

Oxygen Reduction at the Silver / Hydroxide-Exchange Membrane

Interface

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Abstract

A solid-state cell is used to study the electrocatalysis of oxygen reduction at the silver/hydroxide-exchange membrane interface. The catalyst/membrane interface exhibits improved performance in comparison to a catalyst/aqueous sodium hydroxide interface. Surprisingly, the half wave potential for oxygen reduction is shown to shift 185 mV higher at the silver/ Hydroxide-Exchange Membrane Interface than for the silver/aqueous hydroxide solution interface, and the exchange current density is significantly higher at $1.02 \times 10^{-6} \text{ A m}^{-2}$. On a cost/performance basis the use of silver electrocatalysts in a hydroxide-exchange membrane fuel cell may prove better performance than platinum in a proton exchange fuel cell environment.

Keywords

Oxygen reduction reaction; Electrocatalyst; Alkaline membrane; Solid-state cell; Silver

1. Introduction

The electrochemistry of the oxygen reduction reaction (*orr*) on metal electrodes is usually studied in liquid electrolytes such as sulphuric acid and perchloric acid. However, the presence of adsorbing anions in liquid electrolytes results in competitive adsorption on the metal catalyst surface [1], which can lower the rate of reactions such as the *orr*. In solid polymer electrolytes, where ions are not freely mobile, electrode kinetics may differ greatly [2]. It is therefore important to study catalysis at solid polymer electrolyte interfaces.

Anionic-exchange solid polymer membranes are promising for fuel cell applications. One of the advantages of alkaline membranes is enhanced electrokinetics of the *orr* which leads to the use

of cheaper, non-platinum metal catalysts such as silver [3-5]. Also, a wider range of materials can be used in alkaline fuel cells as many more materials show corrosion resistance in alkaline than in acid environments. Another advantage is favourable water and ion management. As water is produced at the anode and consumed at the cathode, the reverse of that in a cationic-exchange membrane such as Nafion, flooding of the cathode is prevented and in fuel cells utilising a liquid fuel such as methanol, fuel crossover is reduced [6].

Silver has been shown to be a promising electrocatalyst for the reduction of oxygen in alkaline systems [7, 8]. In this paper we present a study of the *orr* activity of a high surface area silver catalyst at an anionic-exchange solid polymer membrane. For comparison, results obtained in sodium hydroxide are also included. This experimental approach was previously used to study electrochemical reactions such as methanol oxidation [9] and oxygen reduction [10, 11] at the microdisk electrode/Nafion interface.

2. Experimental

2.1 Chemicals

The catalyst studied was a silver nanopowder (Aldrich, <100nm, 99.5 %, 5 m²g⁻¹ specific surface area). The electrolytic media were 0.5 mol dm⁻³ sodium hydroxide and an anionic exchange membrane, AAEM60 [4, 5, 12]. Sodium hydroxide solutions were prepared using deionised water (18 MΩ cm, Millipore Elix 5). The solutions were deoxygenated with research grade (99.9999%) argon prior to the experiments, and were subsequently oxygenated with research grade (99.9999%) oxygen. Membranes were hydrated prior to experiments in 1 mol dm⁻³ KOH solution for one hour with a change of solution after 30 minutes. They were then rinsed with deionised water to remove excess KOH.

2.2 Preparation of the electrodes

The working electrodes in all experiments were 50 μm diameter silver-wire-in-glass microelectrodes produced in our laboratories following the approach mentioned in ref 2. After manufacture, the microelectrodes were polished sequentially with 30 μm, 9 μm, and 0.5 μm

alumina paper (Agar Scientific). The silver nanopowder catalyst was then abrasively attached to a microelectrode [13, 14].

2.3 Electrochemical measurements

Voltammetric measurements were performed at room temperature ($21 \pm 1^\circ\text{C}$) using an Autolab general purpose electrochemical system (Ecochemie, Netherlands).

In all experiments, the counter electrode was a platinum disk and the reference electrode was a dynamic hydrogen electrode (DHE) [2, 9]. For the experiments in sodium hydroxide electrolyte, a three compartment cell was used with a Luggin capillary for the reference arm and a glass frit between the counter electrode compartment and the main cell. For the experiments at the AAEM60 membrane, a solid-state cell was used, as described by Jiang et al. [2, 9].

3. Results and Discussion

Figure 1 shows the base voltammogram of a silver nanopowder modified microelectrode cycled at an anionic-exchange membrane, AAEM60. For comparison, a voltammogram for the Ag/NaOH system is overlaid. The features are typical of Ag/NaOH electrochemistry [15]. Similar voltammetry is shown for the Ag catalyst in the two different electrolytic media, although the Ag/AAEM60 system shows broader peaks.

The real surface area of the silver microelectrode can be estimated from a voltammogram using the surface charge of a silver oxide monolayer, which has been reported as 2.10 C m^{-2} [16]. For the Ag electrode cycled at the AAEM60 membrane, the electrode surface area was found to be $8.20 \times 10^{-7} \text{ m}^2$. For the Ag/NaOH system this was calculated to be $8.50 \times 10^{-7} \text{ m}^2$ (roughness factors of 420 and 430 respectively). We estimate a loading of silver on the electrode of $0.17 \mu\text{g}$ ($8.5 \times 10^{-3} \text{ g cm}^{-2}$). Figure 2 shows a linear sweep voltammogram at a scan rate of 0.2 mV s^{-1} in the negative direction for oxygen reduction at a silver nanopowder modified $50 \mu\text{m}$ Ag electrode cycled at a AAEM60 membrane. For comparison, the linear sweep voltammogram for oxygen reduction at the Ag/NaOH interface is also shown. In each case, a well-developed limiting current plateau, can be seen, and the currents are reported as a ratio of the limiting current. For the same Ag catalyst, a 185

mV positive shift in the $\frac{1}{2}$ -wave potential is observed at the interface with the anionic-exchange membrane. This suggests that the *orr* is significantly more active at the anion-exchange electrolyte interface than in the aqueous electrolyte. Close observation of the voltammetry in the absence of oxygen (figure 1) shows that the initial formation of oxide, and reduction of the last remaining traces of oxide are both shifted to higher potential for the Ag/anionic-exchange membrane system. This suggests that the shift in $\frac{1}{2}$ - wave potential is due to the reduced coverage of oxide/hydroxide on the Ag surface at high potentials, providing a larger number of reaction sites. Changes of coverage of oxide as a function of electrolyte have been observed before, most notably platinum[2], however in that case OH adsorption commences at lower potential when the Pt is in contact with the solid electrolyte.

The limiting current against the membrane is $-0.033 \mu\text{A}$, smaller in magnitude than in the liquid electrolyte, where the value of i_L is $-0.13 \mu\text{A}$ for the same size electrode. This owes to the lower oxygen permeability of the membrane.

The product of the oxygen diffusion coefficient and the bulk concentration of oxygen in the electrolytes can be calculated from the steady-state diffusion-limited current at a planar microdisk electrode [17]:

$$i_L = 4nFDcr \quad (1)$$

where D is the diffusion coefficient ($\text{m}^2 \text{s}^{-1}$), c is the concentration (mol m^{-3}) and r is the radius of the disk (m). The limiting current for oxygen reduction at the silver catalyst cycled at the AAEM60 membrane was measured as $3.3 \times 10^{-8} \text{ A}$. The value of n for the *orr* is 4 and the radius of the microelectrode is $3 \times 10^{-5} \text{ m}$. These values yield the permeability, $Dc = 7.12 \times 10^{-10} \text{ mol m}^{-1} \text{ s}^{-1}$. At the Ag/NaOH interface, the calculated permeability is, $Dc = 2.80 \times 10^{-9} \text{ mol m}^{-1} \text{ s}^{-1}$. This latter value is close to that of Gubbins et al for oxygen transport in 0.5 M KOH at 25 °C, $1.9 \times 10^{-9} \text{ mol m}^{-1} \text{ s}^{-1}$ [18]. Permeation of oxygen through the membrane is shown to be approximately 3-4 times slower than oxygen diffusion in the sodium hydroxide solution.

Data points from the kinetically controlled regions of the steady-state curve were chosen for Tafel analysis. These data are corrected for mass-transport effects by calculating the parameter $i_L i / (i - i_L)$, where i is the measured current at a given potential and i_L is the limiting current. The inset to Figure 2 shows the mass-transfer corrected Tafel plot. The plot shows two well defined linear regions.

Values for the exchange current densities, j_0 , in the low and high current density regions may be obtained by extrapolation of the Tafel line to the equilibrium potential, E_{eq} , for oxygen reduction (1.23 V vs. RHE). The exchange current densities for oxygen reduction on the silver nanopowder catalyst in each of the electrolytic media are shown in Table 1. For comparison, values in the low current density region for oxygen reduction at a bulk polycrystalline Ag rotating disk electrode have also been included [8]. The Tafel slopes in the low and high current density regimes were shown to be similar between experimental systems. The only exception is oxygen reduction at Ag in 0.5 mol dm⁻³ NaOH, in which the Tafel slope is slightly higher in the low current density region.

Higher exchange current densities were observed for the silver nanopowder modified microelectrode/membrane system in comparison with the same catalyst in sodium hydroxide solution.

How does this catalyst-system compare to other oxygen reduction catalysts? Platinum is acknowledged as the element providing the highest *orr* activity. In a recent paper Gasteiger et al. provide performance information for platinum catalysts of different particle sizes [19]. Larger sized catalysts show higher activity. Table 2 Compares the specific activity of the silver catalyst at 0.9 V vs. RHE in both 0.5 mol dm⁻³ NaOH and at the AAEM60 membrane, with one of equivalent surface area in the Gasteiger et al. paper (Johnson Matthey HiSpec 1000, 4.9 m² g⁻¹). In the paper of Gasteiger et al, the catalysts are tested in 0.1 mol dm⁻³ HClO₄, although they see no difference in testing catalysts in perchloric acid or in contact with a proton-conducting solid polymer electrolyte. The Ag catalyst at the AAEM60 interface shows a specific activity which is 1/200th that of

platinum, although it is important to note that the catalysts in the Gasteiger et al. paper were tested under conditions which would produce larger specific activities than those used in our paper (60 °C, 5 mV s⁻¹ positive scan versus 22 °C, 0.2 mV s⁻¹ negative scan in our results). The *orr* activity of Ag catalysts increase by a factor of five as the temperature is increased from 25 °C to 80 °C [8]. Silver has three benefits over platinum. The first is that it costs 1/100th the price of platinum. The second is that silver is half the density of platinum - for catalysts particles of equivalent size, the silver catalyst will have twice the specific surface area compared to the platinum catalyst. The third is that silver may not suffer from a particle-size effect to the same extent as platinum. Data in reference 8 suggests that the specific activity of high surface area Ag/C (81 m²g⁻¹ based on a particle diameter of 7 nm) in 0.5 mol dm⁻³ NaOH is 0.009 A m⁻² at 900 mV vs.RHE and at 25 °C. Such a value is higher than the value of the silver catalyst we used under the same conditions, but less than the performance of our silver catalyst using the solid-state electrolyte. In comparison, the decrease in *orr* activity of platinum as a function of particle size was first seen in phosphoric acid fuel cells [20]. Gasteiger et al. show a three-fold drop in specific activity in moving from platinum catalysts with surface areas of 5 m² g⁻¹ to one of 79 m² g⁻¹. By moving to smaller Ag particles it may be possible to obtain performance which, although not matching the specific activity of Pt-based catalysts, exceeds them in terms of “cost-activity”. The catalyst costs of a fuel cell of equivalent performance may therefore be less.

4. Conclusion

The reduction of oxygen at silver has been studied at an anionic-exchange membrane and in a sodium hydroxide solution. Cyclic voltammetry of the catalyst in each of the electrolytic media showed that oxygen reduction currents were lower in the Ag/AAEM60 system than in the Ag/NaOH system, even though the surface areas of the electrodes were very similar in both experiments. This owed to the lower oxygen permeability of the membrane; diffusion of oxygen through the membrane is shown to be approximately 3-4 times slower than oxygen diffusion in the

sodium hydroxide solution. The $\frac{1}{2}$ wave potential for oxygen reduction shifts by 185mV in contact with the membrane. The Ag/AAEM60 system also showed a higher exchange current density.

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1. Tables

Table 1 Tafel slope (b) and exchange current density (j_0) for oxygen reduction at high surface area Ag in 0.5 mol dm^{-3} NaOH and at the AAEM60 membrane.

Electrolyte	Low current density		High current density		Reference
	$b(\text{V dec}^{-1})$	$j_0(\text{A m}^{-2})$	$b(\text{V dec}^{-1})$	$j_0(\text{A m}^{-2})$	
0.5 M NaOH (21 °C)	0.0874	4.18×10^{-7}	0.1311	1.48×10^{-5}	This work
AAEM60 (22 °C)	0.0738	1.02×10^{-6}	0.1339	2.20×10^{-4}	This work
0.5 M NaOH (25 °C)	0.070	1.4×10^{-7}			[8]

Table 2 Comparison of specific activity of Ag at 0.9 V vs. RHE in 0.5 mol dm^{-3} NaOH and at AAEM60 membrane. Reported values for platinum are also given.

Catalyst	Temperature (°C)	Electrolyte	$j_{s,0.9 \text{ V (RHE)}} (\text{A m}^{-2})$	$j_{M,0.9 \text{ V (RHE)}} (\text{A g}^{-1})$	$j_{M,0.9 \text{ V (RHE)}} (\text{A \$}^{-1})$	Reference
Ag ($5 \text{ m}^2 \text{g}^{-1}$)	22	AAEM60	0.03	0.15	0.39	This work
Ag ($5 \text{ m}^2 \text{g}^{-1}$)	21	0.5 M NaOH	0.003	0.015	0.039	This work
Pt ($4.9 \text{ m}^2 \text{g}^{-1}$)	60	0.1 M HClO ₄	6.2	31	0.778	[19]

2. Figures

Figure 1 Cyclic voltammograms for a silver nanopowder modified 50 μm Ag electrode cycled at a AAEM60 membrane (—), and in 0.5 mol dm⁻³ NaOH (- - -), at a scan rate of 5 mV s⁻¹ and at room temperature.

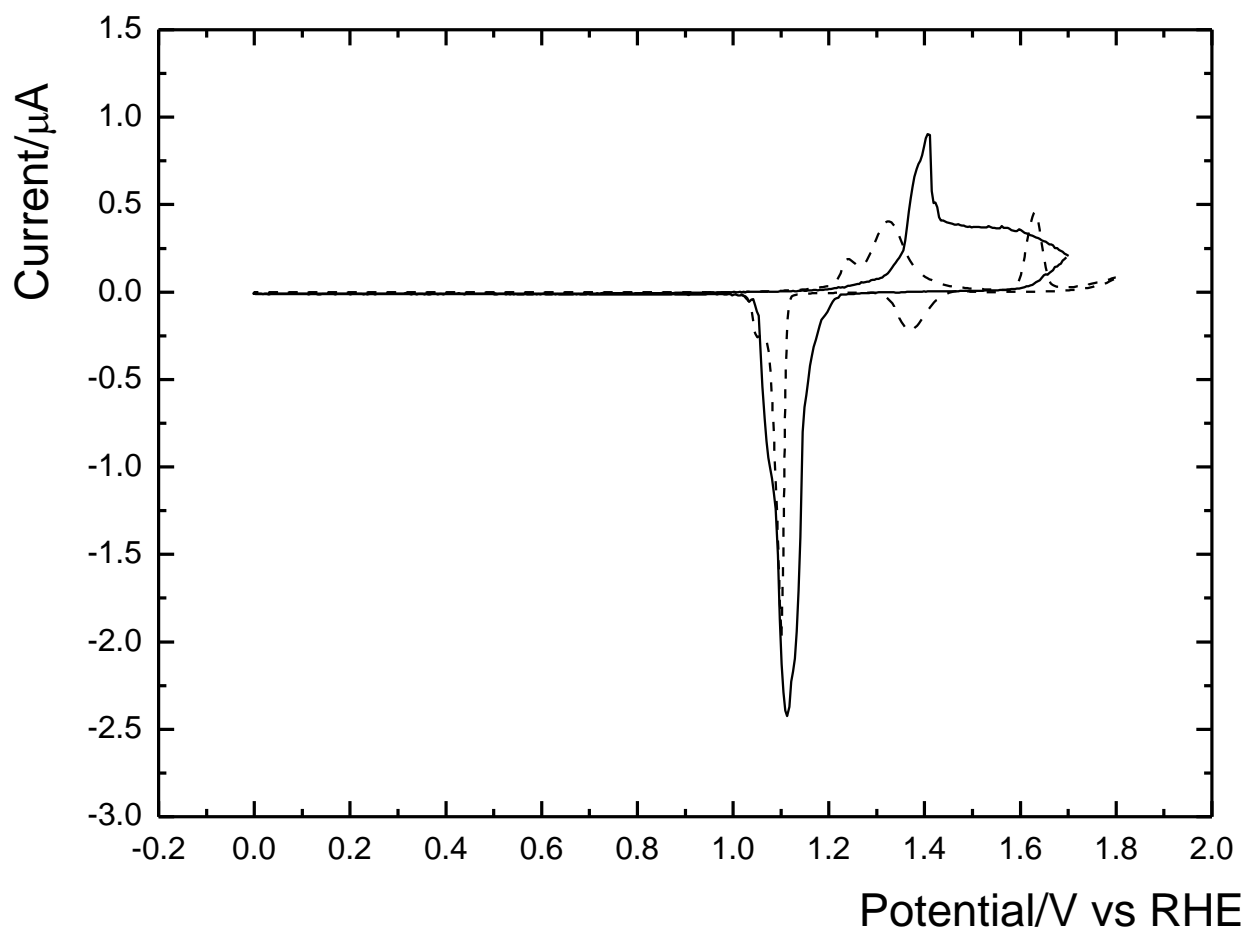


Figure 2 Linear sweep voltammograms for oxygen reduction reaction at a silver nanopowder modified 50 μm Ag electrode cycled at a AAEM60 membrane (—), and in 0.5 mol dm^{-3} NaOH (- - -), at a scan rate of 0.2 mV s^{-1} and at room temperature. Voltammograms are scaled by the limiting currents, see text. Inset: Mass-transfer corrected Tafel plot for oxygen reduction at the Ag/AAEM60 interface.

