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Chemically regenerative redox fuel cells. I Membrane studies

R. LARSSON, B. FOLKESSON

Inorganic Chemistry 1, Chemical Center, University of Lund, P.O. Box 124, S-221 00 Lund, Sweden

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Three different types of membrane have been tested in a chemically regenerative redox fuel cell. It was found that a Nafion membrane gave the best polarization curves, but also that a much cheaper silica-filled polyethylene membrane could be used. A polysulphone membrane ranked number three.

1. Introduction

A redox fuel cell of a chemically regenerative type contains two redox systems (one of low normal potential, and the other one with a high normal potential) which are circulated past the electrodes, the anode and the cathode, respectively, (see Fig. 1). After electrochemical reaction at the electrodes, the solutions are passed into regeneration reactors where they are re-reduced or re-oxidized as the need may be. It is in these regeneration chambers that the catalysts are present, and it is here that the fuel is introduced as is also the oxidant, usually oxygen. After the regeneration step the solutions are once more circulated past the electrodes, and the process proceeds. The work of Kummer and Oei [1, 2] has shown the merits and the limitations of a redox type fuel cell. The attraction of this concept still remains: the possibility of avoiding catalysts at the electrode surface and the possibility of using simple (inexpensive) electrode materials and – even though not stressed by Kummer and Oei – the greater freedom of choice of fuels.

We have investigated the requirements for such a cell and in this paper we describe the results of studies on some membranes. A prime consideration is that the membrane should be made as cheap as possible. This means that the use of ion exchange membranes must be abandoned. Therefore, one has to search for other types of membrane. For instance, silica filled porous polymer membranes might be used: in this way proton conductance through the membrane is maintained.

2. Experimental details

2.1. *The Redox cell*

The cell construction is shown schematically in Fig. 1. 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. Three different kinds of membrane were used:

1. A commercial cationic exchange membrane, Du Pont Nafion 390.
2. A silica filled polyethylene membrane, the 'Submicro' battery separator from Evanite Battery Separator, Inc., Corvallis, Oregon. This membrane has a mean pore diameter $< 0.1\,\mu$ and a resistance of $0.25\,\Omega\,cm^{-2}$ after 24 h acid soaking.
3. A sulphonated polysulphone membrane (SPS), developed by Sandia National Laboratories, Albuquerque, New Mexico, especially for use in a zinc/ferricyanide battery. This membrane is highly conductive and extremely resistant against corrosion.

2.2. *Preparation of redox solutions*

As cathode redox couple we used VO_2^+/VO^{2+} ($E^0 = 1.00$ V [3]). The VO_2^+-solution was prepared by dissolving V_2O_5 in 1 M H_2SO_4. As anode redox couples we used V^{2+}/V^{3+} ($E^0 = -0.225$ V [3]), Ti^{3+}/TiO^{2+} ($E^0 = 0.100$ V [3]) and $Fe(EDTA)^{2-}/Fe(EDTA)^-$ ($E^0 = 0.117$ V [4]). The V^{2+}-solution was prepared by reduction of $VOSO_4$ in sulphuric acid with metallic zinc. The V^{2+}/V^{3+} anolyte solution thus contains Zn^{2+} ions. The Ti^{3+}-solution was commercially obtained as 1 M $TiCl_3$ in 10% hydrochloric acid. The $Fe(EDTA)^{2-}$-solution was prepared by dissolving iron (II) chloride and Na_2EDTA in an acetate buffer of pH 5.0.

The solutions were pumped through the cell in a 'flow-by' arrangement with a flow rate of 35 ml min^{-1}. Some experiments were also performed with a 'flow-through' arrangement, as described by Kummer and Oei [2].

No regeneration of the redox couples was carried out during the experiments described in this paper.

2.3. *Measurements*

Discharge curves for the redox cell were obtained by drawing currents through appropriate external resistors of 110, 50, 20, 10, 5, 2, 1 and 0 Ω for 2 min and recording the voltage and current at the end of these 2 min periods. The current was read on a Norma amperometer and the cell voltage on a Keithley 179A TRMS digital multimeter. The internal resistance of the cell was determined with a Metrohm conductometer E 382.

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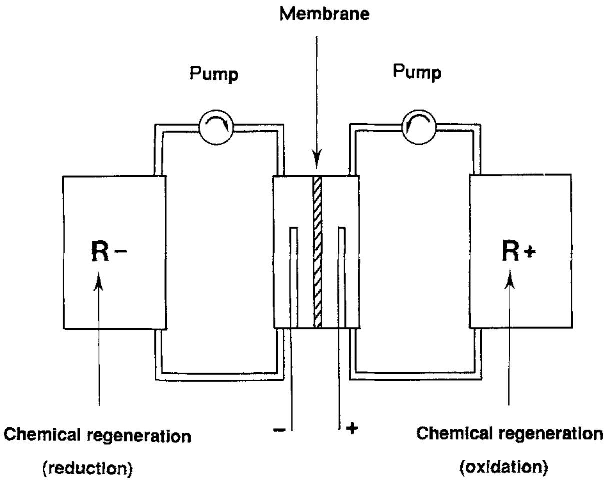

Fig. 1. A schematic picture of the chemically regenerative redox fuel cell.

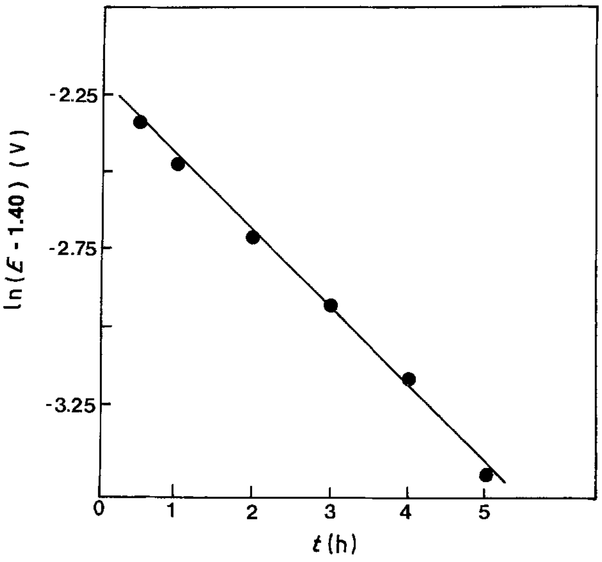

Fig. 3. Graphical analysis of the decay rate of the open cell voltage, E(V), from Fig. 2.

3. Results

3.1. *'Flow-by' cells*

Using the VO_2^+/VO^{2+} couple as cathode and V^{2+}/V^{3+} as anode system in sulphuric acid we have tested the 'Submicro' membrane. In open circuit we found that the cell voltage was tending towards a constant value of about + 1.40 V (Fig. 2). The fall-off curve could be described by a linear logarithmic function (Fig. 3), yielding the following expression for the open cell voltage as a function of time:

$$E = 1.51 - 0.11\,(1 - e^{-0.24t}) \qquad (1)$$

Our interpretation is that a membrane potential of about 0.11 V is set up by the migration of vanadium species across the membrane. The migration of vanadium species through membranes has recently been studied by Oei [5].

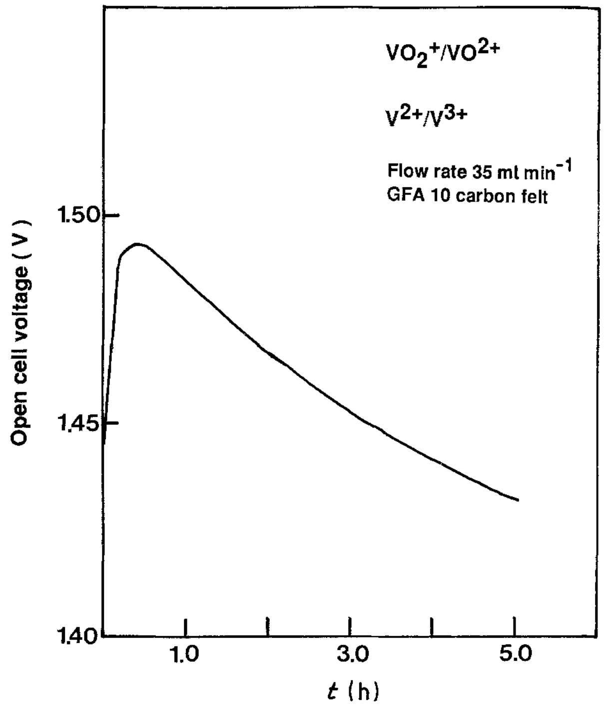

Fig. 2. Open cell voltage for a cell with 'Submicro' membrane as a function of time.

Using the same anode/cathode systems polarization curves have been obtained for the three different membranes (Fig. 4). Clearly, the most expensive Nafion membrane gives the best result. However, up to about 20 mA cm^{-2}, all three curves are more or less parallel but at higher current densities the 'Submicro' and SPS membranes give a lower cell voltage.

We have also tested the membranes using other redox systems. Figure 5 shows the polarization curves for the VO_2^+/VO^{2+} and Ti^{3+}/TiO^{2+} combinations. Nafion is also better in this case.

Figure 6 shows the result using the VO_2^+/VO^{2+} and $Fe(EDTA)^{2-}/Fe(EDTA)^-$ systems in combination. In this case the SPS membrane gives lower cell voltage and current density than the other two membranes. The polysulphone membrane thus presents a much higher ohmic resistance. This is probably to a large extent caused by proton diffusion from low to high pH solutions through the membrane. This diffusion is opposed to the direction of current.

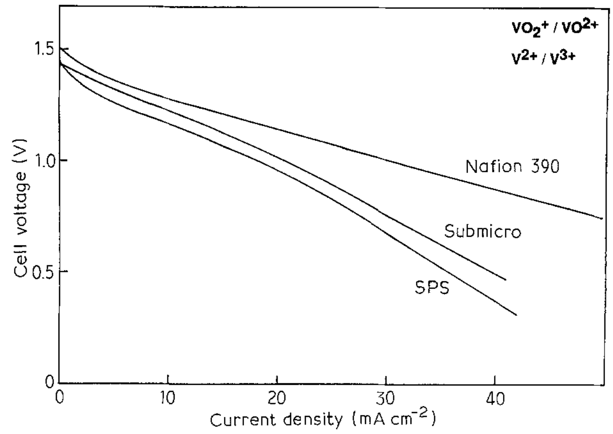

Fig. 4. Potential–current density curves for cells with different membranes. Cathode solution: 0.2 M $(VO_2)_2SO_4$ in 1 M H_2SO_4; anode solution: 0.8 M VSO_4 in 2.3 M H_2SO_4.

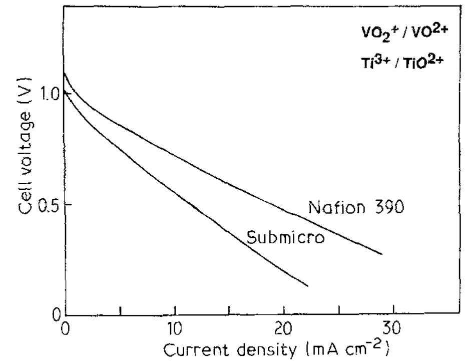

Fig. 5. Potential–current density curves for cells with different membranes. Cathode solution: 0.2 M $(VO_2)_2SO_4$ in 1 M H_2SO_4; anode solution: 1 M $TiCl_3$ in 10 % HCl.

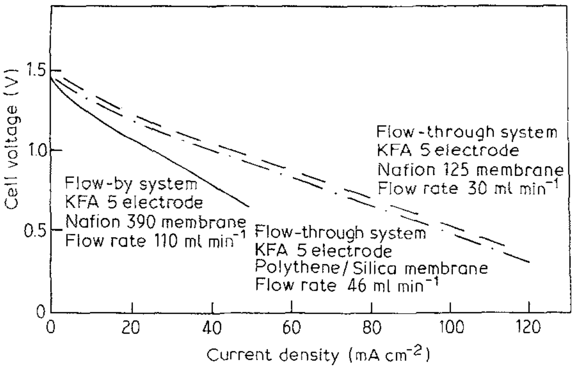

Fig. 7. Potential–current density curves for cells with different membranes. Cathode solution: 0.2 M $(VO_2)_2SO_4$ in 1 M H_2SO_4; anode solution: 0.8 M VSO_4 in 2.3 M H_2SO_4. The two upper curves are obtained with a 'flow-through' cell.

3.2. *'Flow-through' cell*

Using the VO_2^+/VO^{2+} couple as cathode and the V^{2+}/V^{3+} as anode system in sulphuric acid we have also tested the 'Submicro' membrane in a cell with a flow-through arrangement. The results given in Fig. 7 show that it is possible to achieve almost the same polarization curve with this polyethylene–silica membrane as with the Nafion membrane. Figure 7 also illustrates the advantage of using a flow-through system compared to a flow-by one, as much higher current densities are obtained. The difficulty for the flow-through system is to achieve an effective flow in the porous electrode material without seriously increasing the flow resistance. In our approach we have followed Kummer and Oei [2] in forcing the electrolyte through the porous felt electrode perpendicular to the solid electrode surface.

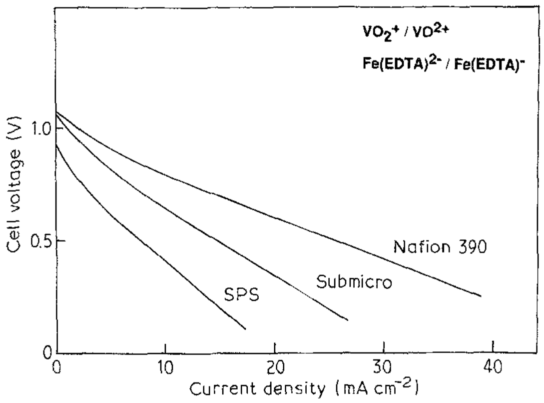

Fig. 6. Potential–current density curves for cells with different membranes. Cathode solution: 0.2 M $(VO_2)_2SO_4$ in 1 M H_2SO_4; anode solution: 0.05 M $Na_2Fe(EDTA)$ in HAc/Ac^- buffer solution of pH 5.0.

4. Conclusion

The experiments show that a simple membrane such as the 'Submicro' can be used with reasonably good results. In this way it is possible to construct less expensive cells of the chemically regenerative type. In spite of the good result (from Fig. 2) in open circuit, it is to be expected that a metal ion leakage will take place through the membrane under current load. However, it is likely that the advantage of reduction in cost will outweigh any disadvantage due to this leakage. The leakage may also be counteracted by a suitable choice of redox system on both sides of the membrane.

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