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A chemically regenerative redox fuel cell. II

J. T. KUMMER, D-G. OEI

Research, Ford Motor Company, Dearborn, MI 48121, USA

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Our previous paper [1] has described an unconventional chemically regenerative redox fuel cell, including a modest amount of performance data, and has pointed out a number of problem areas. This paper describes additional work and some attempts that have been made to improve the cell performance in several of the problem areas described in the first paper. Two different redox fuel cell systems employing the V^{2+}/V^{3+} and Mo^{3+}/Mo^{4+} redox couples as the anolyte, and a new NO_3^-/NO catalyst system for VO^{2+} oxidation were explored and described. The reduction of Na_2MoO_4 to Mo^{4+} and Mo^{3+} by H_2 in concentrated H_2SO_4 solution was studied in small scale laboratory experiments and discussed. The performance of a redox cell in which H_2 was obtained from the Pd-catalysed decomposition of formic acid, HCOOH, is described and the results of experiments with different membranes are reported. The results of experiments using WC as a hydrogenation catalyst at a temperature of 70–90° C with mixed molybdo-tungsto-silicic acids are reported and discussed.

1. Consideration of other anodic redox couples

The redox couple in the anolyte solution of the redox fuel cell described previously [1] utilized the reduction and reoxidation of tungstosilicic acid (TSA). The redox voltage of the large TSA molecule (Mol wt ~ 3 000) matches the redox potential of H_2, but it can undergo only a one-electron exchange redox reaction when H_2 is used as a reducing agent, although it contains 12 tungsten atoms per molecule. The solutions used in the previous redox cell [1] contained approximately 300 g TSA l^{-1} (0.1 M, $\rho = 1.3 \text{ g cm}^{-3}$) and could store 0.1 F of charge in 1 l of completely reduced solution.

In a recent paper, Richens and Sykes [2] described a redox couple based on a trinuclear molybdenum ion.

$$[(Mo^{3+})_2Mo^{4+}] \rightleftarrows [Mo^{4+}]_3 + 2e(E_0 \sim 0 \text{ V vs NHE}) \qquad (1)$$

We have found that highly acidic (~ 3 M H_2SO_4) molybdate solutions can be readily reduced by H_2 using Pt (or Pd) as a catalyst to this trinuclear molybdenum ion, $[(Mo^{3+})_2Mo^{4+}]$. Some laboratory experiments were done in order to investigate this system further.

2. Experimental details

2.1. *Laboratory experiments involving regeneration of the Mo^{3+}/Mo^{4+} system*

The reaction vessel for studying the molybdate reduction was a 125 or 250 cm^3 reaction flask connected to a water manometer and a water lubricated glass syringe (100 cm^3). The vessel was stirred with a Teflon coated stirring bar at approximately 500 r.p.m. The reaction vessel was either at room temperature or thermostated at 50 or 82° C. It was flushed with H_2 and the H_2 uptake was the measured, after the stirrer was turned on, by observing the change of the syringe plunger position with time at constant pressure. The syringe had to be refilled a number of times during a run. The final reduced solution was titrated with either Ce^{4+} or Cr^{6+} solutions.

The salt, Na_2MoO_4, (usually 3 g) was dissolved in 20 cm^3 of H_2O in the reaction flask and 5 cm^3 of strong acid added. The acid strength was such that, after acid addition, the molarity of free H_2SO_4 was as indicated (usually 3 M).

The SiO_2–Pt catalysts were prepared as given in [1]. The SiO_2–Pt–polytetrafluoroethylene (PTFE) catalysts were prepared by adding 2 g of

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Table 1. Reduction of H_2MoO_4 by H_2 catalysed by Pt and Pd

H_2SO_4* (M)	H_2MoO_4 (M)	Temp (°C)	Final degree of reduction equivalent per Mo atom	Observed rate (cm^3 STP H_2/min^{-1})		Stirring bar length (cm)	Catalyst wt (g)	Catalyst description
				Initial†	Final‡			
1.9	0.063	82	2.12	–	–	2.6	0.0096	PtO_2
2.9	0.073	24	2.56	–	–	2.6	0.019	PtO_2
3.1	0.5	82	2.42	0.88	0.88	2.6	0.033	PtO_2
3.4	0.5	25	2.54	0.76	0.68	2.6	0.033	PtO_2
3.1	0.5	24	2.54	1.18	0.94	2.6	0.0074	PtO_2
6.1	0.5	24	2.72	1.28	0.68	2.6	0.077	PtO_2
3.1	0.5	24	–	1.2	–	2.6	0.50	SiO_2 + 3.6% Pt
3.1	0.5	24	–	0.65	0.17	2.6	0.084	$PdSo_4$
3.1	0.5	24	2.56	1.9	1.7	4.0	0.076	PtO_2
3.1	1.0	24	2.54	2.8	1.96	4.0	0.075	PtO_2
5.1	2.0	24	2.57	2.8	–	4.0	0.076	PtO_2
3.1	0.5	24	2.55	4.5	4.5	4.0	0.5	SiO_2 + 3.3% Pt, 28% PTFE
3.1	0.5	25	–	9.5	6.9	4.0	0.43	SiO_2 + 4.4% Pt, 2.8% PTFE
3.1	0.5	50	2.57	6.2	5.2	4.0	0.41	SiO_2 + 4.4% Pt, 2.8% PTFE
3.1	0.5	25	2.55	5.0	–	4.0	2.0	SiO_2 + 1% Pt, 4.7% PTFE
3.1	0.5	25	–	9.5	7.5	4.0	2.0	SiO_2 + 1% Pt, 2.8% PTFE

* In excess of that used to react with Na_2MoO_4 to form H_2MoO_4.
† Rate of Mo^{6+} reduction.
‡ Rate of $(Mo^{4+})_3$ reduction.

fumed SiO_2 (Cab-o-sil) to 9 cm^3 of a water solution containing a calculated volume of a PTFE suspension (DuPont Type 30, 0.18 g solid cm^{-3}). This was dried at 25° C then at 350° C for 1/2 hour in an attempt to remove the dispersing agent. To this was added 4 cm^3 of water containing a calculated amount of H_2PtCl_6. The mixture was dried at 25° C and then reduced for 10 min at 250° C. The resultant catalyst was nonhomogenous with black and white areas.

Table 1 gives the results of a number of reduction runs. The reduction of Mo^{6+} at 25 or 50° C stops at 50% of the way from Mo^{4+} to Mo^{3+} (see Fig. 1). From Equation 1 we would expect reduction to proceed to 67% of completion. In cell operation we would hope to operate in the range $Mo^{4+} \rightleftarrows Mo^{3.5+}$, i.e. at a redox capacity of 1/2 electron per Mo atom.

The extent of reduction increases as the molarity of sulphuric acid increases, and appears to be somewhat less at 82° C than at 25° C. This may be due to either a shift of the equilibrium constant

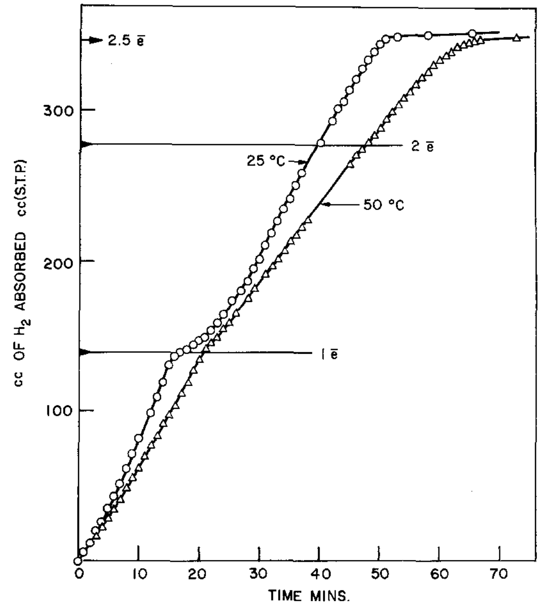


Fig. 1. Reduction of 0.5 M Mo^{6+} by H_2 at 25 and 50° C. Ordinate also gives number of electrons per Mo atoms. Pt/PTFE catalyst, 20 mg Pt.

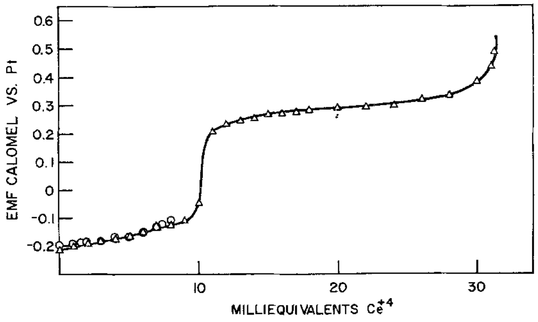


Fig. 2. Potentiometric titration of reduced 0.5 M H_2MoO_4 solution with Ce^{4+}(Δ–Run 1, ○–Run 2).

with temperature or to the reduction of the partial pressure of H_2 (at 1 atm total pressure) in the flask due to the increased water vapour pressure. The titration of the reduced solution at the end of the run agreed with the measured hydrogen uptake and was used to determine the final degree of reduction of the Mo^{6+}. A titration curve is shown in Fig. 2.

In most experiments concerning the reduction of H_2MoO_4 in acid solution there is observed a discontinuity in the rate of H_2 uptake in the region where Mo^{5+} should start to form. This can be seen better at low Mo^{6+} and H^+ concentrations, see Fig. 3. The cause of this is not known. The reduction rates depend on the degree of agitation, indicating that the rates shown in Figs. 1 and 3 are not true intrinsic reaction rates and are probably limited by the low solubility of H_2 in the solution. The final extent of reduction, at equilibrium, is thought to be accurate.

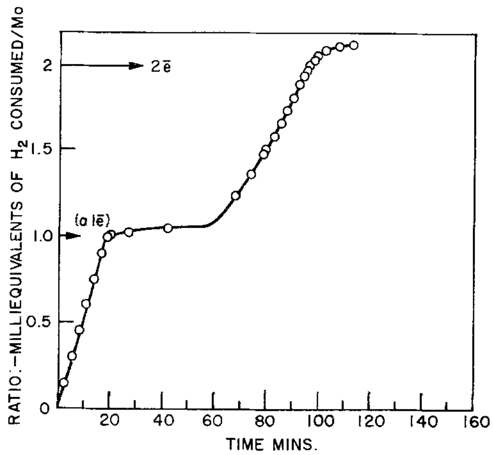


Fig. 3. Hydrogenation of 25 cm³ 0.062 M H_2MoO_4 solution (1 M H^+) under 1 atm total pressure at 82° C using 9.6 mg PtO_2 catalyst.

Recently, Matsuda *et al.* [3] published a paper concerning catalysts prepared containing polytetrafluoroethylene (PTFE). The work is interesting since a $Pt/Al_2O_3(TiO_2)$–PTFE catalyst is used to reduce Cu^{2+} to Cu metal. Usually, Pt is deactivated by Cu deposition on the Pt surface. That this does not occur in Matsuda's experiments could be interpreted in terms of a H_2 spill-over effect from non-wetted Pt across a Teflon barrier to the aqueous phase. Such a hypothesis would suggest that perhaps a Ni or Ni alloys could be used in acid solution without dissolution. However we have not seen any literature reference to this.

We have prepared catalysts with fumed SiO_2 (Cab-o-sil) together with Pt and PTFE. For the hydrogenation of Mo^{6+} in solution these show enhanced activity as compared to Pt–SiO_2 catalysts without PTFE. We believe that this is a result of the ability of the catalysts prepared with PTFE to trap H_2 in the non-wetted portions of the catalyst when they reach the surface of the solution during agitation and to utilize this hydrogen during periods under water and that they are thus much less dependent on the solubility of H_2 in the solution. This is shown by the data in Table 1. Since there is a usable one-electron redox reaction for every 2 Mo atoms in solution this system is more efficient in its utilization of the elements in the compound in solution than is tungstosilicic acid. The solubility of H_2MoO_4 in a strong H_2SO_4 solution at 20° C is 140 g dm^{-3} for a 3 M solution and 200 g dm^{-3} for a 4 M acid solution [4]. The solubility decreases as the temperature increases and is 90 g dm^{-3} for a 3 M acid solution at 50° C. Assuming a concentration of 100 g dm^{-3} (0.617 M) a completely reduced solution would have a redox capacity of 0.3 F l^{-1}. Operation of a redox fuel cell using this Mo^{3+}/Mo^{4+} redox couple is described later.

2.2. *Cathodic redox system regeneration*

As described in the previous report [1] the VO_2^+/VO^{2+} redox catholyte was regenerated with O_2 using as a catalyst the soluble heteropoly acids $H_3PMo_{12}O_{40}$ or $H_5PMo_{10}V_2O_{40}$ at pH ≥ 0.75 [5]. At lower pH the rate of regeneration is very slow. The sensitivity of the catalyst toward the pH of the electrolyte solution makes it necessary to use a strong buffer in order to maintain a constant pH close to 0.75 during the operation of the cell. It is desirable to have a catalyst which is rather insensitive to changes in pH and which will adequately regenerate the VO_2^+ from VO^{2+} and O_2 in highly acidic solutions. It has been found [6] that the reaction between NO_3^- and VO^{2+} to give VO_2^+ and NO is rapidly catalysed in solution by solid V_2O_5. The NO produced can be reacted with O_2 in a static system to regenerate the NO_3^-. The reaction of VO^{2+} with NO_3^- in the presence of solid V_2O_5 is very fast although the reaction is near equilibrium [6]. The $NO + O_2$ reaction has a ΔF of ~ -8 k cal mol^{-1} which represents the free energy expanded to perform this regeneration reaction. At the high H^+ concentration used, the formal VO_2^+/VO^{2+} redox voltage is $\geqslant 1.0$ V which is desirable for fuel cell use. This catholyte regeneration system at a pH ~ 0 was employed in most of the examples of redox cell performance given below.

2.3. *Hydrogenation catalysis*

The hydrogenation catalysts which we have used to regenerate the anolyte with H_2 contains noble metals, Pt, Pd, Ru and Rh. It would be desirable to replace them with an active base metal catalyst. The requirement that the catalyst be insoluble in strong acid solution, however, is difficult to realise. Copper is insoluble in strong acid solution but is inactive in dissociating hydrogen. Nickel is an active catalyst for hydrogenation in aqueous solution but is only thermodynamically stable at 25° C at a $pH > 4.7$ in a 1 N Ni^{2+} solution. An electrolyte of this pH is CO_2 rejecting which is a desirable property of a fuel cell operated with H_2 made from methanol, but the electrolyte resistance is high. (ΔF of dissolution is -10.9 kcal mol^{-1} at $pH = 0$). WC appears to be kinetically stable and has been employed as a catalyst in acid solution. We have observed that Hastelloy B (a Ni–30% Mo alloy), which has a known resistance to dissolution in sulphuric acid [7] is an active catalyst for the hydrogenation of tungstosilicic acid in acid solution. This alloy is also thermodynamically unstable (to about the extent of nickel) but must owe it's acid resistance to kinetic effects. The results of some hydrogenation experiments using this alloy are given in Table 2. No measurable solution of the alloy was observed in these experiments at 25° C (under the same conditions nickel dissolves rapidly), but the absolute hydrogenation reaction rate for these low surface area catalysts is low.

3. Redox cell results

3.1. *Experimental details*

The 'flow-by' redox cell, the equipment for obtaining the discharge curves, and most of the materials used in the experiments were described in previous reports [1, 8]. V^{2+} ions were obtained by reducing a solution of $VOSO_4$ in sulphuric acid with Zn (rods or pellets). The V^{2+}/V^{3+} anolyte contained Zn^{2+} ions. $[(Mo^{3+})_2Mo^{4+}]$ ions were prepared by the reduction of an acidic solution (3 M H_2SO_4) of Na_2MoO_4 with H_2 using a Pt catalyst. [Originally PtO_2 was used and in subsequent studies Cab-o-sil (1% Pt) and PTFE-coated

Table 2. Hydrogenation of tungstosilicic acid using filings of Hastelloy B as a catalyst. $pH = 1$, (H_2SO_4) $Ni^{2+} = 1$ M, $T = 25°$ C

Catalyst	*Moles TSA used*	*molar equivalent (meq) H_2 reacted*	*Rate (meq min^{+1} g^{-1})(average of 3 runs)*
A[b e]	1.39	1.4	3.7×10^{-3}
B[c d e]	4.16	4.06	0.8×10^{-3}

[a] Filings 0.1 mm long aspect ratio 5 to 10.
[b] From Climax Molybdenum Co., 70.33% Ni, 27.82% Mo, 1.25% Fe, 0.42% Cr, 0.18% Mn.
[c] From Alfa Chemical Company.
[d] Pretreated with warm 9 M H_2SO_4 before use, in order to reduce induction period.
[e] Metal catalyst recovery 100% in both runs. Considerable amounts of Teflon found mixed with the recovered metal catalyst from stirrer bar abrasion.
[f] There was observed an induction period which can be as long as 100–200 min before the hydrogenation reaction started.

Cab-o-sil (1% Pt) catalysts were used.] To prevent NO loss, when using the NO_3^-/NO catalyst, the cathode regenerator was exposed to pure O_2 without bubbling the gas through the solution.

3.2. *The redox cell $SiW_{12}O_{40}^{5-}/SiW_{12}O_{40}^{4-}$ vs VO_2^+ VO^{2+} regenerated by NO_3^- + O_2*

The electrode and regeneration reactions for the cathode and anolyte are,

$$\text{cathode:}\quad VO_2^+ + 2H^+ + e \rightleftarrows VO^{2+} + H_2O\,(E_0 \sim 1.0\,\text{V vs NHE}) \qquad (2)$$

$$\text{regeneration:}\quad 4VO^{2+} + 2H_2O + O_2 \xrightarrow{NO_3^-/NO} 4VO_2^+ + 4H^+ \qquad (3)$$

$$\text{anode:}\quad SiW_{12}O_{40}^{5-} \rightleftarrows SiW_{12}O_{40}^{4-} + e \qquad (4)$$

$$\text{regeneration:}\quad 2SiW_{12}O_{40}^{4-} + H_2 \xrightarrow{Pt} 2SiW_{12}O_{40}^{5-} + 2H^+ \qquad (5)$$

The improvement in VO_2^+/VO^{2+} catholyte regeneration using the NO_3^-/NO catalyst (from HNO_3) instead of the heteropoly acid ($H_5PMo_{10}V_2O_{40}$) catalyst is evident from Fig. 4 which shows the performance of a H_2/O_2 redox fuel cell discharged over a 2.1 ohm external resistive load for a 12 h period. The cathodic voltage (VO_2^+/VO^{2+} side) remains almost constant throughout the discharge. The anodic voltage showed increased polarization after 6 h of discharge, which may be a result of Pt catalyst deactivation or loss (the solid accumulates on the top of the walls of the regenerator flask and in the cell).

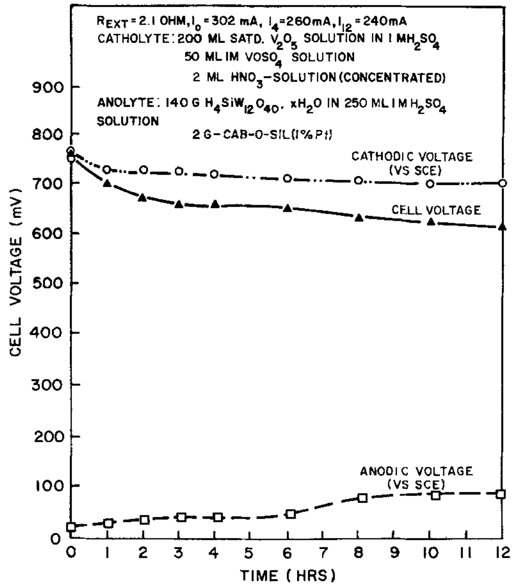


Fig. 4. Discharge curve of VO_2^+/VO^{2+} vs $SiW_{12}O_{40}^{4-}/SiW_{12}O_{40}^{4-}$ redox fuel cell using NO_3^-/NO catalyst for VO_2^+/VO^{2+} regeneration with O_2. 'Flow-by' rate, 230 cm^3 min^{-1}; I_0, I_4, I_{12} are currents at 0, 4, and 12 h; VO_2^+/VO^{2+} regeneration chamber at 75–80° C, TSA regeneration chamber at 25–30° C. Saturated V_2O_5 solution, 0.2 M.

3.3. *The redox cell Mo^{3+}/Mo^{4+} vs VO_2^+/VO^{2+}*

The electrode reactions and redox potentials of the Mo^{3+}/Mo^{4+} vs VO_2^+/VO^{2+} redox fuel cell are,

$$\text{cathode:}\quad VO_2^+ + 2H^+ + e \rightleftarrows VO^{2+} + H_2O\,(E_0 \sim 1.0\,\text{V}) \qquad (6)$$

$$\text{anode:}\quad [(Mo^{3+})_2Mo^{4+}] \rightleftarrows [Mo^{4+}]_3 + 2e\,(E_0 \sim 0\,\text{V}) \qquad (7)$$

The catholyte mixture and its regeneration were described in the account of the preceding redox cells. The anolyte consisted of 30 g $Na_2MoO_4\cdot 2H_2O$ dissolved in a solution of 45 cm^3 concentrated sulphuric acid (18 M H_2SO_4) in 205 cm^3 H_2O to which 0.7 g PtO_2 catalyst was added. This molybdate solution was reduced with hydrogen overnight.

In the low pH (3 M H_2SO_4) environment of the redox cell the redox potential of the Mo^{3+}/Mo^{4+} redox couple is near that of the hydrogen redox potential. The rate of regeneration of the anolyte with H_2 increased approximately 5-fold by using the PTFE-coated Cab-o-sil (1% Pt) catalyst.

A discharge curve of the cell using the Mo^{3+}/Mo^{4+} and VO_2^+/VO^{2+} redox couples is shown in Fig. 5. At a current density of 85 mA cm^{-2} the IR-free voltage of the cell is 725 mV. Under the conditions of the experiment this redox cell has a limiting power density of 0.062 W cm^{-2}.

3.3. *The redox cell V^{2+}/V^{3+} vs VO_2^+/VO^{2+}*

When using the V^{5+}/V^{4+} redox couple for the oxidant in the redox fuel cell it would be desirable to use the V^{2+}/V^{3+} redox couple for the reductant in order to reduce the problem of contamination between anolyte and catholyte. The formal V^{2+}/V^{3+} redox voltage of − 0.25 V in 1 M H_2SO_4,

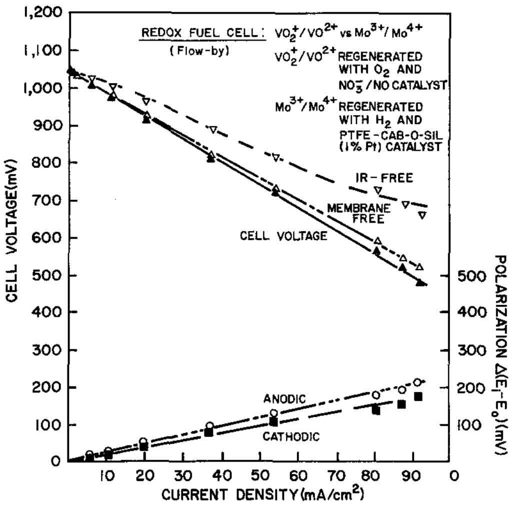


Fig. 5. Performance of VO_2^+/VO^{2+} vs Mo^{3+}/Mo^{4+} redox fuel cell, cell voltage vs current density. IR-free voltage is E_0 minus the cathodic and anodic polarization; membrane-free voltage = cell voltage + calculated membrane IR; 'flow-by' rate, 230 cm³ min⁻¹; VO_2^+/VO^{2+} regeneration chamber at 75–80° C, Mo^{3+}/Mo^{4+} regeneration chamber at 45–50° C.

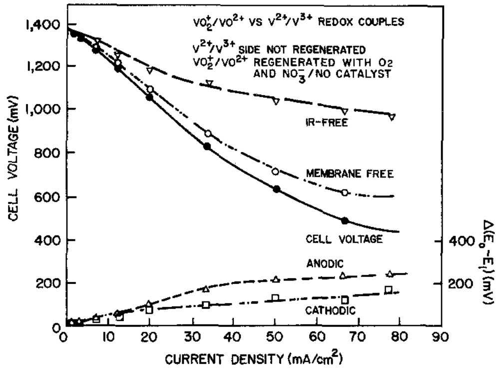


Fig. 6. Performance of a VO_2^+/VO^{2+} vs V^{2+}/V^{3+} redox fuel cell, cell voltage vs current density. IR free voltage is E_0 (Open Circuit Voltage, OCV) minus the cathodic and anodic polarization; membrane-free voltage = cell voltage + calculated membrane IR; 'flow-by' rate, 230 cm³ min⁻¹; VO_2^+/VO^{2+} regeneration chamber at 75–80° C, V^{2+}/V^{3+} flask at room temperature.

however, precludes its use when H_2 is the reducing agent, unless this voltage can be changed more positively by a ligand that will complex V^{2+} with a greater (~6 kcal more negative) free energy of reaction than V^{3+} in relatively strong acid solution. Although the effect of complex formation on the V^{2+}/V^{3+} redox couple has been investigated by Lingane and Meites [9] and King and Garner [10] have suggested that α, α′-dipyridyl will complex V^{2+} rather than V^{3+}, there is no indication in the literature, nor have we seen, that such ligands exist in strong acid solution. We have, however, been able to show that the V^{2+}/V^{3+} redox couple with V^{2+} made by chemical reduction using Zn, can perform adequately in our chemically regenerative redox fuel cell.

The electrode reactions and the redox potentials for the V^{2+}/V^{3+} vs VO_2^+/VO^{2+} system are,

$$\text{cathode:}\quad VO_2^+ + 2H^+ + e \rightleftarrows VO^{2+} + H_2O\,(E_0 \sim 1.0\text{ V}) \tag{8}$$

$$\text{anode:}\quad V^{2+} \rightleftarrows V^{3+} + e\,(E_0 \sim -0.25\text{ V}) \tag{9}$$

The catholyte consisted of a mixture of 200 cm³ saturated V_2O_5 solution in 2 M H_2SO_4 (0.21 M V_2O_5), 50 cm³ 1 M $VOSO_4$ solution in 1 M H_2SO_4, and 3 cm³ concentrated nitric acid solution. The regeneration of the catholyte was carried out with a static pressure of O_2 of 1 atm at 78–80° C using the NO_3^- as the catalyst [6]. The anolyte consisted of 200 cm³ 1 M $VOSO_4$, 50 cm³ concentrated sulphuric acid (16 M H_2SO_4) and 20.5 g Zn in the form of pellets or rods. The performance of such a redox cell is shown in Fig. 6. The pH of the anolyte was ~1 but varied as Zn was consumed during the reduction. The pH of the catholyte was ~0. At a current density of 75 mA cm⁻² the IR-free cell voltage was 980 mV, which gives this redox fuel cell a potential limiting power density of 0.0735 mW cm⁻² at this voltage. These results were obtained from a redox cell with 'flow-by' configuration.

Fig. 7 shows a redox fuel cell discharged over 5 ohm external resistor with an initial anolyte concentration of 1 M V^{2+}. Without regeneration of the anolyte, the cell was able to deliver 170 mA at 900 mV for at least 8 h. The drastic decline in cell voltage after 10 h is related to the decreasing amount of V^{2+} ions as indicated by the large anodic polarization.

Another advantage of using the V^{2+}/V^{3+} redox couple is its low molecular weight (147 for VSO_4), especially compared to the molecular weight of tungstosilicic acid which is around 3 000. High concentrations (1–2 M) of anolyte can be used with only little effect on its viscosity and flow. This cell would have the potential capability of being electrically regenerated for stationary energy

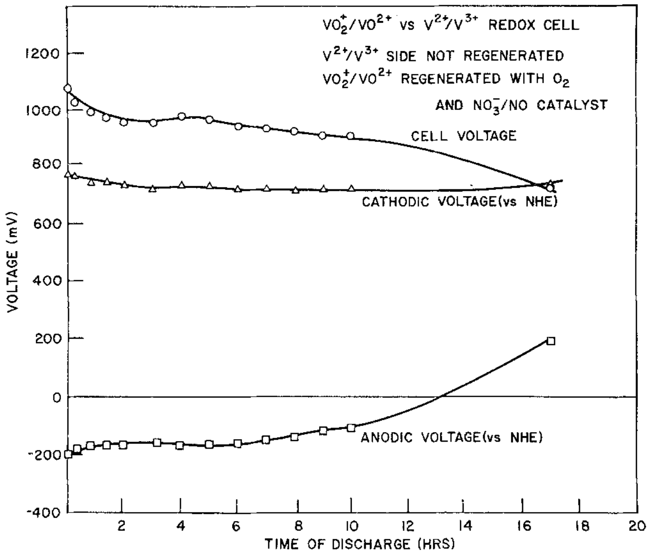


Fig. 7. Discharge curve of VO_2^+/VO^{2+} vs V^{2+}/V^{3+} redox fuel cell, 5 ohm external load; 'flow-by' rate, 230 $cm^3\ min^{-1}$.

storage systems and operate without anolyte–catholyte contamination.

4. Miscellaneous redox fuel cell experiments

4.1. *Formic acid as a H_2 generator*

The use of fuel other than H_2 and the generation of H_2 from other sources using a reformer have been studied and investigated extensively in fuel cell research. In the case of our redox cell it would be advantageous also to have reductants other than H_2. We have obtained data for a regenerative redox fuel cell in which formic acid, HCOOH, was used for the reduction of $H_4SiW_{12}O_{40}$ (TSA), most probably by an initial step involving the decomposition of the acid into H_2 and CO_2. Pd was used to catalyse this decomposition (Equation 10), which is thermodynamically favorable to the extent of 5 to 8 kcal mol^{-1},

$$HCOOH \xrightarrow{Pd} H_2 + CO_2 \qquad (10)$$

The performance of such a cell is shown in Fig. 8. At low current densities the cell performance is comparable to the regenerative redox fuel cell in which pure H_2 was used to regenerate the TSA. At higher current densities and over a longer period of discharge the production of H_2 from the decomposition of the formic acid at 35° C was not adequate for the continuous regeneration of the TSA redox couple. The concurrent production of CO_2 with the H_2 from the formic acid and the consumption of hydrogen has reduced the partial pressure of H_2 above the solution. It is possible of course to produce H_2 and CO_2 from the decomposition of formic acid catalysed by Pd in a separate unit and eliminate the CO_2 by scrubbing with alkali or by other means.

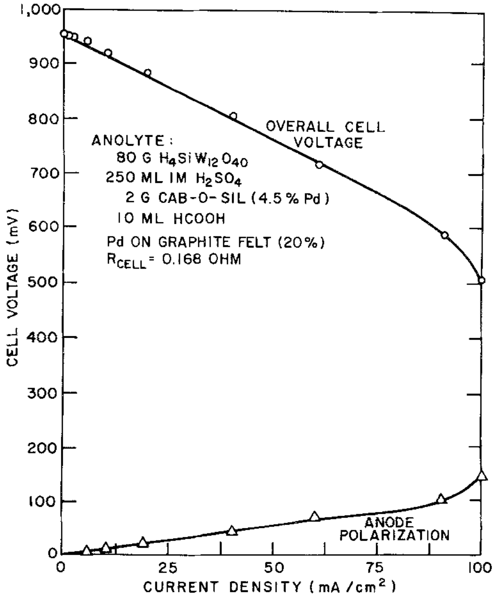


Fig. 8. VO_2^+/VO^{2+} vs $SiW_{12}O_{40}^{5-}/SiW_{12}O_{40}^{4-}$ redox fuel cell with anolyte regenerated by H_2 produced from Pd-catalysed decomposition of formic acid. 'Flow-by' rate, 230 $cm^3\ min^{-1}$, VO_2^+/VO^{2+} regeneration chamber at 75–80° C, TSA regenerated at 35° C.

4.2. *Experiments with different membrane systems*

Although the cationic membranes (DuPont's NAFION and Asahi Glass' SELEMION CMV) have good ionic conductivity, particulary for H^+ ions, they are not sufficiently selective and permit other cations, VO_2^+ and VO^{2+}, to pass through the membrane into the anodic compartment. Transfer of these reducible cations into the anodic half-cell may lead to gradual decline of overall cell performance, principally because of catholyte pH change as a result of the counter-movement of H^+ from anolyte to catholyte.

A redox fuel cell was built using a combination of a cationic and an anionic membrance (SELEMION CMV and AMV) in which one or two pinholes (30–40 μm diameter) were drilled into the anionic membrane. A schematic diagram of the cell using the two membranes is shown in Fig. 9. The performance of such a regenerative redox fuel cell with a combined anionic and cationic membrane is shown in Fig. 10.

A regenerative VO_2^+/VO^{2+} vs $SiW_{12}O_{40}^{4-}$ redox cell was tested in which an anionic membrance, SELEMION DMV, was placed between the anolyte and catholyte. Most anionic membrances have a higher resistance (0.35–0.60 ohm) measured in the acidic medium of the cell which we use. Hara, Okazaki and Fujinaga [11], however, reported that the DMV membrane allows protons to pass through this anodic membrane but essentially no other cations. Therefore this membrane has a better conductance in an acid medium than other anionic membranes. The performance of a cell with a SELEMION DMV anionic membrane is shown in Fig. 11. The overall cell performance is comparable to previous cells using cationic membranes. The internal resistance of the cell is 0.12–0.14 ohm. This membrane greatly inhibits VO_2^+ and VO^{2+} cation transfer [12].

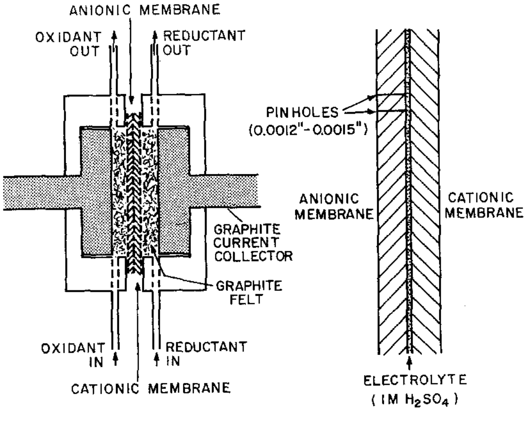


Fig. 9. Diagram of redox fuel cell with dual (cationic and anionic) membrane separator.

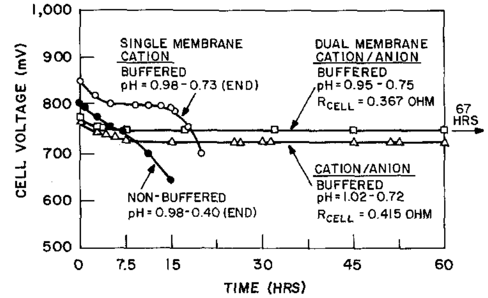


Fig. 10. Comparison of VO_2^+/VO^{2+} vs $SiW_{12}O_{40}^{5-}/SiW_{12}O_{40}^{4-}$ redox fuel cells with dual (cationic/anionic) and single cationic membrane separators; 'flow-by' rate 230 cm^3 min^{-1}, VO_2^+/VO^{2+} regenerated at 70–76° C, TSA regenerated at 25–30° C.

4.3. *Mixed heteropoly molybdo-tungsto-silicic acids*

Tungsten carbide, WC, has been used with some success as a replacement for noble metal catalysts in reduction with H_2. The activity of the WC catalyst is generally considerably lower than for noble metal catalysts and for this reason a higher temperature of reaction and a large catalyst surface area are needed. We have used a WC catalyst with a surface area of 5–10 m^2 g^{-1} in the reduction of TSA with H_2. At room temperature this reduction is very slow, but at higher temperature (70° C) when the WC catalyst showed some activity and the reduction to the dark blue $SiW_{12}O_{40}^{5-}$ takes place more readily, only a fraction of the TSA is reduced; because at the higher temperature the thermodynamic equilibrium is shifted towards H_2 and it is thermodynamically difficult to reduce TSA with H_2 at 1 atm. This shift toward increasing difficulty of reduction with H_2 is also reflected in the shift of the redox potentials of TSA (obtained by a.c. polarography) towards more negative potentials at higher temperatures.

According to Tsigdinos [13] the properties of the mixed heteropoly acids of molybdenum and tungsten are expected to be intermediate between

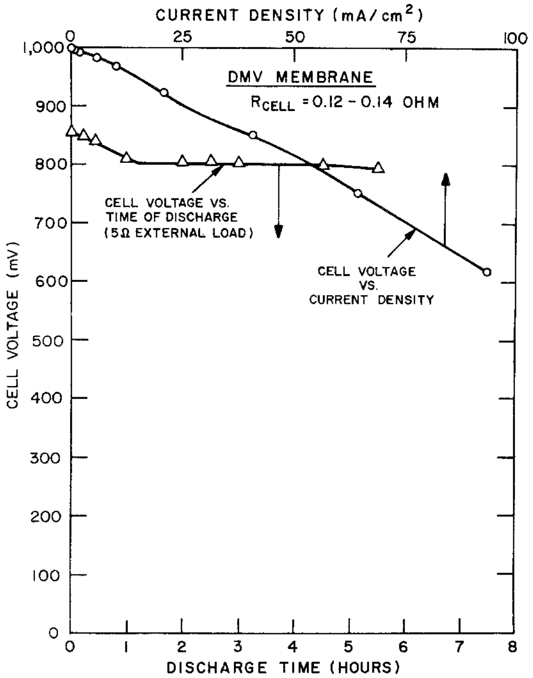


Fig. 11. Performance of VO_2^+/VO^{2+} vs $SiW_{12}O_{40}^{5+}/SiW_{12}O_{40}^{4-}$ redox fuel cell with anionic DMV membrane; 'flow-by' rate, 230 cm^3 min^{-1}.

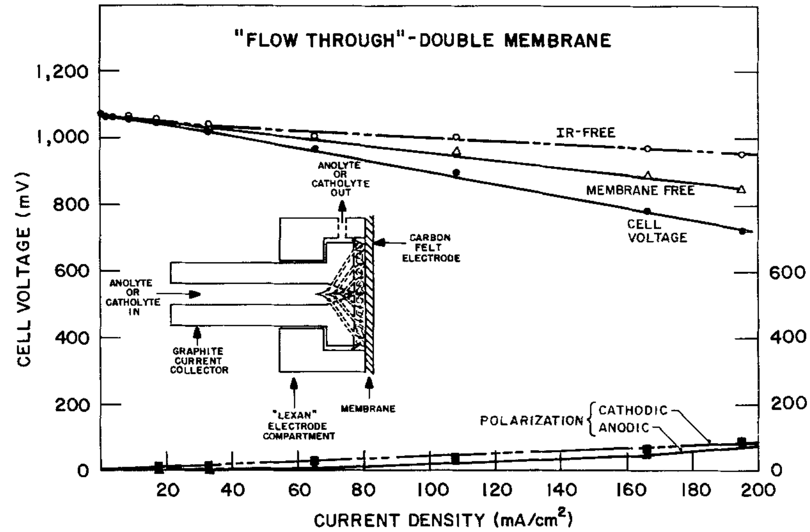
those of molybdosilicic acid and tungstosilicic acid. Molybdosilicic acid, $H_4SiMo_{12}O_{40}$, was synthesized and studied voltametrically; its first redox potential is +0.1 V vs saturated calomel electrode (SCE). The first redox potential of TSA is −0.25 V vs SCE which is very close to the H_2 redox potential. Three of the mixed heteropoly acids, $H_4SiMo_2W_{10}O_{40}$, $H_4SiMo_4W_8O_{40}$, and $H_4SiMo_6W_6O_{40}$, were synthesized and characterized polarographically. At 70° C and in a buffer of pH = 1.4 tetramolybdo-octatungstosilicic acid, $H_4SiMo_4W_8O_{40}$, has a redox potential of −0.15 V, close enough to the H_2 redox potential so that it is expected to be easily reducible with H_2 using the WC catalyst at 70° C. A redox cell was built with the VO_2^+/VO^{2+} catholyte (with $H_5PMo_{10}V_2O_{40}$ catalyst) and an anolyte consisting of a solution of 100 g tetramolybdo-octatungstosilicic acid in 250 cm^3 1 M H_2SO_4 and 4 g WC catalyst. At room temperature with WC catalyst the reduction of the heteropoly acid takes place at a very slow rate. At 60° C or higher the solution became dark blue within 1 h. The overall performance of this redox cell with the mixed heteropoly acid anolyte at low current densities was comparable to our previous cells using the TSA redox couple as the anolyte (using Pt as the regeneration catalyst and at room temperature). At higher current densities the rate of regeneration of the mixed heteropoly acid with H_2 using the WC catalyst at 60° C was slow compared to the rate of reaction at the electrodes as indicated by a large anodic polarization.

4.4. *Redox cell with 'flow-through' configuration*

In the 'flow-by' cell used, the flow distribution of the circulating electrolyte as it passes through the cell is not uniform. The electrolyte tends to pass directly from the inlet hole to the outlet hole and to give poor flow patterns at the edges of the cell away from the direct route from inlet to outlet. The overall cell performance in the 'flow-by' configuration improved at higher flow rates, although this performance seemed to reach its peak at a flow rate of 200–250 cm^3 min^{-1}. In the flow through' configuration, illustrated in Fig. 12 (insert), the freshly regenerated electrolyte flows more uniformly through the surface area of the felt electrode, is discharged electrically, and immediately exits from the felt into the outlet and is returned to the regenerator. The maximum flow rate used in this 'flow-through' configuration was 100–130 cm^3 min^{-1} and in most cases satisfactory performance was obtained at a flow rate of 75–95 cm^3 min^{-1}.

A redox fuel cell with 'flow-through' configuration was built and its performance evaluated. The anolyte consisted of 100 g $H_4SiW_{12}O_{40}$ in 250 cm^3 2 M H_2SO_4 solution and 2 g Cab-o-sil (3.5%Pt) catalyst. Previously we have tried to use the PTFE-coated Cab-o-sil catalyst but have experienced some problems with the circulation pump due to catalyst-clogging of the felt and the holes of the graphite electrode. The PTFE–SiO_2–Pt catalyst cannot be dispersed as well as the SiO_2–Pt catalyst, unless it is vigorously stirred for a number of days.

The catholyte consisted of 0.25 M $VOSO_4$ in 3 M H_2SO_4 solution to which 3 cm^3 concentrated nitric acid (16 M HNO_3) was added as the oxidation catalyst for 250 cm^3 of catholyte. The double membrane (cationic CMV and anionic AMV with two pinholes in the AMV), pressed together in 3 M H_2SO_4, was used as the separator. The high concentration of H^+ ions lowers the internal



$SiW_{12}O_{40}^{4-}$ redox fuel cell with NO_3^-/NO oxidation catalyst in 3 M H_2SO_4 solution and dual membrane separator. 'Flow-through' rate, 95 cm^3 min^{-1}; VO_2^+/VO^{2+} regenerated at 75–80° C, TSA regenerated at 25–30° C.

resistance of the cell (0.098–0.109 ohm) measured during the cell operation.

The discharge curve in Fig. 12 shows that at a current density of 180 mA cm^{-2} the cell voltage is 755 mV and the IR-free voltage is 960 mV. In this 'flow-through' configuration this novel chemically regenerative redox cell has a power density of 0.136 W cm^{-2}. Previously the highest power density obtained with a 'flow-through' redox cell with a double membrane (and having an internal cell resistance of 0.205 ohm) was 0.048 W cm^{-2}. The IR-free voltage of this acid redox fuel cell approaches that of alkaline cells.

If the regeneration of the VO_2^+/VO^{2+} catholyte was due to direct oxidation by HNO_3, and did not involve O_2, the stoichiometry of the oxidation reaction shows that the addition of each cm^3 of concentrated HNO_3 solution (16 M) would deliver $3 \times 16 \times 10^{-3}$ F of electricity or a total of $48 \times 10^{-3} \times 96\,500$ coulombs (1 287 m A h). Since we have added 3 cm^3 of HNO_3 (16 M) solution the redox cell would last for 19.3 h at 200 mA discharge current. Experiments with a 'flow-through' configuration using the above catholyte showed that the redox fuel cell could deliver 200 mA for 72 h or longer, thus showing that the NO_3^-/NO system acted as a catalyst for the regeneration of VO_2^+ from VO^{2+} and O_2.

5. Discussion and conclusions

The various redox fuel cell systems described in the previous paragraphs are of interest because the performance of the cell, as separate from the regenerator, is not a great deal less than that of a normal fuel cell.

Because of the relatively low H^+ ion concentration in the catholyte when a heteropoly acid catalyst is used for regeneration with O_2, compared to normal acid fuel cells, the cell has relatively higher internal resistance. It is possible that this can be overcome by a bipolar thin cell construction similar to the Alsthom fuel cell described by Warszawski *et al.* [14], since only two phases, liquid–solid, are present.

The use of the NO_3^-/NO catalyst system for the oxidation of VO^{2+} has improved the rate of catholyte regeneration and enables the cell to operate in a highly acidic medium thereby lowering the internal cell resistance. This improvement might not be sufficient for practical mobile application because it requires pure O_2 in order to prevent NO loss from the regenerator, unless a complexing agent for NO can be found that does not inhibit its reoxidation to nitrate ion by O_2. The oxidized vanadium solutions are not a strong adsorbent for NO [6].

Many fuel-cell concept vehicles assume the use of storage batteries to start-up when the fuel cell and reformer, if used, are cold and for added power during acceleration. In concept, the regenerated anolyte and catholyte solutions could also fulfil this task if sufficient amounts were present and if the maximum power output capability of the cell was in excess of the catalytic regeneration capacity so that short demands of high power could be met by regeneration during long lower power operation. It is instructive to investigate this possibility.

In order for the combined stored reductant and oxidant alone (exclusive of cell) to equal the specific energy density of a leadacid storage battery of 30 W kg^{-1} we would require the anolyte and catholyte to each contain 4 F (26.8 A h F^{-1}) of reductant and oxidant respectively per kg of each solution (2 kg total) assuming a cell voltage of 0.6 V.

If one considers the anolyte alone, the completely reduced TSA solution of 300 g dm^{-3} would represent only 0.077 F – much too low. Even if the concentration of the TSA solution were increased to the limit of solubility of 2 500 g dm^{-3} (0.8 M; $\rho = 3.0\ \mathrm{g\ cm}^{-3}$) the storage capacity would still be inadequate and the solution too expensive to replace batteries. This illustrates the futility of attempting to match the energy storage density of a battery with aqueous solutions in the 1 M range. The results with the 'flow-through' design and the use of the $\mathrm{Mo}^{3+}/\mathrm{Mo}^{4+}$ anolyte redox couple are encouraging and might provide some impetus towards solving some of the other problems associated with the cell. The high solubility and low molecular weight of the $\mathrm{Mo}^{3+}/\mathrm{Mo}^{4+}$ redox couple provides us an opportunity to work with an anolyte redox solution containing more 'fuel' per unit volume, and the improved mass transfer using the 'flow-through' design increases the power density of the cell. The separation of the catalyst system from the fuel cell proper can simplify repair in case of catalyst deactivation. The improvements in the electrochemical operation of the chemically regenerable redox fuel cell system, combined with possible improvements in the oxidation and/or reduction catalysts and regeneration reactions in the regenerator system, may improve the practical feasibility of the chemically regenerative redox fuel cell.

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