JOURNAL OF APPLIED ELECTROCHEMISTRY 15 (1985) 231–235

Permeation of vanadium cations through anionic and cationic membranes

DJONG-GIE OEI

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

Received 21 May 1984; revised 19 June 1984

The permeability of four commercially available ion-exchange membranes, the cationic Nafion 125 (duPont) and Selemion CMV (Asahi Glass) membranes and the anionic Selemion AMV and DMV membranes, to vanadyl, VO^{2+}, and vanadic, VO_2^+, ions was studied. The results show that two important variables determine the usefulness of a membrane as a membrane separator in a redox cell. These are selectivity and membrane–electrolyte resistance. Only the DMV membrane was considered to meet the requirements of low permeability to vanadium cations and at the same time permitting H^+ ions to go through the membrane, thereby providing a very low membrane–electrolyte resistance in the redox fuel cell.

1. Introduction

Commercially available membranes are mostly developed for the industrial separation of cations and anions and are ion-selective rather than ion-specific. For special applications as a membrane separator in redox cells it is generally necessary to develop special membranes [1] to meet the specific requirements of the redox cell. Redox cells require a membrane separator to avoid mixing and direct chemical reaction of the oxidant and reductant electrolyte of the electrochemical power source. The function of the membrane separator is not only to physically separate the anolyte and catholyte, but also to provide a conduction path between the electrolytes. The logical choice for a membrane is therefore an ion-exchange membrane which will provide a conduction path for the electrolytes and at the same time provide a physical barrier for the separation of anolyte and catholyte.

In our chemically regenerative redox fuel cell [2, 3] using the VO_2^+/VO^{2+} vs $SiW_{12}O_{40}^{5-}/SiW_{12}O_{40}^{4-}$ redox couples, we have tried various types of ion-exchange membranes, both cationic and anionic, and have analysed the anodic reservoir for the presence of cationic vanadium species. The large size of the tungstosilicic acid (TSA) molecule, $H_4SiW_{12}O_{40}$, would inhibit its anion from easy passage through a membrane. Although the presence of vanadium cations in the anolyte does not have any detectable and deleterious effect on the anolyte performance in the redox cell, which was in continuous operation for 10 days (240 h), it is desirable to study the rate of permeation of these vanadium cations through the membranes.

2. Experimental details

Fig. 1 illustrates the equipment used for studying the permeability of the membranes to the VO_2^+ and VO^{2+} cations. One reservoir was filled with pure H_2SO_4 solution (1 M and 3 M) and the other reservoir was filled with a saturated V_2O_5 (for VO_2^+ ions) solution or a 0.25 M $VOSO_4$ solution in either 1 M or 3 M H_2SO_4. The concentration of a saturated V_2O_5 solution is 0.165 M in 1 M H_2SO_4 and 0.245 M in 3 M H_2SO_4 solution. Both the solution containing vanadium ions and the pure H_2SO_4 solution were circulated simultaneously through the cell compartments of the redox cell which were separated by the ion-exchange membrane. The graphite felt electrode, graphite current collector and the membrane are assembled in the same way as in the 'flow-by' redox cell [2], but is not used electrically. The geometrical area of the exposed membrane is 6.05 cm^2. Samples (5 ml) were withdrawn as a function of time from the reservoir which previously contained a H_2SO_4

0021-891X/85 $03.00 + .12

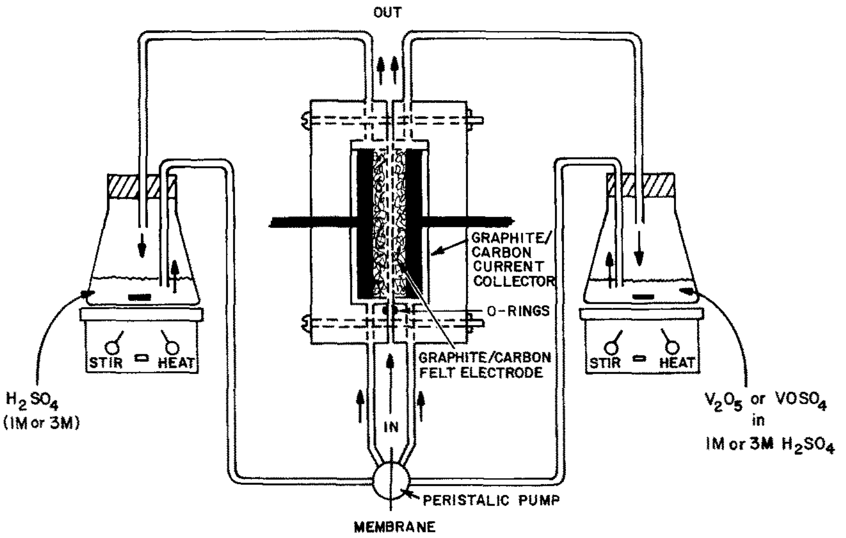

Fig. 1. Equipment for studying the permeability of membranes to vanadyl, VO^{2+}, and vanadic, VO_2^+, ions. Exposed membrane area: 6.05 cm^2.

solution only, and the samples were analysed for vanadium with an atomic absorption (AA) spectrophotometer. The temperatures of both reservoirs were held constant at 40, 50 and 60° C, respectively. The cationic membranes tested were Selemion CMV (Asahi Glass Co. Ltd) (0.11–0.15 mm thick) (CMV) and Nafion 125 (duPont) (0.125–0.13 mm) (NAF), and the anionic membranes tested were Selemion AMV (0.11–0.15 mm) (AMV) and DMV (0.13–0.17 mm). Pre-treatment of the membranes consisted of boiling in H_2O for 30 min and storing the membranes in distilled water until they were used.

3. Results and discussion

The permeability of two cationic and two anionic membranes to VO_2^+ ions were determined at 40, 50 and 60° C. Changes in the trend of permeability of the membranes as a function of temperature were similar for each of the membranes and in essence the permeability of the membrane increased at higher temperatures. The permeability of the membranes to the vanadium cations as a function of temperature did not follow the Arrhenius rate equation; the logarithm of the flux of vanadium ions plotted against $1/T$ was not linear. A temperature coefficient of the permeability would be valid for a narrow temperature range only. The results of measuring the permeability to VO_2^+ ions of the four membranes in 1 M and 3 M H_2SO_4 solutions at 50° C are shown in Fig. 2. As expected the anion selective membranes, AMV and DMV, were also permeable to the vanadium cations although to a lesser degree.

Fig. 2 shows that the permeability of the membranes to the vanadic, VO_2^+ ions is reduced as the concentration of sulphuric acid increases from 1 M to 3 M. This phenomenon is contrary to the fact that the solubility of V_2O_5, and therefore the VO_2^+ concentration, is higher in 3 M H_2SO_4 (0.245 M V_2O_5 per dm^3) than in 1 M H_2SO_4 (0.165 M V_2O_5 per dm^3). Although the concentration gradient is the driving force in transporting ions through the membrane, it is also obvious that the permeability of the membrane is a function of the solvent medium. The pre-treatment of the membrane by boiling in distilled water for 30 min and storing in water before its use in the experiment causes the membrane to 'swell', that is to allow water molecules to reside in the pores of the membrane and thus to provide paths for the transport of the ions through the membrane [4]. As the concentration of the sulphuric acid increases, so does the external osmotic pressure, and the membrane shrinks and inhibits the transport of ions through the membrane. This agrees with the results shown in Fig. 2.

For the cationic membranes, NAF and CMV, the number of vanadium ions passing through the membrane (6.05 cm^2) in 3 M H_2SO_4 after 30 h was still high, that is 400 and 840 ppm V, respectively, even though this was smaller than the number going through the membrane in 1 M H_2SO_4, 820 ppm V for NAF and 3075 ppm V for CMV. The anionic membranes, AMV and DMV,

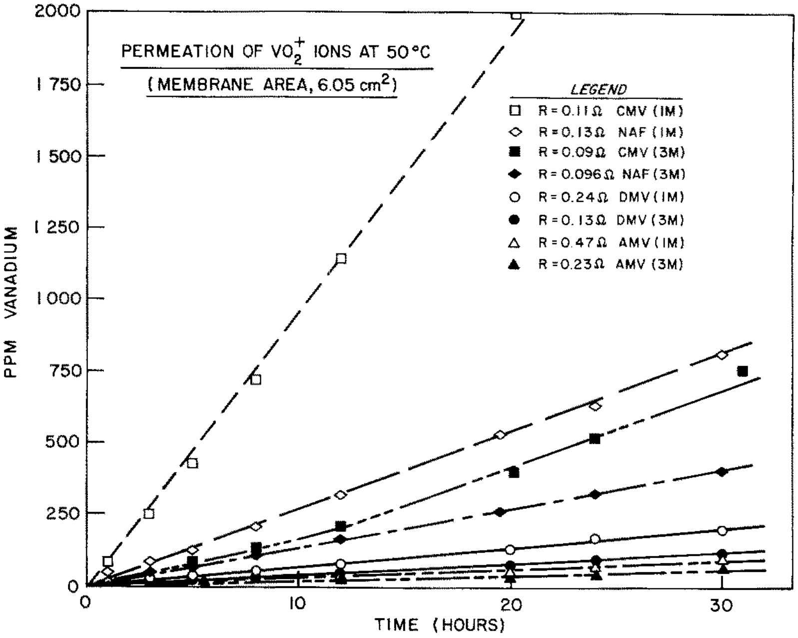

Fig. 2. Permeability of 2 cationic (NAF and CMV) and 2 anionic (AMV and DMV) membranes to vanadic, VO$_2^+$, ions at 50° C.

have a much lower permeability to the vanadium cations, even in 1 M H_2SO_4, because of their anion-selective property. In 1 M H_2SO_4 solution the amount of V found on the other side of the membrane after 30 h was 72 ppm V for the AMV membrane and 200 ppm V for the DMV membrane, and in 3 M H_2SO_4 even lower values were obtained, 48 ppm V for AMV and 116 ppm V for DMV.

In the chemically regenerative redox fuel cell [2], although the catholyte primary contains vanodic, VO$_2^+$, ions, the discharge reaction at the electrode produces vanadyl, VO^{2+}, ions according to the reaction,

$$VO_2^+ + 2H^+ + e \rightarrow VO^{2+} + H_2O \qquad (1)$$

Fig. 3 shows the permeation of the vanadic and vanadyl ions through the cationic CMV and

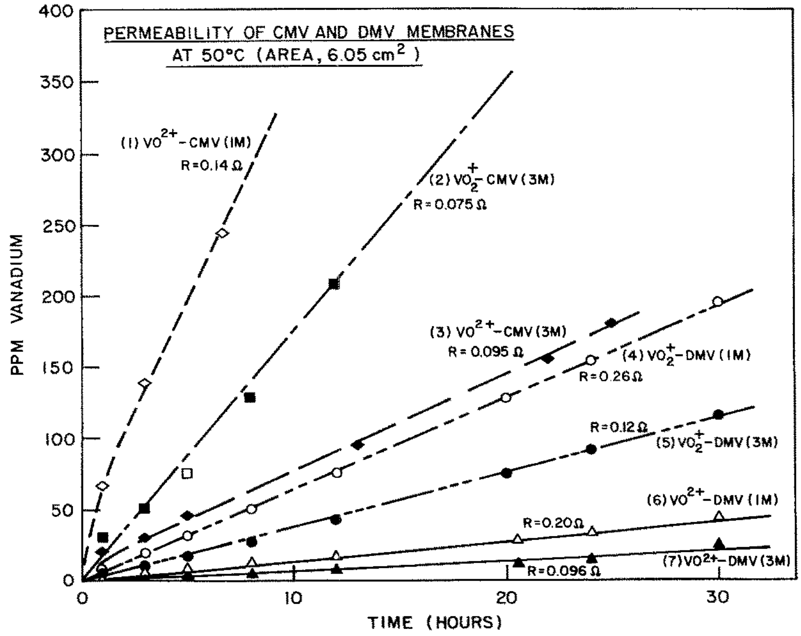

Fig. 3. Permeability of CMV and DMV membranes to vanadyl, VO^{2+}, and vanadic, VO$_2^+$, ions at 50° C.

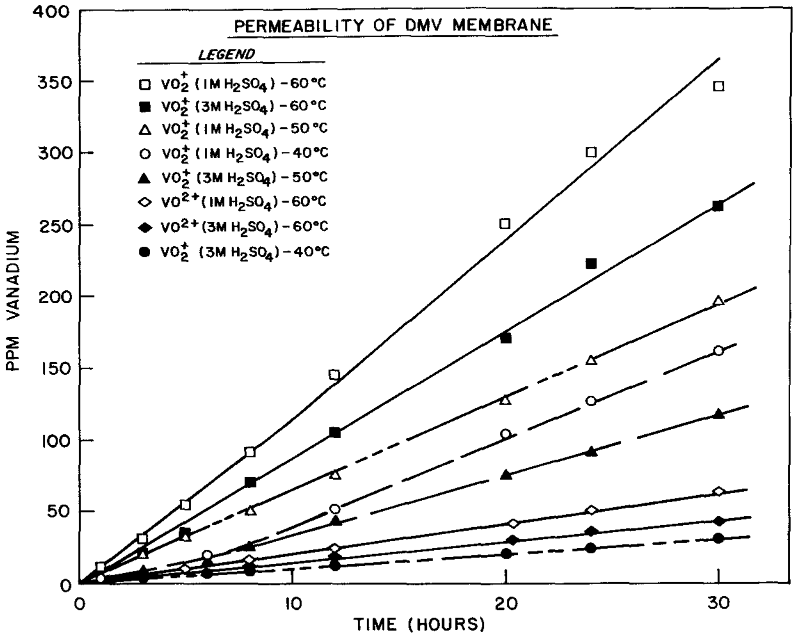

Fig. 4. Permeability of DMV membrane to VO_2^+ ions at 40, 50 and 60° C, and to VO^{2+} ions at 60° C.

anionic DMV membranes. The graphs (1–7) in Fig. 3 show that the membranes were less permeable to the divalent vanadyl ions, VO^{2+}, than to the monovalent vanadic ions, VO_2^+.

The permeability of the anionic DMV membrane to both the VO_2^+ and VO^{2+} ions at 40, 50 and 60° C is summarized in Fig. 4. At 50° C only 115 ppm V in the form of VO_2^+ ions was found to pass through the DMV membrane in 3 M H_2SO_4 after 30 h, and much less in the form of VO^{2+} ions, 25 ppm V (the results at 50° C were not plotted because the graphs were somewhat overlapping). The graph in Fig. 4 for the permeation of VO^{2+} ions through the DMV membrane is for the data obtained at 60° C; it shows that only 40 ppm V was found to pass through the membrane in 3 M H_2SO_4 solution after 30 h.

In our redox fuel cell [2] the catholyte consists of the VO_2^+/VO^{2+} redox couple and the anolyte consists of the $SiW_{12}O_{40}^{5-}/SiW_{12}O_{40}^{4-}$ redox couple. It is assumed that the large and bulky $SiW_{12}O_{40}^{n-}$ anion has considerably less mobility in the electrolyte solution and is expected not to permeate the membrane. The graphs in Fig. 2 show that the anionic AMV membrane has the lowest permeability to the vanadic, VO_2^+, ions and next to lowest is the anionic DMV membrane.

In a redox fuel cell a high internal (membrane–electrolyte) resistance causes a large internal IR drop and therefore a large undesirable internal energy loss. The total resistance of membrane and electrolyte in the cell was measured and indicated in the graphs of Fig. 2 corresponding to the membranes tested. Each of the membranes was tested in the same cell configuration and the same area of the membrane (6.05 cm^2) was exposed. The specific resistances ($\Omega\,cm^2$) of the membrane–electrolyte combinations are tabulated in Table 1.

In the highly acidic medium of the redox cell the internal resistance of the membrane–electrolyte is expected to be lower for the cationic membranes than for the anionic membranes, and this was borne out by the experimental results. The anionic AMV membrane has the highest membrane–electrolyte resistance, 0.47 Ω in 1 M H_2SO_4 and 0.23 Ω in 3 M H_2SO_4. The DMV membrane, although an anion selective membrane, will transport H^+ ions [5] and this rather unique

Table 1. Membrane–electrolyte resistance

Membrane	*Resistance* ($\Omega\,cm^2$)	
	1 M H_2SO_4	3 M H_2SO_4
NAF	0.78	0.58
CMV	0.67	0.54
AMV	2.84	1.39
DMV	1.45	0.79

property translates into a lower membrane–electrolyte resistance in highly acidic media. The measured resistances for the DMV membrane were 0.10–0.13 Ω in 3 M H_2SO_4 and 0.22–0.24 Ω in 1 M H_2SO_4. For the cationic membranes the measured membrane–electrolyte resistances were 0.13 Ω in 1 M H_2SO_4 and 0.10 Ω in 3 M H_2SO_4 for the NAF membrane, and 0.11 Ω in 1 M H_2SO_4 and 0.09 Ω in 3 M H_2SO_4 for the CMV membrane. The electrical resistance and permeabilities were measured on membranes of almost equal thickness, 0.11–0.15 mm. This dimension may be a practical limit for obtaining a membrane with sufficient mechanical strength and low electrical resistance.

These results show that, although the AMV membrane has the lowest permeability for the VO_2^+ cations, the internal membrane–electrolyte resistance for this membrane is too high for a membrane separator in a redox fuel cell. A resistance of less than 0.10 Ω was frequently achieved in experiments with a DMV membrane. This rather unique combination of properties of the DMV membrane, namely anion-selectivity (less permeable to cations) except for H^+ ions (highly conductive in acids), has guided our choice in selecting membranes for the redox fuel cell.

4. Conclusion

This study of four commercially available membranes showed that for the chemically regenerative redox fuel cell operating in highly acidic solutions it is desirable to choose a membrane separator with similar properties to the anionic DMV membrane. The DMV membrane has good anion selectivity and because it is permeable to H^+ ions it has low resistivity [5]. Presently most of our experiments with the chemically regenerative redox cell are based on the use of the DMV membrane as the separator. The choice of membrane separator is important for improved overall cell performance and to avoid excessive contamination of the anolyte by cations.

Acknowledgements

The author wishes to thank Mr Y. T. Lu and Dr L. C. Westwood for the V analysis by AA, and Dr J. T. Kummer for discussions, suggestions and advice.

References

[1] S. S. Alexander and R. B. Hodgdon, 'Anion Permselective Membrane', NASA CR-135316 (1978).

[2] J. T. Kummer and D-G. Oei, *J. Appl. Electrochem.* 12 (1982) 87.

[3] *Idem,* 'Chemically Regenerative Redox Fuel Cells' Paper presented at the 183rd ACS National Meeting, Division of Industrial and Engineering Chemistry, Abstract 62, Las Vegas, Nevada, April 1982.

[4] W. G. F. Grot, G. N. Munn and P. N. Walmsley, 'Perfluorinated Ion Exchange Membranes', Paper presented at the 141st National Meeting, The Electrochemical Society, Houston, Texas, May 1972.

[5] H. Hara, S. Okazaki and T. Fujinaga, *Bull. Chem. Soc. Jpn.* 54 (1981) 1257.