

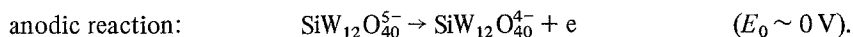
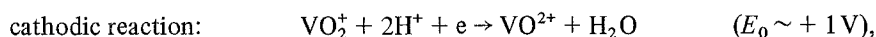
A chemically regenerative redox fuel cell

J. T. KUMMER, D-G. OEI

Engineering and Research Staff Research, Ford Motor Company, Dearborn, Michigan 48121, USA

Received 26 March 1981

A novel chemically regenerative redox fuel cell is described. The electrode reactions are based on the following redox reactions:



Regeneration of the oxidant by direct oxidation with O_2 was achieved by using the soluble heteropoly acid catalysts, $\text{H}_3\text{PMo}_{12}\text{O}_{40}$ or $\text{H}_5\text{PMo}_{10}\text{V}_2\text{O}_{40}$, whereas regeneration of the tungstosilicic acid, $\text{H}_3\text{SiW}_{12}\text{O}_{40}$, was accomplished by direct reduction with H_2 utilizing small amounts of Pt, Pd, Rh, Ru or the soluble Pd-4, 4', 4'', 4'''-tetrasulphophthalocyanine complex as catalysts. Some aspects of the regeneration kinetics and their influence on the overall performance of the redox fuel cell are discussed.

1. Chemically regenerative redox fuel cells

Although the chemically regenerative redox fuel cell was proposed a number of years ago [1], it has received little experimental attention. The direct fuel cell in which hydrogen and oxygen react at the fuel cell electrodes appears to be a more desirable approach because it eliminates regeneration reactions and because the large porous partially wetted electrode surface enables the gases, H_2 and O_2 , which have very low solubility in water, to react rapidly because of the short diffusion distances of the gases in the electrolyte and the very large electrolyte gas interface area. Since the latter problem will have to be solved by any fuel system, it would be desirable to have the solution of the problem built into the electrode itself.

However, the estimated high cost of such electrodes is \$300-1000 per m^2 in sizeable production, and the modest power levels that are expected for ambient pressure aqueous electrolyte fuel cell systems of approximately 2 kW m^{-2} have made it difficult for fuel cells designed for vehicle propulsion to compete economically with internal combustion engines (40 kW dm^{-3} displacement and \$5-10 per kW). Because chemically regenerative redox fuel cells have the possibility of using less expensive fuel cell electrodes and have more

degrees of freedom as a result of the separation of the regeneration system from the electrochemical reactions, we have carried out a series of experiments to see if a viable chemically regenerative redox fuel cell can be constructed.

Previous work from this laboratory [2] has shown that inexpensive electrodes can be used for the fuel cell section of the redox fuel cell. The work reported here was done to investigate the rates at which some selected redox systems can be regenerated by hydrogen and oxygen or air, and, to a limited extent, to investigate the performance of the regenerators and fuel cell together.

2. Laboratory studies of oxidation and reduction regeneration reactions

In order to select the proper redox systems for use in the chemically regenerative redox fuel cell it is necessary to obtain some data for the regeneration rates of promising redox couples. This involves the measurement of the oxidation rate with O_2 of the reduced redox couple used at the cathode, and the reduction rate with H_2 of the oxidized redox system used at the anode. Promising cathodic couples are those whose redox potentials are near that for oxygen, and promising anodic couples are those whose redox potentials are near that for hydrogen. In addition the exchange currents

for both couples should be high. Since complexing the ions in the redox couples can change the redox potential, the exchange currents and the regeneration rates, i.e. the number of promising redox couples, may be substantial. In general, there are little data in the literature showing the change of these three characteristics of a redox couple in the presence of complexing agents. In this work we have limited ourselves to the measurement of the regeneration rates of a few promising systems in acid solution using H_2 and O_2 as reductant and oxidant, respectively.

2.1. Experimental procedure

The reactor consisted of a 125 cm³ Erlenmeyer flask containing a Teflon stirring bar. This was positioned on a hot-plate under which was located a motor driven magnet. The reaction was run at room temperature or at elevated temperatures and the usual volume of liquid used was 25 cm³. One outlet from the rubber stopper in the top of the flask went to a water bubbler and the other to a source of O_2 , H_2 or Ar. The flask was flushed with the appropriate gas saturated with water vapour with the stirrer off, and the experiment started by turning the gas off and the stirrer on. The rate of reaction was followed by observing the rise of the water level in the glass tube in the water bubbler or by titration of the product produced in a given time. Ceric and ferrous ion solutions were used as reagents for titration and the system volume was calibrated by observing the rise in the water level in the water bubbler produced when a hypodermic syringe was inserted into the system rubber tubing and was used to suck out a known volume of gas. The redox voltage was measured by inserting a Pt and calomel electrode in the final product, and this electrode couple was also used to determine the titration end-points.

2.2. Materials

The PtO_2 , H_2PtCl_6 , H_2PtCl_4 and silicotungstic acid were purchased from commercial sources. The Ru for catalytic use was made by reducing an acid solution of $RuCl_3$ with Zn, filtering and washing the product. The PtS was made by treating H_2PtCl_4 with H_2S . The WC was made by treating $WO_3 + 10\% NH_4Br$ with CO at 900° C for 2 h. The

Pt-SiO₂ catalysts were made by mixing 9 cm³ of water containing an appropriate amount of H_2PtCl_6 with 2 g of fumed SiO₂ (Cab-o-sil, Cabot Corp.) and drying the resultant gel at room temperature overnight, followed by reduction at 200° C in H_2 .

The palladium 4, 4', 4'', 4'''-tetrasulphophthalocyanine (PdPc) was made by the method of Weber and Busch [3] with $PdCl_2$ as the inorganic salt and with $(NH_4)_2SO_4$ used in place of NH_4Cl . The analogous Pt^{2+} compound was made in a similar manner.

The molybdovanadophosphoric acid, $H_5PMo_{10}V_2O_{40}$, was made by mixing 454 g of MoO_3 , 58 g of V_2O_5 and 22 cm³ of concentrated phosphoric acid with 900 cm³ of water and heating with stirring at 80° C overnight. The small amount of unreacted solid was filtered off leaving a red solution of the molybdovanadophosphoric acid. A similar procedure was used, without the V_2O_5 , to make the yellow molybdophosphoric acid.

2.3. Oxidation of vanadyl ion

Post [4] has shown that the uncatalysed rate of oxidation of vanadyl ion, VO^{2+} , by oxygen is slow (1×10^{-4} mol dm⁻³ min⁻¹ at 80° C, 1 atm O_2 total pressure, pH = 1 and 1 M vanadyl) and is inversely proportional to the H^+ concentration. Kuznetsova and Matveev [5] have reported that Na_2MoO_4 is a catalyst for the oxidation of vanadyl ion by oxygen at pH = 3.4. Otake and Onoda [6] have shown that $H_5PMo_{10}V_2O_{40}$ can be used as a heterogeneous catalyst for the partial oxidation of aldehydes by air, and a Chemical Abstract reference [7] reports the use of $H_9PMo_6V_6O_{40}$ with Pd as a liquid phase catalyst for alkene oxidation by oxygen. Bett and Lynch [8] have reported the use of iron phthalocyanine as a heterogeneous catalyst for the oxidation of vanadyl ion by oxygen in strong acid solution. They report, however, conversions of only 0.3% in 300 min at 70° C, and that the rate is pH independent. In this paper we report data for the oxidation of vanadyl ion catalysed by heteropolymolybdates. The chemistry and electrochemistry of the heteropolymolybdic acids have been reviewed by Tsigdinos [9, 10].

We have confirmed the work of Kuznetsova and Matveev [5]. Molybdic acid is a catalyst for vanadyl oxidation by oxygen, but is ineffective

Table 1. Oxidation of vanadyl solutions using polyion catalysts*

VOSO ₄ solution molarity	Solution pH [†]		Gas used, 1 atm total pressure	Temperature (°C)	Time (min)	Catalyst composition	Concentration (g dm ⁻³)	V ⁴⁺ oxidized (%)	Voltage vs saturated calomel electrode [‡]
	Start	End							
1	1.3	1.0	O ₂	76	15	H ₃ PMO ₁₂ O ₄₀	24	11.8	0.64
0.5	1.4	1.3	O ₂	82	30	H ₃ PMO ₁₂ O ₄₀	4.5	14.0	0.61
0.5	2.0	1.3	O ₂	82	30	H ₃ PMO ₁₂ O ₄₀	4.5	26.7	0.60
1.0	1.0	0.9	O ₂	76	15	H ₅ PMO ₁₀ V ₂ O ₄₀	20	13.5	0.63
1.0	1.0	0.9	Air	76	30	H ₅ PMO ₁₀ V ₂ O ₄₀	24	7.0	0.58
1.0	0.7	0.6	O ₂	76	15	H ₅ PMO ₁₀ V ₂ O ₄₀	40	8.3	0.63
0.5	1.0	1.0	O ₂	82	30	No catalyst		0.1	0.54

* Solution (25 cm³) agitated with a Teflon-coated bar magnetic stirrer in a 125 cm³ flask.† Solution pH adjusted at start of experiment with H₃PO₄.

‡ Oxidized solution.

at $\text{pH} < 1.5$. Molybdophosphoric acid solutions are effective catalysts for vanadyl oxidation at $\text{pH} > 1$, and molybdovanadophosphoric acid ($\text{H}_5\text{PMo}_{10}\text{V}_2\text{O}_{40}$) is an effective catalyst for vanadyl oxidation at $\text{pH} > 0.5$, see Table 1. The rate falls off rapidly at a lower initial pH. The acidity of the vanadium containing polyacid is greater than that of molybdophosphoric acid, which is greater than that of molybdic acid. This may indicate that the ionized anion is the effective catalyst. At low initial pH it has been observed experimentally that, in the range of 5 to 15% conversions, the rate of reaction is very nearly independent of the percentage conversion. The catalysed rate is ~ 100 times faster than the uncatalysed rate at $\text{pH} = 1$. For the redox fuel cell where the cathodic solution is circulated through a flow-through electrode, the extremely high solubility of the polyacids is a desirable property of the catalyst.

2.4. Reduction of silicotungstic acid

The data of Pope and Varga [11] indicate that the redox potential of silicotungstic acid ($\text{H}_4\text{SiW}_{12}\text{O}_{40}$) is close to that of hydrogen so that this material can be considered as a promising redox couple for the anolyte solution. For this reason we have measured the rate of reduction of silicotungstic acid by hydrogen in acid solution ($\text{pH} = 0.5$ to 1).

At 25°C the uncatalysed reduction of silicotungstic acid solution is too slow to be measured in our apparatus. However, the reduction at 25°C can easily be catalysed by noble metal catalysts and slowly by tungsten carbide. See Table 2 and Figs 1 and 2. The reduced solution is oxidized by O_2 gas very rapidly as shown in Fig. 3 so that many reduction-oxidation cycles can be run on one sample. No change in reduction rate has been observed after use for one month. The soluble palladium catalyst, palladium 4, 4', 4'', 4'''-tetrasulphophthalocyanine, had low activity when first used as a reduction catalyst, but its activity rapidly increased with use at 25°C or after briefly heating the solution during a reduction run to 76°C . Filtering the solution (Whatman filter No. 42) did not reduce its activity. Experiments in which the soluble Pd-phthalocyanine compound alone was reduced with hydrogen showed that it is rapidly reduced to the extent of

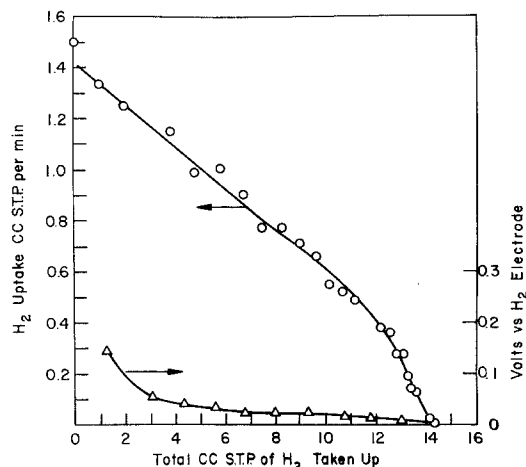


Fig. 1. Reduction of tungstosilicic acid with hydrogen.

one electron per molecule. Platinum (+ 2) 4, 4', 4'', 4'''-tetrasulphophthalocyanine was made and found to be inactive as a reduction catalyst. It is not known to what extent, if any, the reaction rates that were measured are affected by the degree of liquid phase mass transfer of H_2 that can be obtained in our Teflon bar stirred reactor. Because of the large size of a silicotungstic acid molecule it is thought that catalyst supports with very small pore sizes should be avoided.

At 76°C the degree of reduction of silicotungstic acid is only about one-third that observed at 25°C . This is due to the shift in equilibrium with increased temperature towards unreduced silicotungstic acid and hydrogen. Indeed hydrogen is evolved if a silicotungstic acid solution that had

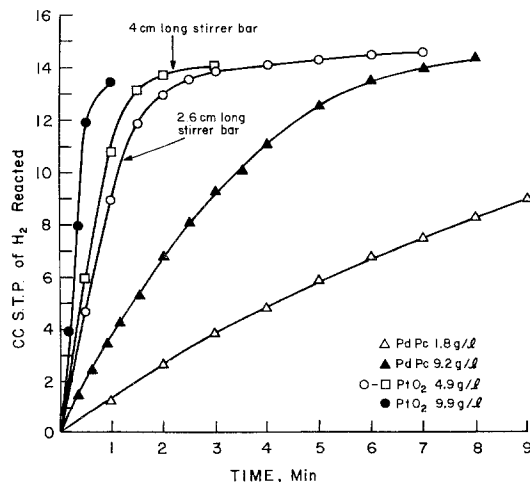


Fig. 2. Reduction of tungstosilicic acid with hydrogen using different catalysts.

Table 2. Reduction of silicotungstic acid*

$H_2SiW_{12}O_{40} \cdot 24H_2O$ concentration ($g\ dm^{-3}$)	H_3PO_4 concentration ($g\ dm^{-3}$)	Gas used, 1 atm total pressure	Temperature ($^{\circ}C$)	Time (min)	Catalyst composition	Concentration ($g\ dm^{-3}$)	Reduced (1-electron reduction) (%)	Voltage of reduced solution vs saturated calomel
152	57.42	H ₂	25	8	PtO ₂	0.8	82	-0.27
152	57.42	H ₂	76	8	PtO ₂	0.8	29	-0.25
152	57.42	H ₂	25	16	PtCl ₄	0.2	92	-
152	57.42	H ₂	25	20	Ru	2.9	92	-
152	57.42	H ₂	25	100	WC	18.4	13	-
152	57.42	H ₂	25	9	PtS ₂	1.0	86	-
152	57.42	H ₂	25	11	PdPc [†]	1.8	71	-
152	57.42	H ₂	25	1.5	PtO ₂	4.9	86	-
152	57.42	H ₂	25	0.8	PtO ₂	9.9	92	-
152	57.42	H ₂	25	2.9	1.1% Pt on SiO ₂	12.8	46	-
304	57.42	H ₂	25	5.2	1.1% Pt on SiO ₂	12.8	91	-
304	57.42	H ₂	25	4.0	1.1% Pt on SiO ₂	25.6	75	-

* Solution (25 cm³) agitated with a Teflon-coated bar magnet stirrer in a 125 cm³ flask.

† Palladium 4, 4', 4'', 4'''-tetrasulphophthalocyanine.

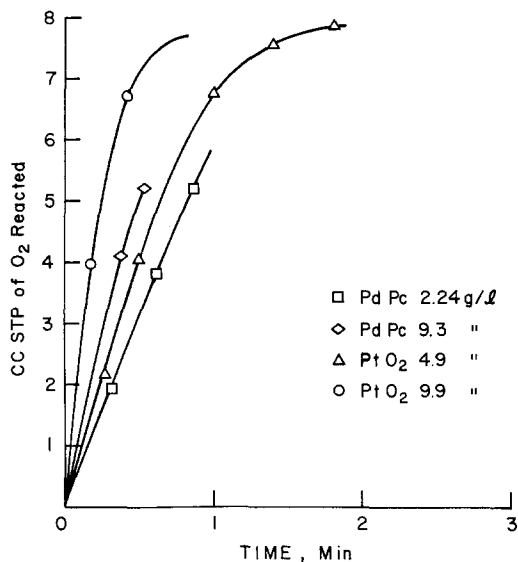


Fig. 3. Oxidation of reduced tungstosilicic acid.

been reduced at 25° C is heated to 76° C or if the partial pressure of hydrogen over the reduced silicotungstic acid solution at 25° C is lowered. Such a system can be used to transfer H₂ from one gas stream to another.

2.5. Reduction of other oxidized members of redox couples

Noble metal catalysts can also catalyse the reduction of a phosphotungstic acid solution (pH = 0.5) by hydrogen, but upon repeated oxidation and reduction this compound decomposes to tungstic acid.

Noble metals catalyse the reduction of a molybdophosphoric acid solution by hydrogen, but the redox voltage only becomes favourable for fuel cell use towards the end of reduction, see Fig. 4. It was also noted that this solution was highly viscous after reduction.

Noble metal catalysts readily catalyse the reduction by hydrogen in solution, of V⁴⁺ to V³⁺ and UO₂²⁺ to U⁴⁺. This latter reduction has been reported by Naqvi [12]. The redox voltages of these systems do not appear to be very suitable for fuel cell use because they differ too much (> 0.3 V) from that of the hydrogen electrode.

3. A chemically regenerative redox fuel cell

The oxidation and reduction reactions of redox

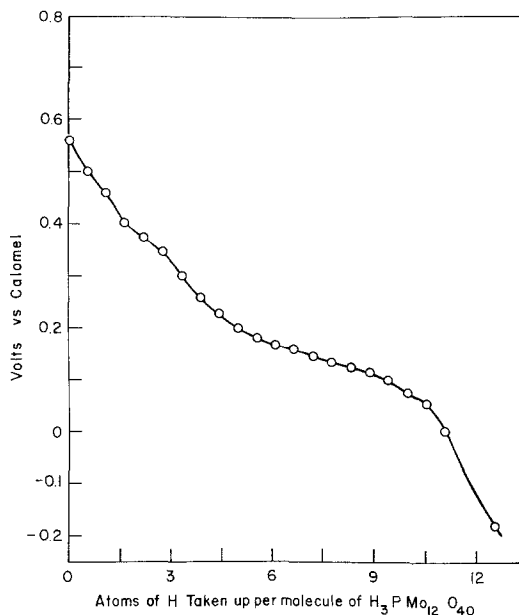
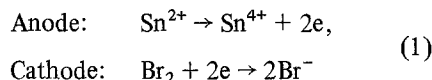


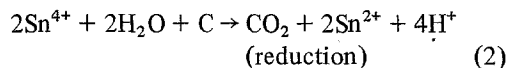
Fig. 4. Reduction of 12-molybdophosphoric acid, H₃PMo₁₂O₄₀, with hydrogen.

couples employed in redox fuel cells are in principle 'reversible reactions'. Electrochemical reversibility implies adequate exchange current densities from the redox electrode reactions, thus assuring adequate current flow at the electrodes. Chemical reversibility means that the reductant and oxidant can be regenerated chemically by oxidation and reduction with O₂ and H₂.

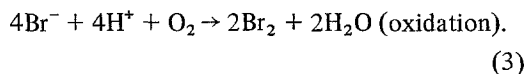
In the past, several redox couples were proposed as suitable materials for redox fuel cells and even though the redox couples satisfied the requirements of both chemical and electrochemical reversibility, none emerged successfully as a practical unit. The principal reason was the slow and inadequate rate of regeneration of the oxidant or reductant. Thus, Posner [1] operated the following redox fuel cell:



with the accompanying regenerating reaction:

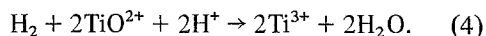


and

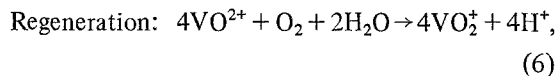
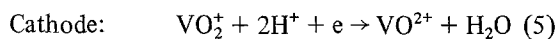


Although the rate of oxidation of bromide ion to

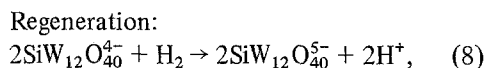
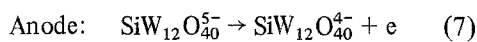
bromine by O_2 (catalysed by NO) was adequate to support the cathodic reaction, the reduction of Sn^{4+} to Sn^{2+} proceeded at a much slower rate and in order to obtain adequate rates of regeneration it was necessary to employ an autoclave at 160–180° C. Similarly Carson and Feldman [13], using the redox couples, $2Ti^{3+} + 2H_2O \rightarrow 2TiO^{2+} + 4H^+ + 2e$ (anode) and $Br_2 + 2e \rightarrow 2Br^-$, failed to obtain adequately fast rates of regeneration for the reaction:



The preceding laboratory work on the regeneration kinetics of several redox couples resulted in the identification of the following novel chemically regenerative redox cell.



using the soluble oxidation catalysts, $H_3PMo_{12}O_{40}$ or $H_5PMo_{10}V_2O_{40}$.



using a noble metal or $Pd-4, 4', 4'', 4'''$ -tetrasulphophthalocyanine as a reduction catalyst at room temperature. The experiments reported in this part pertain to the operation of such a chemically regenerative redox fuel cell.

4. Experimental

Sources and methods for obtaining the materials, redox couples, catalysts, and electrolytes were mentioned in Section 2.

The chemically regenerative redox fuel cell is illustrated in Fig. 5. A description of this redox cell was presented in a previous report [2]. The redox regenerator flask was made of a 1 dm³ wide-mouthed, wide-bottom Erlenmeyer flask. The regenerator flasks were placed on a magnetic stirrer/hot-plate. Approximately 250 cm³ of reactants and electrolyte were used during the experiments. The solutions in the flasks were vigorously stirred in order to promote gas-liquid contact. The regeneration of the oxidant, VO_2^+ , by direct oxidation with O_2 employing the soluble heteropolymolybdic acid catalysts, $H_3PMo_{12}O_{40}$ and $H_5PMo_{10}V_2O_{40}$, was carried out at 70° C with the appropriate solution pH. The regeneration of the reductance, $SiW_{12}O_{40}^{5-}$, by direct H_2 reduction with a heterogeneous noble metal catalyst or with the soluble catalyst $Pd-4, 4', 4'', 4'''$ -tetrasulphophthalocyanine, was carried out at room temperature.

A Soltec 1330 3-channel recorder was employed to record the overall cell voltage and the anodic and cathodic half-cell voltages (versus a saturated KCl calomel electrode) during each 4 min cell discharge through external resistors of 100, 50, 20, 10, 5, 2, 1, 0.5, 0.2 and 0.1 ohms. The current was displayed on a Keithley 179-20A

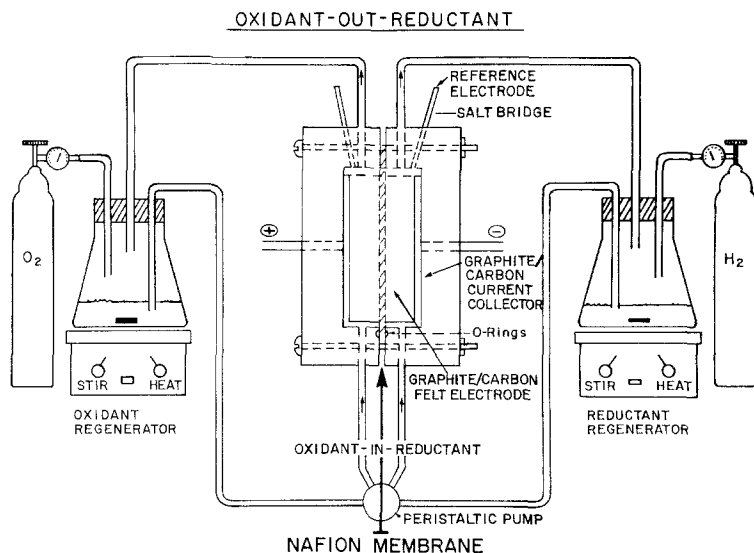


Fig. 5. Chemically regenerative redox fuel cell assembly.

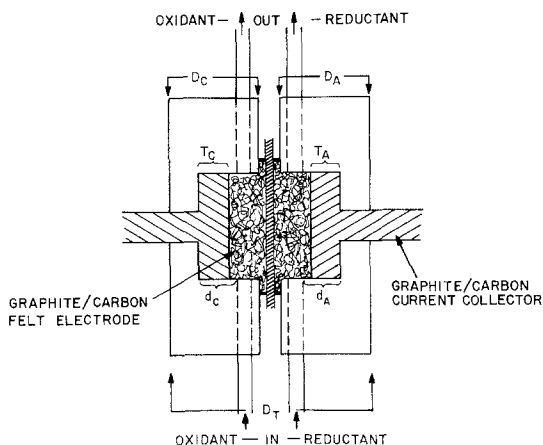


Fig. 6. Cross-section of redox fuel cell electrode compartments.

digital multi-meter. A glass electrode/calomel electrode combination attached to a Radiometer PHM-64 pH meter was used to determine the pH of the electrolyte solutions.

A cross-section of the redox fuel cell is shown in Fig. 6. Throughout the experiments, Type VDG graphite felt (Union Carbide) (0.375 in = 0.466 cm thick) and Nafion-415 membranes (DuPont) (5 mils = 0.013 cm) were used in the cell. The felt density was 0.064 g cm^{-3} and the fibre diameter was $\sim 0.0013 \text{ cm}$. The current collector and electrode were made from UF-4S graphite rods (Ultra Carbon Corp.), with geometrical surface areas of 9.6 and 9.1 cm^2 , respectively. The electrolytes were pumped through the anodic and cathodic compartments by means of a Masterflex peristaltic pump, entering the lower inlet hole of each compartment and emerging at the top outlet channel to be returned to the appropriate regenerating

reservoir. In the present configuration the graphite felt electrodes functioned as 'flow-by' electrodes. Teflon tubing and silicone rubber tubing were used to make connections.

5. Results and discussion

The regenerative cathodic and anodic redox couples, $\text{VO}_2^+/\text{VO}^{2+}$ and $\text{SiW}_{12}\text{O}_{40}^{5-}/\text{SiW}_{12}\text{O}_{40}^{4-}$, were tested separately with another appropriate counter redox couple in a redox fuel cell, and then combined into the proposed redox fuel cell. Results of these tests and the influence of various factors, such as pH and conduction, on the performance of the fuel cell are presented and discussed in the following paragraphs.

5.1. Regenerative $\text{VO}_2^+/\text{VO}^{2+}$ versus Cu/Cu^{2+} redox fuel cell

The feasibility of using $\text{VO}_2^+/\text{VO}^{2+}$ and Cu/Cu^{2+} redox couples in a redox fuel cell has been established in previous experiments, using a saturated V_2O_5 -30% H_2SO_4 solution as the catholyte and Cu-wool as the reactant/electrode in a 30% H_2SO_4 anolyte solution. In the experiments described here the starting catholyte solution was an aqueous $0.8 \text{ M VO}_2^+ + 0.055 \text{ M H}_5\text{PMo}_{12}\text{V}_2\text{O}_{40}$ (or $0.28 \text{ M H}_3\text{PMo}_{12}\text{O}_{40}$) solution (250 cm^3), VO_2^+ ions were generated from this solution by direct oxidation with O_2 for several hours at 70°C . The anolyte consisted of a solution containing 30% H_2SO_4 and 10^{-4} M CuSO_4 with Cu-wool as reactant/electrode.

The overall cell voltage-current density plot of such a redox cell is shown in Fig. 7. Previous

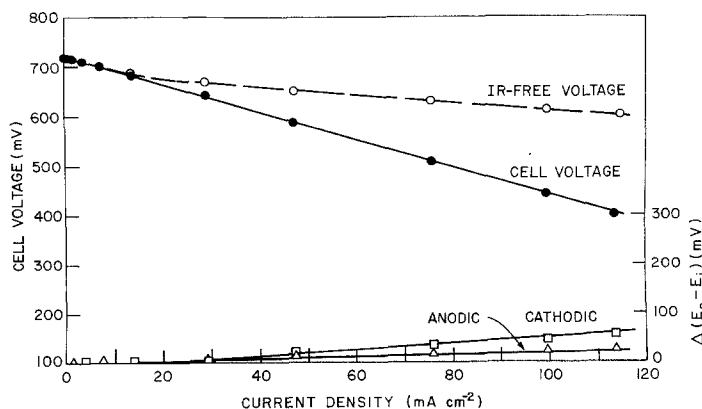


Fig. 7. Redox fuel cell with regenerative $\text{VO}_2^+/\text{VO}^{2+}$ catholyte and Cu/Cu^{2+} anode.

experience with the Cu/Cu^{2+} redox couple showed a small polarization (30 mV at 100 mA cm^{-2}) at this anode [2]. Similar results were obtained with the present redox cell. The cathodic polarization at the $\text{VO}_2^+/\text{VO}^{2+}$ side, although larger than at the anode, is still within manageable range (approximately 100 mV at 100 mA cm^{-2}). With the present configuration, namely using 'flow-by' felt electrodes, an electrolyte recirculating rate of $180 \text{ cm}^3 \text{ min}^{-1}$, and approximately 250 cm^3 each of catholyte and anolyte, this partially regenerative redox fuel cell delivers 100 mA cm^{-2} at 450 mV. This is equivalent to a power density of 0.045 W cm^{-2} (41.8 W ft^{-2}). From the plot of the internal resistance (IR)-free cell voltage versus the current density one can calculate that, for a cell with zero internal resistance the cell voltage would be 615 mV at 100 mA cm^{-2} , corresponding to a power density of 0.0615 W cm^{-2} (57.1 W ft^{-2}). This cell has an internal resistance of 0.17 ohms and it would have to be reduced to 0.1 ohm or less in order to prevent unnecessary losses due to the IR voltage drop. This study has shown that a vanadyl solution, which has been regenerated by oxygen, can support interesting current densities using our graphite fibre fuel cell electrode.

5.2. $\text{VO}_2^+/\text{VO}^{2+}$ versus silicotungstic acid ($\text{SiW}_{12}\text{O}_{40}^{5-}/\text{SiW}_{12}\text{O}_{40}^{4-}$) redox couple

In this redox cell the anolyte consists of 80 g silicotungstic acid, $\text{H}_4\text{SiW}_{12}\text{O}_{40} \cdot 24\text{H}_2\text{O}$, in $250 \text{ cm}^3 \text{ H}_2\text{O}$ to which was added 7 cm^3 concentrated sulphuric acid. The silicotungstic acid was

converted to the reduced form by direct H_2 reduction in the presence of noble metal catalysts. The catholyte was a saturated V_2O_5 solution in 30% H_2SO_4 . In this experiment no attempt was made to regenerate the catholyte. Using a pumping speed corresponding to a circulation rate of $3 \text{ cm}^3 \text{ s}^{-1}$ for this partially regenerative redox cell (internal resistance of 0.13 ohm), a promising performance was observed. The voltage versus current density relation is shown in Fig. 8. At a discharge rate of 100 mA cm^{-2} the overall cell voltage was 835 mV, giving the redox cell a power density of 0.0835 W cm^{-2} (77.6 W ft^{-2}). The corresponding IR-free cell would deliver 100 mA cm^{-2} at 1020 mV giving the IR-free cell a power density of 0.102 W cm^{-2} (94.8 W ft^{-2}).

During cell discharge the cathodic polarization was larger than the anodic polarization. At 100 mA cm^{-2} the cathodic polarization was 140 mV compared to 55 mV for the anodic polarization. The low polarization of the anode was a strong indication that the exchange current density for the redox reaction, $\text{SiW}_{12}\text{O}_{40}^{5-} \rightarrow \text{SiW}_{12}\text{O}_{40}^{4-} + e$, was reasonably large and that this redox couple functioned satisfactorily as the anodic couple in a redox cell provided adequate mass transfer was maintained.

In the cell described above, 50 mg of reduced Pt oxide was added to the silicotungstic acid solution, and the reduction of the colourless $\text{SiW}_{12}\text{O}_{40}^{4-}$ solution to the dark blue $\text{SiW}_{12}\text{O}_{40}^{5-}$ species proceeded rather rapidly within about 10 min. Neither the amount of catalyst nor the form in which the catalyst was made were varied

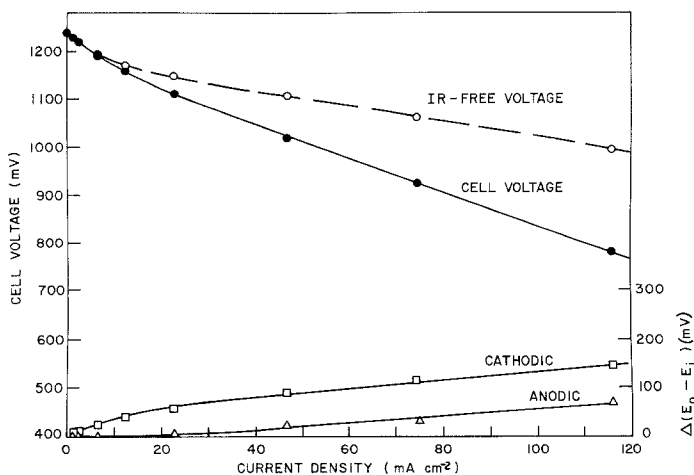


Fig. 8. Redox fuel cell with regenerative $\text{SiW}_{12}\text{O}_{40}^{5-}/\text{SiW}_{12}\text{O}_{40}^{4-}$ anode and $\text{VO}_2^+/\text{VO}^{2+}$ cathode.

in these preliminary studies of the regenerative anodic half-cell using the silicotungstic acid redox couple. The main purpose of the experiment was to demonstrate the ability of the silicotungstic acid redox couple to support adequate current densities.

5.3. Regenerative VO_2^+/VO^{2+} - $SiW_{12}O_{40}^{5-}/SiW_{12}O_{40}^{4-}$ redox cell

The complete regenerative redox fuel cell system consisted of the following components: the oxidant regenerator (Fig. 5) which contains 250 cm³ of catholyte solution (0.8M $VOSO_4$ and 0.055M $H_5PMo_{10}V_2O_{40}$ or 0.28M $H_3PMo_{12}O_{40}$), the reductant regenerator which contained 250 cm³ of anolyte solution (0.112M $H_4SiW_{12}O_{40}$ and 1M H_3PO_4), and the redox fuel cell at which the electrode reactions took place generating the electric current. Generation and regeneration of VO_2^+ took place in the oxidant regenerator by direct oxidation with O_2 catalysed by the soluble heteropolymolybdic acid catalysts.

During the oxidation reaction the bluish-green $VOSO_4$ solution became increasingly reddish-brown indicating the formation of increasing amounts of VO_2^+ . In the reductant regenerator the reduction of $H_4SiW_{12}O_{40}$ to $H_5SiW_{12}O_{40}$ was accompanied by a change from the clear $SiW_{12}O_{40}^{4-}$ solution to the intense dark-blue $SiW_{12}O_{40}^{5-}$ solution. Before the addition of H_2 and O_2 to the regenerators (previously purged with

argon) the cell voltage with circulation was ~ -0.2 V when $H_3PMo_{12}O_{40}$ was used as an oxidation catalyst. After regeneration for 0.5 h the open circuit voltage was + 0.9 V. Previous experiments in which the regeneration of the reduced silicotungstic acid was accomplished by direct H_2 reduction using finely divided Pt powder as a catalyst, showed that the catalyst lost its activity with time because the finely divided Pt powder tended to agglomerate into coarser particles and accumulated in the felt in the fuel cell anode compartment. Using a catalyst made from Pt on fumed SiO_2 (Cab-o-sil Cabot Corp.) alleviated this problem and no decrease in catalyst activity should be detected during the course of the experiments. This form of Pt catalyst, which is nearly colloidal since it is difficult to remove by filtration, was employed in the anolyte regenerator in all subsequent redox cell experiments.

The performance of a regenerative VO_2^+/VO^{2+} - $SiW_{12}O_{40}^{5-}/SiW_{12}O_{40}^{4-}$ redox fuel is shown in Fig. 9. The anolyte contained 2.0 g of the Cab-o-sil (1.1% Pt) reduction catalyst. The internal cell resistance was 0.228 ohm. In a series of experiments, the rate of recirculation of the electrolytes was varied from 65 cm³ min⁻¹ to 105 cm³ min⁻¹ and the results at these two limits are displayed in Fig. 9. At the higher current densities the influence of the rate of circulation of the electrolyte became very pronounced. In this particular case the overall cell voltages at a current density of 80 mA cm⁻² were 450 mV (at 65 cm³ min⁻¹) and 568 mV (at

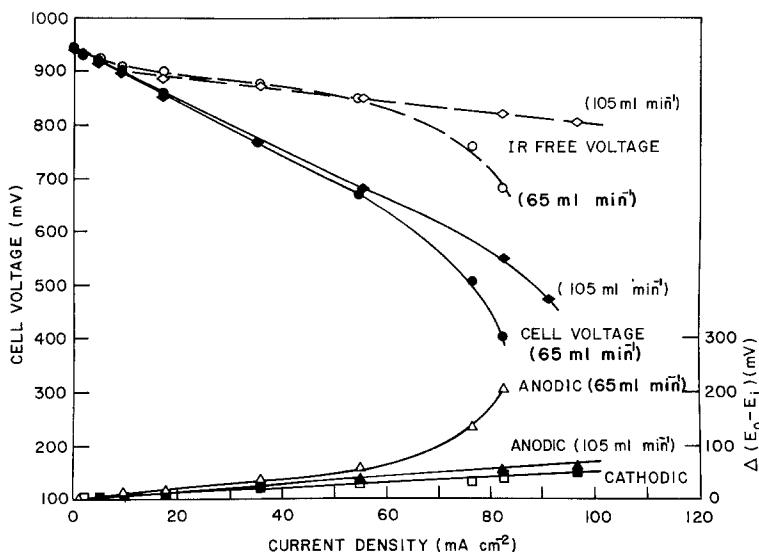


Fig. 9. Chemically regenerative VO_2^+/VO^{2+} - $SiW_{12}O_{40}^{5-}/SiW_{12}O_{40}^{4-}$ redox fuel cell.

105 cm³ min⁻¹). The anodic polarization was also much larger at the slower rate of circulation, whereas the cathodic polarization was not noticeably influenced by the recirculation rate. This can be explained in terms of the difference in size of the much larger silicotungstic acid molecule or ion compared to the smaller VO₂⁺ and VO²⁺ ions, and the influence of the recirculation rate on the mass transfer rate of the individual species to the electrode surface. These results indicate that the performance of the redox cell can be improved by the improvements in mass transfer rates which can be expected to result from improvements in electrode and overall cell design.

By comparing the IR-free cell voltage and the overall cell voltage of the redox cell it becomes very obvious that better performance of the cell can be achieved by lowering the internal resistance of the cell below the present value of 0.228 ohm. In order to reduce the cell resistance, either the electrolyte conductivity must be increased, or the separation between anode and cathode decreased. We have not attempted the latter, but have attempted to decrease the electrolyte resistance. For the anode compartment, acid can be added to lower the resistance. This had little effect on the regeneration rate. As stated before, it is not possible to increase the hydrogen ion concentration of the catholyte above 0.3M (preferably 0.1 to 0.2M) because this would greatly decrease the regeneration rate with oxygen. However, neutral salts can be added to increase electrolyte conductivity.

The performance of another regenerative redox fuel cell is displayed in Fig. 10. Originally the cell contained 250 cm³ catholyte solution (0.8M VOSO₄ and 0.055M H₅PMo₁₀V₂O₄₀) at pH = 0.67 and 250 cm³ anolyte solution (0.112M H₄SiW₁₂O₄₀) at pH = 0.97 to which 2.0 g Pd-4, 4', 4'', 4'''-tetrasulphophthalocyanine was added. The internal resistance of the cell was 0.262 ohm. To lower the internal resistance of the cell, 50 g NaHSO₄ · H₂O and 5 g Na₂SO₄ was added to the catholyte and 5 cm³ concentrated sulphuric acid was added to the anolyte. The purpose of adding the bisulphate-sulphate mixture was to improve the electrolyte conductance and to buffer the pH. This particular buffer mixture, however, lowered the pH of the catholyte to 0.54, which was the lower limit for obtaining a reasonable rate of regeneration with the molybdovanadophosphoric acid catalyst. The internal resistance of the cell decreased to 0.205 ohm. From the cell voltage versus current density plots of Fig. 10 the improvement in cell performance after addition of the electrolytes to lower the internal resistance is quite obvious. The cell voltage was measured at a discharge current corresponding to 80 mA cm⁻², before and after the addition of the NaHSO₄ + Na₂SO₄ buffer to the catholyte and the concentrated H₂SO₄ to the anolyte. The overall cell voltage is 440 mV (circulation rate 50 cm³ min⁻¹) before buffer addition, and is 560 mV (circulation rate 50 cm³ min⁻¹) and 594 mV (circulation rate 90 cm³ min⁻¹) after buffer addition. These results also showed again that for the same cell, the higher

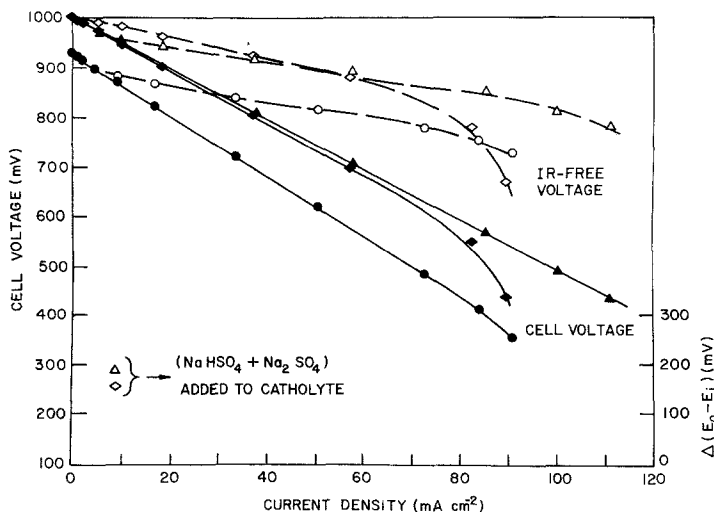


Fig. 10. Buffer addition to catholyte of chemically regenerative VO₂⁺/VO²⁺-SiW₁₂O₄₀⁵⁻/SiW₁₂O₄₀⁴⁻ redox fuel cell.

rate of circulation, and consequently the better mass transfer, resulted in improved cell performance.

In this redox cell we used the Pd-4, 4', 4'', 4'''-tetrasulphophthalocyanine catalyst for regeneration of the anolyte. The results showed that this catalyst can be used for the reduction of silicotungstic acid with H_2 in the regenerator.

The IR-free voltage versus current density plots showed that the cell was still incurring a considerable loss of voltage due to internal resistance. Even at the lower internal resistance of 0.205 ohm the voltage drop was 148 mV at a current density of 80 mA cm^{-2} . Improved performance will have to come from improved cell design with smaller cathode-anode distances. The contribution of the ohmic resistance of the felt (Table II of Oei [2]) is significant and must be reduced.

Another regenerative redox fuel cell, using molybdophosphoric acid catalyst in the oxidant regenerator, was used in an experiment to evaluate this catalyst (see Fig. 11). The catholyte consisted of 250 cm^3 (0.8M $VOSO_4$ and 0.28M $H_3PMo_{12}O_{40}$) solution at $pH = 0.75$ and the anolyte consisted of 250 cm^3 H_2SO_4 solution at $pH = 0.14$ with 0.112M silicotungstic acid. At a circulation rate of $180 \text{ cm}^3 \text{ min}^{-1}$, the maximum discharge current that could be obtained was 75 mA cm^{-2} , at 510 mV. At higher current densities the cell voltage decreased drastically. It is only at very high rates of circulation, $360 \text{ cm}^3 \text{ min}^{-1}$, that this redox cell performed in a manner similar to the previous redox cells, delivering 80 mA cm^{-2} at 550 mV.

The above results show that this chemically regenerative redox fuel cell can operate for a short time with current densities and voltages near those obtained with conventional fuel cells. The long-time performance under constant load will be determined by the size of the regenerators and the regeneration rates measured in the first part of this paper. The limiting rate is that for the re-oxidation of VO^{2+} to VO_2^+ and is sufficiently slow for the catalysts that we have used so that regenerator weight would be too large for vehicle use ($\sim 5000 \text{ lb}$ for 20 kW at a 0.6 V cell voltage, and at an oxidation rate of the 1M $VOSO_4$ solution of 1% per min at 1 atm O_2 , 76° C). It could conceivably be of use for a stationary power plant. Other problems of concern are, the use of noble metals in the anolyte regenerator, the cost of silicotungstic acid, the high recirculation rates and the diffusion of vanadyl ion through the Nafion membrane. Fuels other than hydrogen would be desirable. Although methanol and Pt can reduce phosphomolybdic acid at 76° C they cannot reduce silicotungstic acid at 100° C .

The regenerative capacity of the VO_2^+/VO^{2+} - $SiW_{12}O_{40}^{5-}/SiW_{12}O_{40}^{4-}$ redox fuel cell system was evaluated by discharging the cell through an external 5 ohm resistive load. Originally the regenerators contained 250 cm^3 0.8M $VOSO_4$ + 0.055M $H_5PMo_{10}V_2O_{40}$ (oxidized with O_2) and 250 cm^3 0.112M $H_4SiW_{12}O_{40}$ + 2 g Pt (1%) on Cab-o-sil (reduced with H_2). The overall cell voltage, cathodic and anodic voltages were recorded as a function of time of discharge and the results are shown in Fig. 12.

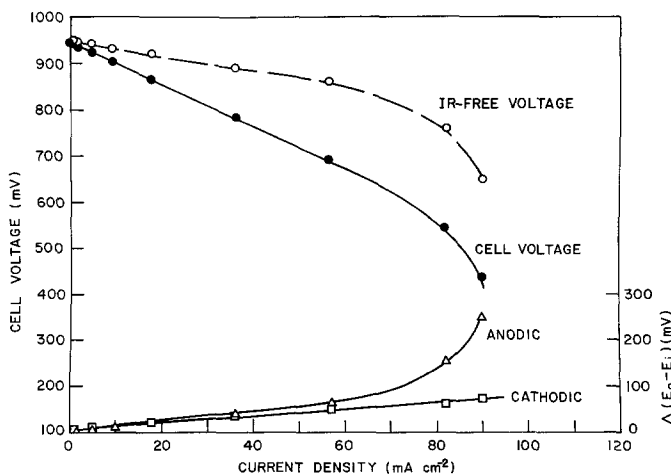


Fig. 11. Chemically regenerative VO_2^+/VO^{2+} - $SiW_{12}O_{40}^{5-}/SiW_{12}O_{40}^{4-}$ redox fuel cell with $H_3PMo_{12}O_{40}^{4-}$ oxidation catalyst.

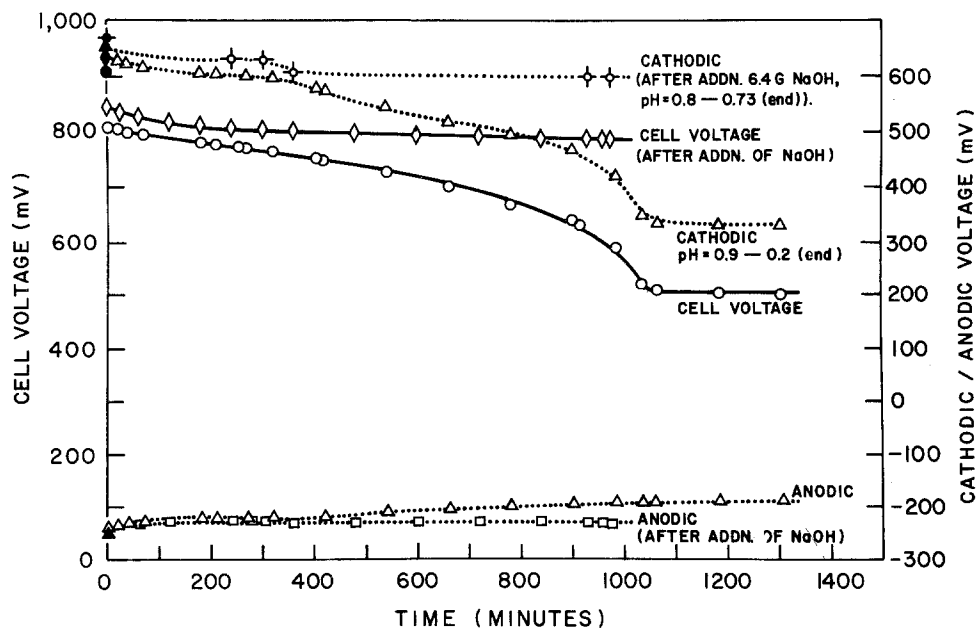


Fig. 12. Chemically regenerative redox fuel cell, voltage versus time of discharge.

The anodic cell voltage remained steady after 1200 min of cell operation. During the first 660 min the change in anode voltage was 4.4 mV h^{-1} , and between 660 and 1200 min of discharge it was 2.3 mV h^{-1} . After readjustment of the pH of the catholyte the change in the anodic voltage during discharge was practically zero.

Poor performance of the redox fuel can be traced to the poor performance of the cathodic side of the cell. Indeed, the curves showing the changes in the overall cell voltage and the cathodic cell voltage with time exhibited similar trends. A parallel decline in both the overall cell voltage and cathodic voltage during the discharge was observed, and after 900 min of cell operation the voltages decreased sharply from 638 mV overall cell voltage and 468 mV cathodic voltage to a steady voltage of 500 mV and 330 mV, respectively. This low cathodic voltage is indicative of the low rate of regeneration of VO_2^+ leading to poor overall cell performance. At the end of the discharge the pH of the catholyte was 0.2, a drastic change from pH 0.9 for the starting solution. Such a large change in pH was caused by the migration of H^+ ions from the anolyte through the Nafion membrane to counteract the movement of VO_2^+ ions from the catholyte through the membrane. The anolyte solution was found to contain 0.13M

vanadium ions. The regeneration of VO_2^+ with O_2 using the phospho-10-molybdo-2-vanadic acid catalyst requires a $\text{pH} > 0.5$. Thus the changing pH of the catholyte, from 0.9 to 0.2, made this catalyst ineffective and was the cause of the slow regeneration rate of the catholyte.

Addition of 6.4 g NaOH to restore the pH of the catholyte (to pH 0.82) seemed to have another beneficial effect, namely the buffering of the pH of the catholyte. Performance of the catholyte and the overall cell improved considerably and the regeneration rate of the catholyte seemed to be adequate for the redox fuel cell to deliver 147 mA at 785 mV for at least 1000 min. During the discharge the pH of the catholyte changed from 0.82 to 0.73. Although the Nafion membrane used has high ion conductivity, it lacks sufficient selectivity for ion transfer to be useful in this application.

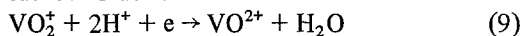
6. Conclusion

Laboratory studies on the oxidation of VO^{2+} to VO_2^+ showed that the reaction is catalysed by molybdic acid, H_2MoO_4 , molybdophosphoric acid, $\text{H}_3\text{PMO}_{12}\text{O}_{40}$, and molybdovanadophosphoric acid, $\text{H}_5\text{PMO}_{10}\text{V}_2\text{O}_{40}$. The rate of oxidation using the above catalysts depended strongly on the pH of the solution. The molybdovanadophosphoric acid

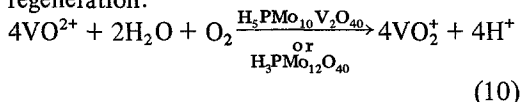
catalyst operated at the lower pH (preferably from 0.7 to 1); the molybdophosphoric acid operated at a solution pH of 1; and the molybdic acid operated at a pH of 1.5. The regeneration of the reduced anolyte, $\text{SiW}_{12}\text{O}_{40}^{5-}$, by direct reduction with H_2 and a noble metal catalyst, took place over a wider pH range, and was most effectively performed at or near room temperature.

Based on the previous results, the following novel regenerative redox fuel cell is proposed,

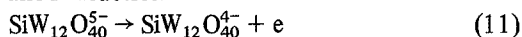
cathode reaction:



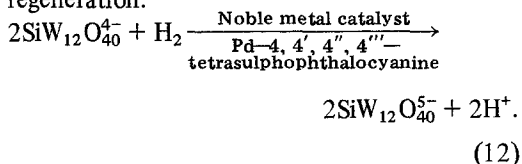
regeneration:



anode reaction:



regeneration:



The results of the experiments have demonstrated the feasibility of operating and constructing a regenerative redox fuel cell using the above redox couples. We have identified a number of problems and suggested possible solutions to a few of them. The design of the cell and the conditions under which it operates (for example, temperature and pH of catholyte and anolyte) have not been optimized for maximum cell performance and

regeneration rates in these early experimental cells. Improvements in cell performance can be achieved by lowering the internal resistance of the cell through addition of appropriate conducting electrolytes, and through improved design of electrodes and cell. An improved cell and electrode design should also improve mass transfer rates of the ions involved in the redox reactions to the electrode surface and lead to better overall cell performance at lower recirculation rates. A more selective ion exchange membrane or membrane system will be required before long-term durability can be achieved.

References

- [1] A. M. Posner, *Fuel* **34** (1955) 330.
- [2] D-G. Oei, *J. Appl. Electrochem.* **11** (1981) 330.
- [3] J. H. Weber and D. H. Busch, *Inorg. Chem.* **4** (1965) 469.
- [4] K. Post, *Chem. Abs.* **85** (1976) 131240.
- [5] L. I. Kuznetsova and K. I. Matveev, *Reaction Kinetics Catal. Lett.* **3** (1975) 305.
- [6] M. Otake and T. Onoda, *7th Inter. Congress on Catalysis, Tokyo* (1980) paper B3-1.
- [7] *Chem. Abs.* **86** (1977) 161908.
- [8] J. A. S. Bett and K. R. Lynch, 'Power Sources No. 3', Pergamon Press, Oxford (1971) p. 439.
- [9] G. A. Tsigdinos, 'Topics in Current Chemistry', Vol. 76, Springer-Verlag Berlin, Heidelberg (1978).
- [10] G. A. Tsigdinos, 'Electrochemical Properties of Heteropoly Molybdates', Bulletin Cdb-15, Climax Molybdenum Co., Greenwich, Connecticut (1971).
- [11] M. T. Pope and G. M. Varga Jr, *Inorg. Chem.* **5** (1966) 1249.
- [12] I. I. Naqvi, *Pak. J. Sci. Res.* **31** (1979) 151.
- [13] W. N. Carson and M. Feldman, *Proc. 13th Ann. Power Sources Conf.* (1959).