reactor a very fast regeneration reaction can be obtained and consequently the Ti^{3+}/TiO^{2+} redox couple can be used as anode system in the chemically regenerative fuel cell. It is also interesting to note that the reduction of TiO^{2+} with hydrogen proceeds with about the same rate at 50° C as at 70° C. This means that the redox cell can be operated at a relatively low temperature. The results of the chemically regenerative redox fuel cell experiments using the Ti^{3+}/TiO^{2+} couple as anode system are presented below.

2.2. Regeneration of the $Fe(EDTA)^{2-}/Fe(EDTA)^{-}$ redox couple

The $Fe(EDTA)^{2-}/Fe(EDTA)^{-}$ redox couple has a redox potential $E = 0.117\,V$ [6]. The regeneration reaction

$$2Fe(EDTA)^- + H_2 \rightleftharpoons 2Fe(EDTA)^{2-} + 2H^+ \qquad (5)$$
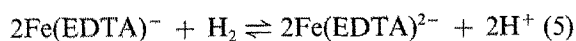
has been described by Schwarzenbach [6]. We have tested the reduction of $Fe(EDTA)^-$ with hydrogen using various catalysts in acetate buffer solutions at pH = 5.0. It has been found that the fastest reduction

Fig. 2. The Arrhenius plot for determination of the activation energy for the reduction of TiO^{2+} with hydrogen.

of $Fe(EDTA)^-$ with hydrogen was obtained with a Johnson Matthey palladium catalyst on alumina (3 mm pellets). A counter current flow reactor for the regeneration of the $Fe(EDTA)^{2-}/Fe(EDTA)^-$ system was used (Fig. 3). In this reactor the hydrogen gas was supplied beneath and the $Fe(EDTA)^-$-solution was supplied from the top of the reactor. This reactor was used for the regeneration reaction in the redox fuel cell and the results are presented below.

3. Chemically regenerative redox fuel cell results

3.1. Experimental details

The 'flow-by' redox fuel cell and the equipment for obtaining the discharge curves were described in our previous paper [3]. As electrodes we used Sigratherm graphite felt (GFA 10) of thickness 10 mm and with electrode area 12.6 cm^2. Solid graphite was used as current collector. Du Pont Nafion 390 cationic exchange membrane or a 'Submicro' membrane was used in the cell. As cathode system we used the VO_2^+/VO^{2+} redox couple in all experiments. The VO_2^+-
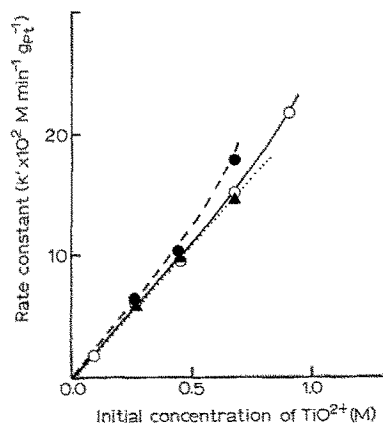
Fig. 1. Plot of the rate constants k' against the initial concentration of TiO^{2+} at the different temperatures: (▲) 50° C; (●) 60° C and (○) 70° C.
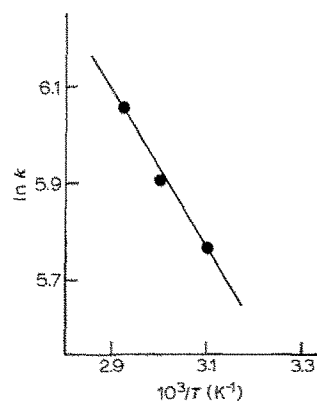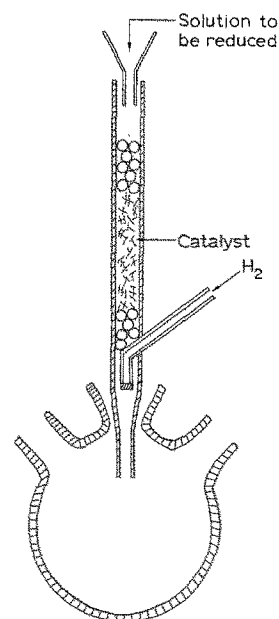
Fig. 3. Schematic picture of the counter current flow reactor used for regeneration of the $Fe(EDTA)^{2-}/Fe(EDTA)^-$ redox couple.

Fig. 4. Discharge curve of VO_2^+/VO^{2+} against Ti^{3+}/TiO^{2+} redox fuel cell (1 Ω external load). Cathode solution: saturated V_2O_5 solution in 1 M H_2SO_4 (0.2 M VO_2^+). Anode solution: 1 M $TiCl_3$ in 10% HCl.

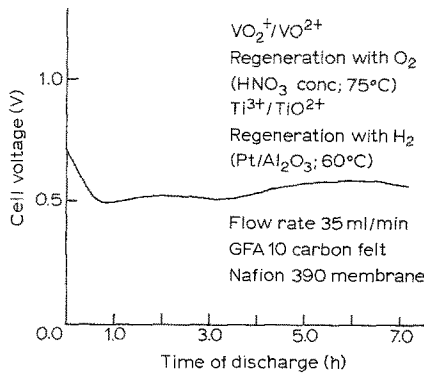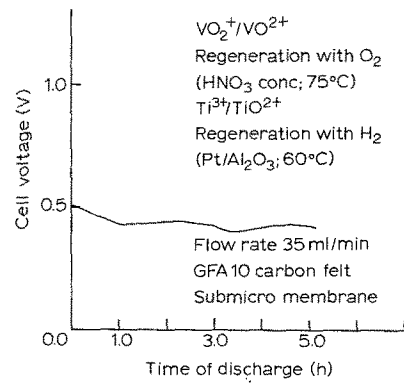

Fig. 5. Discharge curve of VO_2^+/VO^{2+} against Ti^{3+}/TiO^{2+} redox fuel cell (1 Ω external load). Cathode solution: saturated V_2O_5 solution in 1 M H_2SO_4 (0.2 M VO_2^+). Anode solution: 1 M $TiCl_3$ in 10% HCl.

solution was prepared by dissolving V_2O_5 in 1 M H_2SO_4. The concentration of VO_2^+ was approximately 0.2 M. To prevent NO loss when using the NO_3^-/NO catalyst, the cathode regenerator was exposed to pure oxygen without bubbling the gas through the solution. The Ti^{3+}-solution was obtained commercially as 1 M $TiCl_3$ in 10% hydrochloric acid and used without any dilution. The $Fe(EDTA)^{2-}$-solution was prepared by dissolving iron(II) chloride and an appropriate amount of Na_2EDTA in an acetate buffer of pH = 5.0. The concentration of the $Fe(EDTA)^{2-}$-complex was 0.075 M. The regeneration of the $Fe(EDTA)^{2-}$/$Fe(EDTA)^-$-system was done with the counter current flow reactor as described above.

3.2. The redox cell VO_2^+/VO^{2+} against Ti^{3+}/TiO^{2+}

The electrode and regeneration reactions for the cathode and the anode are:

$$\text{cathode:} \quad VO_2^+ + 2H^+ + e^- \rightleftharpoons VO^{2+} + H_2O \tag{6}$$

$$\text{regeneration:} \quad 4VO^{2+} + O_2 + 2H_2O$$

$$\xrightarrow{NO_3^-/NO} 4VO_2^+ + 4H^+ \tag{7}$$

$$\text{anode:} \quad Ti^{3+} + H_2O \rightleftharpoons TiO^{2+} + 2H^+ + e^- \tag{8}$$

$$\text{regeneration:} \quad 2TiO^{2+} + H_2 + 2H^+$$
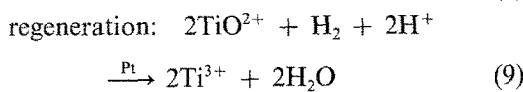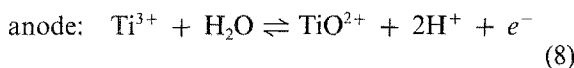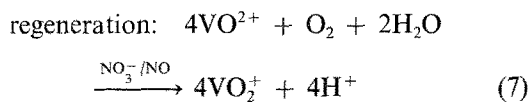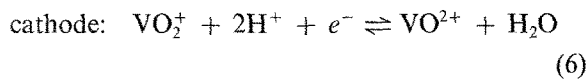
$$\xrightarrow{Pt} 2Ti^{3+} + 2H_2O \tag{9}$$

Figure 4 shows the performance of a H_2/O_2 redox fuel cell discharged over a 1 Ω external load for about 7 h. This cell could deliver 350 mA at about 550 mV, which means a power density of about 0.015 W cm^{-2}. In order to understand if the regeneration reactions work well one can estimate the potential for the anode and cathode solutions with the assumption that no regeneration reactions occur. From the polarization curve (Fig. 5, Ref. [3]) we obtain an open circuit voltage of 1.1 V. This gives the possibility of estimating the changes in concentrations from the Nernst equation and, furthermore, the potential of the cathode and the anode solutions at zero time (cf. Table 2). Figure 4 of the present paper indicates a cell voltage of 0.7 V at zero discharge time. Thus the cell voltage has decreased by 400 mV due to the current output (ohmic resistance, transport polarization and membrane potential).

A current output of 0.35 A corresponds to a decrease in concentration of 0.05 M during one hour for the cell volume used. From Fig. 4 it can be seen that there is a decrease in cell voltage of about 200 mV during the first hour of discharge. We can estimate the change in potential for the anode solution (1 M Ti^{3+}) during the same time as +33 mV. Similarly for the cathode solution (0.2 M VO_2^+) we find a decrease in potential of 70 mV. Thus a total decrease in cell voltage of about 100 mV should be expected. This value is somewhat lower than the value obtained from Fig. 4. Perhaps the drop of an extra 100 mV is caused by a current

Table 2. Changes in cell voltage estimated from the assumption that about 2% of red and ox forms are originally present in the VO_2^+/VO^{2+}- and Ti^{3+}/TiO^{2+}-solutions, respectively and that no regeneration takes place

Discharge time (h)	Current mA	[Ox]/[Red] Anode solution	[Ox]/[Red] Cathode solution	Potential (mV) Anode solution	Potential (mV) Cathode solution	Change in cell voltge (V) Calc.	Change in cell voltge (V) Obs.	Cell voltage (V) Calc.	Cell voltage (V) Obs.
0	0	0.02/0.98	0.195/0.005	0	1095	–	–	1.095	1.10
0	350	0.02/0.98	0.195/0.005	–	–	–	–0.40*	–	0.70
1	350	0.07/0.93	0.145/0.055	33	1025	–0.103	–0.20	0.99–0.40	0.50
2	350	0.12/0.88	0.095/0.105	48	997	–0.043	+0.02	0.95–0.40	0.52
3	350	0.17/0.83	0.045/0.155	59	968	–0.040	±0.00	0.91–0.40	0.52

* This drop in cell voltage is caused by ohmic resistance, other polarizations at the electrodes than concentration polarization and the membrane potential
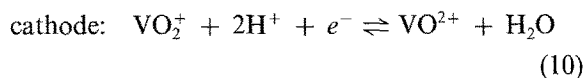
induced membrane potential. The concentration change for the next hour is estimated to be 0.05 M and we estimate an increase in potential for the anode solution of 15 mV and a decrease in potential for the cathode solution of 28 mV. Thus a decrease in cell voltage of 43 mV h^{-1} is expected if no regeneration reactions occur. From Fig. 4 and Table 2 it can be seen that a rather constant or indeed slightly increasing cell voltage is obtained which must mean that the regeneration reactions work well. The regeneration of the anode system can certainly be improved by a more suitable reactor.

It is of interest to compare our results with those of Kummer and Oei [2] on similar systems. They report a limiting power density of 0.062 W cm^{-2} for a chemically regenerative redox fuel cell using the VO_2^+/VO^{2+} and Mo^{3+}/Mo^{4+} redox systems. Our value of power density is somewhat smaller but still of the same order of magnitude.

The performance of the similar redox cell but with a silica filled polyethene membrane 'Submicro' instead of the Nafion 390 membrane discharged over a 1 Ω external load for about 5 h is shown in Fig. 5. This cell could deliver about 280 mA at about 450 mV, corresponding to a power density of 0.010 W cm^{-2}. Thus a reasonable power density can be sustained by using the Submicro membrane in this laboratory cell. The Submicro membrane has been described and tested in our previous paper [3].

3.3. The redox cell VO_2^+/VO^{2+} against $Fe(EDTA)^{2-}/Fe(EDTA)^-$

The electrode and regeneration reactions for the cathode and the anode are:

cathode: $VO_2^+ + 2H^+ + e^- \rightleftharpoons VO^{2+} + H_2O$

(10)

regeneration: as above Equation 7

anode: $Fe(EDTA)^{2-} \rightleftharpoons Fe(EDTA)^- + e^-$

(11)
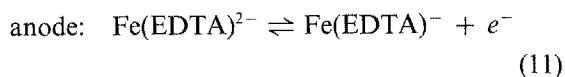
regeneration: as above Equation 5

Figure 6 shows the performance of a H_2/O_2 redox fuel cell discharged over a 1 Ω external load for about 5 h. This cell only delivered 150 mA at about 230 mV,
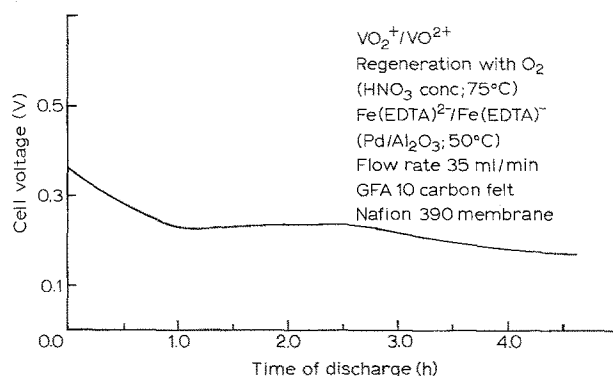

Fig. 6. Discharge curve of VO_2^+/VO^{2+} against $Fe(EDTA)^{2-}/Fe(EDTA)^-$ redox fuel cell (1 Ω external load). Cathode solution: saturated V_2O_5 solution in 1 M H_2SO_4 (0.2 M VO_2^+). Anode solution: 0.075 M $Na_2Fe(EDTA)$ in HAc/Ac$^-$ buffer solution of pH = 5.0.

which corresponds to a power density of 0.003 W cm^{-2}. The concentration of the $Fe(EDTA)^{2-}$-solution was only 0.075 M and the regeneration reaction was performed at a temperature of about 50° C. As above we can estimate the change in cell voltage that would have been observed if no regeneration reactions occur. From the polarization curve (Fig. 6, Ref. [3]) we obtain an open cell voltage of 1.07 V. We can then obtain the changes in concentration at time zero from the Nernst equation and also estimate the potential of the cathode and the anode solutions (cf. Table 3).

Figure 6 of the present paper indicates a cell voltage of 0.36 V at zero discharge time. Thus the cell voltage decreases by 710 mV because of the current output. The low concentration of the $Fe(EDTA)^{2-}$-solution probably gives a large transport polarization. Also pH changes at the membrane contribute to a larger decrease of cell voltage than in the Ti^{3+}/TiO^{2+} case.

A current output of 0.150 A corresponds to a decrease in concentration of 0.06 M during 1 h. If we consider the anode solution (0.075 M) this concentration change corresponds to an increase in potential of 135 mV from the value obtained at time zero. Similarly for the cathode solution (0.2 M) a concentration change of 0.06 M corresponds to a decrease in potential of 76 mV. Thus a total decrease in cell voltage of about 211 mV h^{-1} should be expected if no regeneration reactions occurred. It can be seen from Fig. 6 that the cell voltage decreases by about 130 mV during

Table 3. Changes in cell voltage estimated from the assumption that about 2% of red and ox forms are originally present in the VO_2^+/VO^{2+}- and $Fe(EDTA)^{2-}/Fe(EDTA)^-$-solutions, respectively and that no regeneration takes place

Discharge time (h)	Current mA	[Ox]/[Red]		Potential (mV)		Change in cell voltge (V)		Cell voltage (V)	
		Anode solution	Cathode solution	Anode solution	Cathode solution	Calc.	Obs.	Calc.	Obs.
0	0	0.002/0.073	0.195/0.005	23	1095	–	–	1.07	1.07
0	150	0.002/0.073	0.195/0.005	–	–	–	−0.71*	–	0.36
1	150	0.062/0.013	0.135/0.065	158	1019	−0.211	−0.13	0.86–0.71	0.23

* This drop in cell voltage is caused by ohmic resistance, other polarizations at the electrodes than concentration polarization and the membrane potential

the first hour of discharge and then becomes fairly constant. Thus we can conclude that the regeneration reactions work well.

It is possible that the regeneration rate may be increased at higher reactor temperatures. Also the flow rate through the reactor is of importance. Experiments have only been performed at one flow rate, *viz.* 35 ml min^{-1}. Thus by optimizing various parameters, this fuel cell could give higher power density.

4. Conclusion

The results have demonstrated the feasibility of operating a regenerative redox fuel cell using the above redox couples. The design of the cell and the conditions under which it operates (for example, temperature of catholyte and anolyte, regeneration reactor design and flow rate) have not been optimized for maximum cell performance and regeneration rates in these experimental cells. Improvements in cell performance, combined with possible improvements in the

oxidation and/or reduction catalysts and regeneration reactions in the regenerator system must be achieved.

Acknowledgements

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