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SHORT COMMUNICATION

Electrocatalysis on solid oxide electrolytes

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1. Introduction

It is generally accepted that the nature of the metal electrode is very critical in determining the rate of electrochemical reactions in cells employing solid oxides as electrolytes. On the other hand, the role of the oxide electrolyte itself in catalysing electrochemical reactions involving gases has not been given much attention. The purpose of this paper is to discuss some aspects of the electrocatalytic nature of the oxide electrolyte including enhancement of the rate of the cathodic reduction of oxygen by the presence of point defects such as interstitial protons on the electrolyte surface formed by water in the vapour phase. In the anodic oxidation of H_2, the solid electrolyte is implicated but CO was found to be practically electrochemically inactive compared with H_2. In a previous investigation [1] of the decomposition of nitric oxide on scandia-stabilized zirconia by the electrolytic removal of oxygen, it was the electrolyte itself that mainly catalysed the process, leading to an increase of several orders of magnitude in rates of decomposition over reaction on stabilized-zirconia in an electrochemically inactive system [2].

2. Experimental

The experimental set-up is shown schematically in Fig. 1. The essential part of the cell comprised an 8 mol % scandia-stabilized zirconia disc pressed between two alumina tubes with two gold rings as seals which also served as current collectors. Porous gold and platinum electrodes were prepared by firing at 850° C pastes of the particular metal provided by Englehard Industries and numbered: A-1560 and 6926 respectively. A gold wire 0·3 mm in diameter was welded to the gold seals by a spot-welder to provide the electrical leads. Generally, the gas samples were passed through a water saturator or a liquid nitrogen cold trap depending upon the purpose of experiment. Purified He gas was maintained in the chamber of the furnace. All electrical measurements were made on a Fluke 8200A digital voltmeter with an impedance of $10^{14}\,\Omega$.

The experimental observations consisted of measuring the current–potential characteristics, the cell overpotential, η, at a given current, I, being calculated from the following equation:

$$E = E_o \pm IR_{ac} \pm \eta. \quad (1)$$

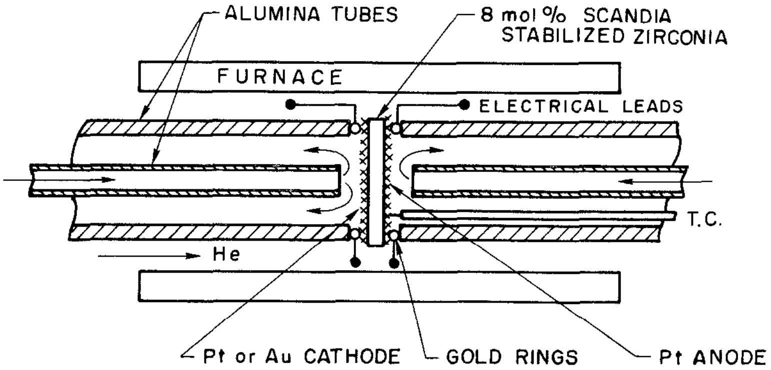

Fig. 1. Schematic diagram of the solid-electrolyte cell assembly.

E is the measured cell potential, E_0 is the open-circuit potential, and R_{ac} is the cell resistance obtained by a.c. techniques at 1 kHz. The positive and negative signs in Equation 1 represent the situations for externally driven cells and self-generating cells (fuel cells) respectively. Temperature was measured with a chromel–alumel thermocouple.

3. Results and discussion

3.1. *Cathodic reduction of oxygen*

Until recently the metallic electrodes were thought to play the predominant role in catalysing the electrochemical reactions of gaseous oxygen compounds in oxide electrolyte systems. Fabry and Kleitz [3] have noted that the reactivity of these oxygen electrode systems is accounted for by both the nature of the metal electrode and the composition of the oxide electrolyte. Also in some recent work of Pancharatnam *et al.* [1], it was observed that the rate of NO decomposition electrochemically on stabilized zirconia with platinum as the electrode was several orders of magnitude greater on the zirconia electrolyte than on platinum itself. It was hypothesized that point defects such as F-centres on the surface of the oxide electrolyte created by the presence of the electric field were responsible for the electrocatalytic processes of NO decomposition. In addition, the electrochemical system gave decomposition rates about 10^8 times that observed by Amirnazmi *et al.* [2] on bare zirconia in the absence of an applied electric potential at the temperature of 800° C. Furthermore, it was demonstrated [1] that NO could be decomposed at an appreciable rate with a porous electrode on an oxide electrolyte cell, even when the metallic electrode material such as gold is not itself catalytic for this reaction.

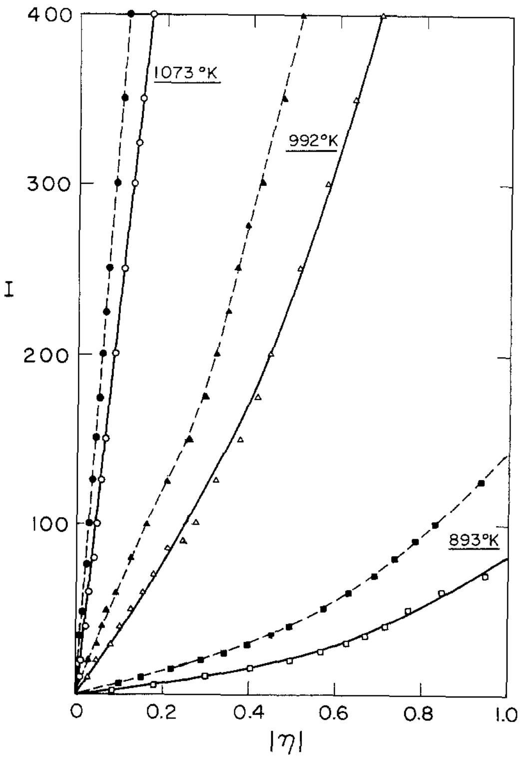

Fig. 2. Influence of water vapour on the cathodic overpotential in the reduction of oxygen on a gold electrode. (+) Air, Pt/$ZrO_2 \cdot Sc_2O_3$/Au, $O_2 + H_2O$(−).
—— 100% O_2 0% H_2O; – – – 96·9% O_2 23·1% H_2O.

In the present study Fig. 2 shows the influence of water vapour on the cathodic reduction of oxygen on an electrolyte coated with a porous Au electrode. As can be seen, the total current at a given overpotential η is substantially increased by adding a small amount (approximately 3% by volume) of water vapour to the oxygen-feed stream at the cathode. The same behaviour has been reported in the study of oxygen pumps using stabilized zirconia by Yuan and Kröger [4]. Similarly, the cathodic overpotential of an electrochemical cell using calcia-stabilized zirconia as the electrolyte with porous Pt paste electrodes has been observed by Yanagida *et al.* [5] to increase significantly in the absence of water vapour. In fact, this catalytic effect of water vapour on the current–overpotential characteristics has been reported not only in the reduction of O_2 on Pt [4, 5] but also in the decomposition of CO_2 as observed by Weisbart *et al.* [6]. For those runs [6] in which the feed gas consisting of CO + CO_2 is mixed with a small amount of water vapour, the cathode current efficiency was much higher than for runs using dry gaseous mixtures.

In order to interpret this electrocatalytic behaviour, the overall cathodic reduction of oxygen via the following defect reaction is one scheme to be considered:

$$O_2(g) + 2V_0^{\circ\circ}(ZrO_2) + 4e'(Au) \rightarrow 2O_0^x(ZrO_2) \quad (2)$$

where $V_O^{\circ\circ}$ denotes the doubly ionized oxygen-ion vacancies, and O_O^x represents the oxygen ions occupying the normal sites. It is clear that the three-phase contact zone where the electrode, electrolyte and gas are in mutual contact, is the most reasonable location for the preponderance of electrochemically active sites. As a matter of fact, the necessity of maintaining as much three-phase contact as possible has been shown by Karapachev and Filayev [7]. Furthermore, it has been pointed out by Casselton [8] that the charge transfer overpotential for the cathodic reduction of oxygen is not negligibly small. As a consequence, the rate of formation of oxygen ions (O_O^x) depends upon the electron transfer steps and the cathodic overpotential arising partially as a result of the irreversibilities of the electrochemical reactions.

In the presence of the water vapour, the oxygen ions (O_O^x), however, can be produced directly according to the defect reaction involving no net charge-transfer as follows:

$$H_2O(g) + V_O^{\circ\circ}(ZrO_2) \rightleftarrows O_O^x(ZrO_2) + 2H_i^{\circ}(ZrO_2). \qquad (3)$$

Wagner [9] has reported that the solubility of hydrogen in the $ZrO_2 + Y_2O_3$ solid solution as interstitial protons is proportional to the square root of the partial pressure of the ambient water vapor P_{H_2O} as expressed by the equation:

$$[H_i^{\circ}] = (K_s P_{H_2O}[V_O^{\circ\circ}]/[O_O^x])^{1/2} \qquad (4)$$

where K_s is the defect equilibrium constant of Reaction 3. The mole fraction of H_i° was estimated to be about 2×10^{-4} at 1000° C and 1 atm H_2O. The temperature dependence was small. Moreover, the diffusion coefficient of H_i° is of the order of $10^{-6}\,cm^2\,s^{-1}$ at 900–1000° C. This value is at least two orders of magnitude higher than that of oxygen ions by a vacancy mechanism reported by Kingery *et al.* [10].

Therefore, the catalytic effect of water vapour on oxygen reduction possibly may be attributed to its solubility on the surface of the oxide electrolyte. A possible electrode process involving the interstitial protons (H_i°) and leading to charge transfer and overall enhancement of the cathodic current is:

$$2e'(Pt) + 2H_i^{\circ}(ZrO_2) \rightleftarrows H_2(g). \qquad (5)$$

Or conceivably an overall process of reducing water such as: $H_2O(g) + 2e'(Pt) \rightarrow H_2(g) + O_O^x(ZrO_2)$ might be involved. Pursuant to further experiments, the interstitial proton formation and reaction via Equation 5 seem more plausible.

3.2. *Effects of anodic reactions on total cell overpotential*

It has been suggested by Weisbart and Ruka [11] that the anodic oxidation of fuel can occur in one of two ways: either (i) the oxygen ions (O_O^x) forming oxygen ($1/2\ O_2$) at the electrode surface and the latter then reacting with the fuel, or (ii) the oxygen ions (O_O^x) reacting directly with the fuel possibly at the electrode–electrolyte interface.

The experimental results of current versus overpotential shown in Fig. 3 were obtained by passing various gases through the anode compartment. Although the data points denoted by different symbols are quite scattered, they generally fall into a single curve except for H_2. It should be noted that the anodic overpotential at a given current for H_2 is considerably less than those of

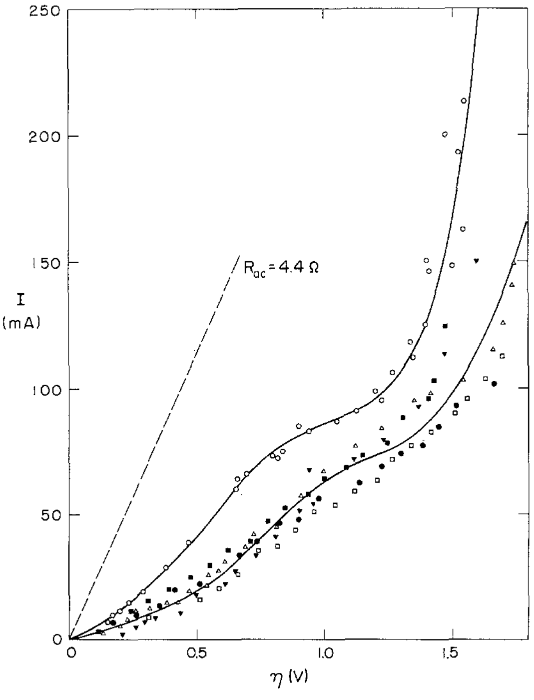

Fig. 3. Influence of anodic gases on overpotential behaviour. ○ H_2 (—) Air, Pt/$ZrO_2 \cdot Sc_2O_3$/Pt, X(+); △ CO; ▼ CO_2; □ He; ■ O_2; ● air. $T = 980°$ K, flow rate of gases $= 50\ ml\ min^{-1}$.

other gaseous species studied. For these other gases it is assumed that the elementary electrochemical step at the anode is:

$$2O_O^x(ZrO_2) \rightarrow O_2(Pt) + 4e'(Pt) + 2V_O^{oo}(ZrO_2). \qquad (6)$$

The exact state of the O_2 is unknown, but for a given overpotential the extent of this reaction appears to be similar for the series of gases represented by the lower curve. It would appear that with the family of various species represented by the lower curve, O_2 is being pumped from the cathode to the anode where little or no reaction occurs with the O_2. There is so much scatter that the detection of any significant reactivity of CO compared to anodically unreactive species such as He and CO_2, must await more refined experiments. However, it can be concluded that CO is electrochemically unreactive compared to H_2. The hydrogen may directly interact with oxygen on the electrolyte near the electrode or more possibly at the electrode–electrolyte interface via mechanisms (i) or (ii) above respectively. Or H_2 might form interstitial protons (reverse of reaction of Equation 5) and thence react with oxygen ions:

$$2H_i^o(ZrO_2) + O_O^x(ZrO_2) \rightleftarrows H_2O(g) + V_O^{oo}(ZrO_2). \qquad (7)$$

The high H_2 reactivity at the anode compared to that of CO may be due to this latter mechanism.

That there is no significant difference in overpotential characteristics for H_2 between a self-generating cell (or fuel cell) and a driven cell is depicted in Fig. 4 by the excellent reproducibility of current versus overpotential at 980 K. The trend towards current plateaus shown in Figs. 3 and 4 is most likely due to diffusional processes at the cathode, either surface-diffusion control or gas-diffusion control. The external gas flow rates were not sufficiently varied to establish which mechanism prevailed. The sharp rise in current near 1·5 V is probably due to the onset of electronic conduction.

4. Conclusion

Based on the preceding discussion, it is tentatively concluded that the oxide electrolyte cell acts as an oxygen concentration cell and the presence of point defects, such as interstitial protons on the oxide electrolyte surface, enhances the electrochemical reduction of O_2 at the cathode and may be responsible for catalysing the anodic oxidation of H_2.

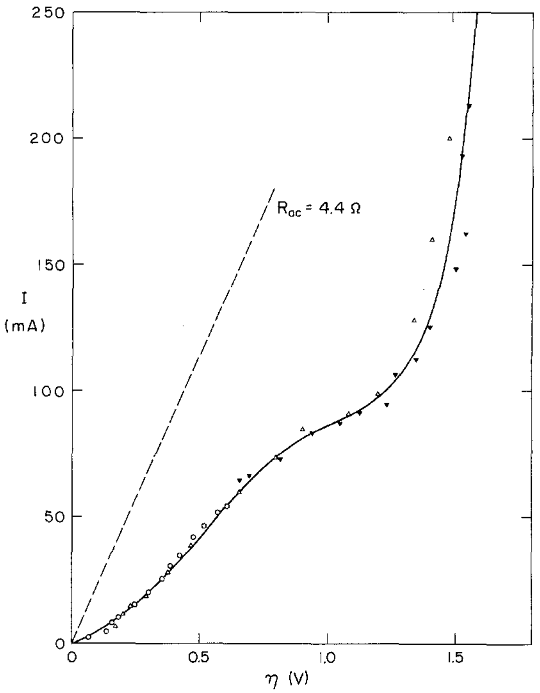

Fig. 4. Reproducibility of current-overpotential behaviour at 980° K. ○ (+) Air, $Pt/ZrO_2 \cdot Sc_2O_3/Pt$, H_2(—) fuel cell; (—) air, $Pt/ZrO_2 \cdot Sc_2O_3/Pt$, H_2 (+) driven cell; △ (—) air, $Pt/ZrO_2 \cdot Sc_2O_3/Pt$, H_2 (+) driven cell.

In order to obtain a much better understanding of the fundamentals of electrode processes involving point defects like interstitial protons and F-centres (V_O^x), it is necessary to investigate the current-overpotential characteristics by performing systematic experiments using various metals as electrodes and a variety of oxides (e.g. ceria) over a wide range of compositions as electrolytes. It is planned to examine the influence of the morphology of the surface on the current-overpotential characteristics by making electron-microscopic, and Auger spectroscopic, measurements. In future work, the magnitude of the individual cathodic and anodic overpotentials will be measured by the introduction of reference electrodes to the system. Having reference electrodes available will greatly facilitate the interpretation of the data and confirmation of proposed electrochemical mechanisms. Also, with the experimental arrangement of Fig. 1

variation of flow-rates normal to the disc, resulting in stagnation flows, will allow gas phase mass-transfer rates to be varied, thus allowing the mechanism of the limiting current behaviour in the plateaus of Figs. 3 and 4 to be ascertained.

Acknowledgement

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References

[1] S. Pancharatnam, R. A. Huggins and David M. Mason, *J. Electrochem. Soc.* **122** (1975) 869.
[2] A. Amirnazmi, J. E. Benson and M. Boudart, *J. Catalysis* **30** (1973) 55.
[3] P. Fabry and M. Kleitz, *J. Electroanal. Chem. and Interf. Chem.* **57** (1974) 165.
[4] D. Yuan and F. A. Kröger, *J. Electrochem. Soc.* **116** (1969) 594.
[5] H. Yanagida, R. J. Brook and F. A. Kröger, *ibid* **117** (1970) 593.
[6] J. Weisbart, W. H. Smart and T. Wydeven, *Aerospace Med.* **40** (1969) 136.
[7] S. V. Karpachev and A. T. Filayev, *Sov. Electrochem.* **2** (1966) 1215.
[8] R. E. W. Casselton, *J. Appl. Electrochem.* **4** (1974) 25.
[9] C. Wagner, *Ber Bunsenqes. physik. Chem.* **72** (1968) 778.
[10] W. D. Kingery, J. Pappis, M. E. Pappis and D. C. Hill, *J. Amer. Cer. Soc.* **42** (1959) 393.
[11] J. Weisbart and R. Ruka, 'Fuel Cells', Vol. 2, (Ed. G. J. Young), Chapter 4, Reinhold New York (1963) p. 45.