A POSSIBLE REACTION MECHANISM FOR THE OXIDATION OF H₂ ON Ni/YSZ CERMET ELECTRODES

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ABSTRACT

Polarisation curves and ac-impedance spectra have been recorded for Ni/YSZ cermet electrodes and for Ni point electrodes on a YSZ electrolyte at 1000°C. Kinetic data fit the rate equations derived for a reaction scheme where the electrochemical step is near equilibrium and a subsequent chemical reaction is rate determining, assumed to be the reaction between protons and oxide ions on the electrolyte surface. The very high capacitance observed for the cermet electrodes is briefly discussed.

INTRODUCTION

The porous composite of nickel and yttria stabilised zirconia (Ni/YSZ cermet) is the most commonly used anode material for solid oxide fuel cell (SOFC) applications. Although the reaction mechanisms of this electrode system have been studied by many investigators, there is still no comprehensive understanding of the reaction processes (1). Impedance spectra with two or three distinct arcs indicate that more than one process may contribute to the reaction control (1,2,3) on cermet electrodes. For simple electrode geometries only one, although distorted, semicircle is observed (4,5). Mogensen et al. suggest that the high frequency response of the cermet electrode is suggested to originate from the three dimensional morphology of the composite electrode. In a recent report, Aaberg et al. (2) found the low frequency capacitance of the cermet electrode to increase exponentially when polarised anodically in H₂-H₂O atmospheres. This behaviour was not observed for CO-CO₂ atmospheres and was taken as an indication of protons being absorbed in the electrolyte. In this work we present a more detailed discussion of the
polarisation curves and steady state kinetic data with respect to the proposed reaction mechanism.

EXPERIMENTAL

Porous Ni/YSZ cermet electrodes were made by spray painting a slurry of NiO (Johnson Matthey) and YSZ (Tosoh TZ8Y) powders onto a TZ8Y electrolyte (Riso 3-electrode pellet). The electrodes were sintered in air at 1300°C for 6 hours. Three electrodes were tested (A, B and C). Their respective Ni/YSZ volume ratios were 2:3, 2:3 and 1:1 in the reduced state. A current collector layer with the Ni/YSZ volume ratio 1:1 was spray painted on top of anode A. After reduction, the cermet thickness was 50 - 70 μm and the anode area $0.43 \text{ cm}^2$ for all three samples. Before being mounted in a three electrode (four wire) set-up a Pt-paste counter electrode was painted on the electrolyte. The reference was a Pt-point electrode in air. Steady state polarisation curves were obtained after allowing the system to equilibrate (up to 60 minutes) at each voltage. The ac-impedance was recorded at all potentials with an applied amplitude of 30 mV over the frequency range from 0.1 Hz - 100 kHz (Solartron 1255/1286 frequency response analyser).

Mixtures of H$_2$ and N$_2$ were bubbled through distilled water at 18°C to obtain a H$_2$O pressure of 0.02 atm. The resulting hydrogen pressures ranged from 0.001 to 0.98 atm. All experiments were performed at 1000°C and a total pressure of 1 atmosphere. The electrochemical characteristics of the H$_2$-H$_2$O mixtures were compared to mixtures of 10-90% CO in CO$_2$ as described in more detail earlier (2).

RESULTS AND DISCUSSION

A simplified reaction mechanism was presented by Aaberg et al. (2) to explain experimentally observed features of the H$_2$-H$_2$O / Ni / YSZ - electrode. The following reaction steps were proposed:

$$\begin{align*}
\text{H}_2(\text{g}) & \leftrightarrow 2 \text{H}_{\text{ads, Ni}} \quad [1] \\
\text{H}_{\text{ads, Ni}} & \leftrightarrow \text{H}^*_{\text{ads, YSZ}} + e^{\cdot}_{\text{Ni}} \quad |2\text{[2]} \\
2 \text{H}^*_{\text{ads, YSZ}} + \text{O}_0 & \leftrightarrow \text{H}_2\text{O} + \text{V}_0^{**} \quad \text{(rds)} \quad [3]
\end{align*}$$

In principle this reaction mechanism is equivalent to the reaction scheme suggested by Lindegård and Mogensen (6), but they gave another interpretation of the kinetic data. According to Skaarup et al. (7) the adsorption and mobility of hydrogen on Ni is fast. Consequently, it is reasonable to presume that adsorbed hydrogen atoms

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are abundantly present at the Ni/YSZ boundary even when the electrode is moderately polarised to anodic potentials. The electrochemical transfer of protons from the metal to the electrolyte is assumed to be the potential dependant step, which in the simplified evaluations below, is assumed to be near equilibrium. The rate determining step will then be the combination of protons and oxide ions on the electrolyte surface. This is probably a multi step process, but in the following evaluation it is not necessary to account for this. From the assumptions above, the anodic current density can be expressed as:

\[ i_a = 2Fk_3[O]_0^2\theta_{H,YSZ} \]  \[ \text{[4]} \]

where \( k_3 \) is a general rate constant and \( \theta_{H,YSZ} \) is the surface coverage of protons on the electrolyte. \([O]\) is the oxide ion activity which is assumed to be constant. If reaction [2] is not too far from equilibrium, the surface concentration of protons is given by the Nernst's equation:

\[ \theta_{H,YSZ} = K_2p(H_2)^{1/2}\exp(FE/RT) \]  \[ \text{[5]} \]

and when substituting into equation [5] we derive:

\[ i_a = 2Fk_3'p(H_2)\exp(2FE/RT) \]  \[ \text{[6]} \]

Equation [6] is identical to the relationship found by Mizusaki et al. (8) for anodic polarisation which fits their experimental data for Ni-stripe electrodes at 700°C. A charge transfer factor, \( \beta = 2 \), as above, is found by Kawada et al. (9) on Ni/YSZ cermet electrodes and by Guindet, Roux and Hammou (5) for Ni-point electrodes. The charge transfer factor is usually obtained from Tafel plots, but the validity of these plots can be questioned because of the narrow polarisation range and the possibility that more than one reaction is rate limiting (1). In figure 1 the apparent charge transfer factor varies from \( \beta = 1 \) to \( \beta = 2 \). Even if the graphs are not extended far into the linear Tafel region, this is clearly larger than expected if the rate determining step is a single charge transfer reaction with a transfer coefficient \( \alpha = \frac{1}{2} \). Since the two electrodes show different inclinations, one can suppose that the reaction mechanism and the rate determining step varies with the cermet structure.

Equation [6] above implicates a reaction order with respect to the hydrogen pressure to unity at anodic potentials. The experimental data shown in figure 2, indicate an apparent reaction order of \( \frac{1}{2} \), which certainly deviates from the
calculated value. A plausible explanation may be given by Skaarup et al. (7), who calculated the hydrogen coverage on Ni. They presume a saturation of H\textsubscript{ads,Ni} in the high pressure range and thus a reduced reaction order with respect to hydrogen. The experimental results are also partly in accordance with Divisek et al. (3) who found the reaction order to decrease from 0.6 to 0.1 at increasing anodic potentials and a temperature of 950°C.

The exchange current density as found from equation [6] is given by:

$$i_0 = 2Fk_0'p(H_2)^0 p(H_2O)^1$$  \[7\]

With respect to p(H\textsubscript{2}) this is in fair accordance with our experimental data for pressures higher than 0.1 atm. Furthermore, equation [7] is in agreement with the results of Mizusaki et al. (4) for roughly the same p(H\textsubscript{2}) range, but on geometrically well defined electrodes at temperatures from 700 - 850°C. The admittance of the H\textsubscript{2}-H\textsubscript{2}O electrode varies insignificantly with the p(H\textsubscript{2}) at pressures higher than 0.1 atm (figure 3). At lower p(H\textsubscript{2}), \(\sigma_0\) is nearly proportional to p(H\textsubscript{2})\(^{1/2}\). This is also found by Kawada et al. (9).

The impedance spectra are fitted to an 'equivalent circuit' consisting of a series of three resistors and constant phase elements in parallel (2). The constant phase element is defined as \(Q = \rho/(j\omega)^\nu\) where \(\rho\) and \(\nu\) are real constants, \(j = \sqrt{-1}\) and \(\omega\) is the cyclic frequency. When evaluating the low frequency arc in the impedance spectra, an almost purely capacitive behaviour is identified for the H\textsubscript{2}-H\textsubscript{2}O cermet electrode. The values of the constant phase elements are plotted versus potential in figure 4 together with constant phase elements of the CO-CO\textsubscript{2} electrode. The observed capacitance is several orders of magnitude higher then expected for an ordinary double layer capacity. The same phenomenon is also reported by Mogensen et al. (10) and an equivalently high capacitance is reported by Jacobsen et al. (11) for air Pt/YSZ point electrodes. Aaberg et al. (2) suggested that the difference in capacitive behaviour between the H\textsubscript{2}-H\textsubscript{2}O and CO-CO\textsubscript{2} electrode could be ascribed to absorption of protons in the electrolyte, according to the reaction:

$$\text{H}_{ads/abs,Ni} \leftrightarrow H^*_{i,Ni} + e^-_{Ni}$$  \[8\]

Wagner (12) showed that hydrogen is soluble in zirconia as interstitial protons to a mol fraction in the order of 10\textsuperscript{-3}. Consequently, the equilibrium solubility of H\textsuperscript{*} is too low to account for the observed capacitance. Since a high capacitance is found on the CO-CO\textsubscript{2} electrode as well as on the air electrode one may speculate that this
is a representation of some physical process rather than an electrochemical or chemical step.

Whether the protons are transferred across the three phase boundary in an adsorbed state only, or additionally across the metal-zirconia interface as hydrogen dissolved in the metal to interstitial protons in the zirconia, is not obvious. However, these details will not affect the general discussion presented here.

CONCLUSIONS

A reaction mechanism is evaluated for the H2-H2O oxidation on the Ni/YSZ cermet electrode that accounts for the majority of the experimental observations. Further investigations, including non-electrochemical methods are necessary to elucidate the processes taking place at the Ni/YSZ electrodes.

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Figure 1: Log \( i \) versus potential for selected gas mixtures. \( \bullet \), \( \square \) and \( \circ \) denotes 0.98, 0.50 and 0.30 atm \( \text{H}_2 \), respectively. \( p(\text{H}_2\text{O}) = 0.02 \text{ atm} \). Anode A (solid line) and anode B (dashed line).

Figure 2: Apparent reaction order for the oxidation of hydrogen with respect to \( p(\text{H}_2) \) on anode A (solid lines) and anode C (dashed lines) at selected potentials.
**Figure 3:** Exchange current density expressed as OCV-admittance. • = anode A, ▲ = anode C. Dashed lines are obtained from the ac-measurements, while the solid line represents $(di/dn)_{p=0}$ in the linear polarisation curves.

**Figure 4:** Values of the constant phase element versus potential in some representative atmospheres. ■, ● and ○ denote 0.98, 0.50 and 0.10 atm H₂, respectively. p(H₂O) = 0.02 atm. □, ▲, △ denote 0.90 and 0.20 atm CO in CO₂. V(H₂) = 0.97, V(CO) = 0.75.