REACTION RESISTANCE IN RELATION TO THREE PHASE BOUNDARY LENGTH OF Ni/YSZ ELECTRODES

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ABSTRACT

H₂+H₂O+Ar/Ni//YSZ electrodes have been studied by impedance spectroscopy at 1173 K vs three-phase boundary length (3pbl) (0.003 to 120 m). At moderate p(H₂) the charge transfer resistance Rct varied linearly with the inverse of 3pbl, and Rct=10²±0.4 ohm*m at p(H₂)=120 Pa, p(H₂O)=630 Pa. At high 3pbl the kinetics become dominated by an additional reaction resistance probably given by the limited available surface area per unit 3pbl. The resistances generally decrease with p(H₂O) and increase with p(H₂), indicating cathodic limitations. At high p(H₂) it is difficult to establish consistent dependencies of resistances vs 3pbl and partial pressures.

INTRODUCTION

Nickel-zirconia cermets (Ni-YSZ) are the most commonly used anodes in solid oxide fuel cells (SOFC). Nevertheless, poor reproducibility, reduced performance over time and reduced performance in carbon- and sulfur-containing gases seem to be common problems with such electrodes. These effects may reflect reduced gas/Ni/YSZ three-phase boundary length (3pbl) due to sintering of Ni or deactivation (blocking) of the active sites. On the other hand, if adsorption/desorption or other surface processes are rate-limiting, changes in the area or properties of surfaces may account for the reduced performance.

We have initiated studies aiming to contribute to clarify this. We decided to start by trying to obtain a relationship between the 3pbl and kinetic characteristics of the electrode. In the present paper we report electrochemical resistances obtained by impedance spectroscopy on geometrically simple H₂+H₂O+Ar/Ni//YSZ electrodes with
different three-phase boundary lengths.

EXPERIMENTAL

Specimen

Yttria stabilized zirconia with 8 mol% Y₂O₃ (YSZ) was used as electrolyte in the form of sintered cold-pressed tablets or tape-cast membranes. Counter and reference electrodes were made from Pt paint on one side of the electrolyte. Two types of Ni working electrodes were used:

In type 1, Ni wire was wound around an alumina rod 2 mm in diameter. This was pressed against the electrolyte surface by means of a spring-loaded alumina assembly in the measurement cell. The effective contact areas were determined by SEM imaging as the flat parts of the Ni wire, and the effective 3pbl taken as the circumference of these areas, increased by an average roughness factor estimated from the SEM images.

In type 2, Ni was deposited by evaporation and subsequent electroplating to a thickness of 2 μm. Ni was then removed in a pattern of circular holes by microlithography to form the desired three-phase boundaries.

Both types of Ni electrodes were confined to the area of the electrolyte covered by the counter electrode on the opposite face.

After measurements it was observed that the electrode of type 2 had exhibited sintering and contraction of the unetched parts of the Ni. This had formed a fine-structured Ni-network with holes of open YSZ surface, as shown in Figure 1. The dimensions of the network and holes were 3-4 μm throughout the electrode. A representative picture was loaded into an image analysis system where an estimate of the 3pbl could be calculated.

Measurement cell

The sample subject to measurement was placed on top of a 40 cm long alumina support tube and held in place by a spring-loaded alumina assembly(1). The electrical contacts to the electrodes were made by Pt leads, and the temperature was controlled and monitored by a Pt/Pt10Rh thermocouple located next to the sample. The cell was enclosed in an outer alumina tube, and the different parts of the cell were fitted to a common brass cup.

Gas mixtures of H₂+H₂O+Ar were made with a rotameter-based mixing system(2). The water vapour level was fixed by mixing in the desired ratio a portion of the gas mixture wetted over a saturated solution of (NH₄)₂SO₄ with another portion dried over P₂O₅. The final gas mixture was led to both faces of the electrolyte.
Impedance measurements

The electrical properties of the electrode were examined with impedance spectroscopy using a Solartron 1260 impedance analyzer interfaced to a Hewlett-Packard series 9000 computer with custom made software. The impedance spectra were transformed to ASCII format and analyzed with the "EQUIVCRT" software (3).

The impedance was recorded from high to low frequency in the range 1 MHz to 0.01 Hz. The ac signal applied between the working and counter electrodes had an amplitude of 10 mV. The voltage probes were connected to the working and reference electrodes, and the measured impedance thus represents the electrochemical impedance of the working electrode plus part of the ohmic resistance of the electrolyte.

The measurements were performed at 1173 K. Prior to this each sample was annealed for two hours at 1273 K in order to stabilize the morphology of the electrodes. (It is assumed that the abovementioned change in the Ni electrode of type 2 took place during this treatment.)

RESULTS

Three-phase boundary length (3pbl)

Four different Ni electrodes were investigated in this work. Three of the electrodes were of type 1 and one was of type 2, with 3pbl of 3.3 mm, 11.1 mm, 15.7 mm, and 121 m, respectively. An uncertainty of 20% was estimated for the 3pbl for all samples.

Deconvolution of spectra and equivalent circuit

The samples of type 1 had impedance spectra with a single arc which could be fitted to and interpreted as the equivalent circuit LRc(RoQa) (see ref. (3) for notation). Here, L is a system inductance, Ro is the ohmic resistance of the electrolyte, Rc is the charge transfer resistance, and Qa is a constant phase element (CPE) representing the double layer capacitance.

The sample of type 2 had impedance spectra with a composite arc which could be better fitted to the equivalent circuit LRc(RoQd)(RoQr). The last part of the circuit may reflect some reaction resistance (Rr) and surface coverage of adsorbed species (Qr) (4).

Charge transfer resistance Rc

At low p(H2), the charge transfer resistance Rc varied with approximately p(H2O)1/2.

Rc plotted versus 3pbl exhibited a linear inverse relationship at moderate p(H2).
Figure 2 shows this for \( p(\text{H}_2)=120 \text{ Pa} \) and \( p(\text{H}_2\text{O})=630 \text{ Pa} \) at 1173 K, and under these conditions the specific charge transfer resistance is \( R_{ct} = 10^{2.34} \text{ ohm} \cdot \text{m} \).

At higher \( p(\text{H}_2) \), \( R_{ct} \) deviates from this linear relationship and exhibits less clearcut and consistent partial pressure dependencies. An explanation of this must await further studies. Other investigators have also noted a more complex behaviour of the impedance characteristics with increasing \( p(\text{H}_2) \)(4).

**Reaction resistance \( R_r \)**

\( R_r \) found in electrode type 2 decreased with increasing \( p(\text{H}_2\text{O}) \) and increased with increasing \( p(\text{H}_2) \) at 1173 K.

The total electrode resistance for electrode type 2, mainly representing the reaction resistance, \( R_r \), had an Arrhenius type temperature dependence in wet hydrogen, with an enthalpy of 29 ±2.4 kJ/mol (973-1223 K).

**DISCUSSION**

The general picture of the electrode impedance is that it decreases with \( p(\text{H}_2\text{O}) \) and increases with \( p(\text{H}_2) \), suggesting that the kinetics is cathodically limited under the conditions used.

The three electrodes with small 3pbl have large available Ni and YSZ area per unit 3pbl. The kinetics of these electrodes seem to be rate limited by charge transfer, i.e., by the 3pbl. On the other hand, a reaction resistance (\( R_r \)) dominates in the electrode with large 3pbl and smaller Ni and YSZ area per unit 3pbl. This suggests that the kinetics of the latter electrode, and probably of most real Ni-YSZ cermet electrodes, is limited by too small or inactive surfaces rather than small 3pbl. This may be further investigated for instance by using electrodes with larger and varying 3pbl, but with constant and limited area.

**SUMMARY**

The kinetics of simple Ni electrodes on YSZ electrolytes in \( \text{H}_2+\text{H}_2\text{O}+\text{Ar} \) appear to be cathodically limited. In gases dilute in \( \text{H}_2 \) the expected inverse linear relationship between \( R_{ct} \) and the 3pbl is observed. At \( p(\text{H}_2)=120 \text{ Pa} \) and \( p(\text{H}_2\text{O})=630 \text{ Pa} \) and 1173 K the specific charge transfer resistance was found to be \( R_{ct} = 10^{2.34} \text{ ohm} \cdot \text{m} \) for 3pbl in the range 0.003 to 120 m. At the highest 3pbl studied there was an additional and dominating resistance to the electrode kinetics, interpreted as reaction resistance caused by the limited Ni and YSZ surface area per unit 3pbl.
ACKNOWLEDGEMENTS

This work was carried out at the Center for Materials Research, University of Oslo (UiO), and the Center for Industrial Research (SI), Oslo, in partial fulfillment of the requirements for the degree of Civil Engineer at The Norwegian Institute of Technology by Håkon Leth-Olsen with financial support from the Norcell-II project. The authors are grateful to Ivar Dahl, Siri Halvorsen, and Kari Baardseth, SI, and Sissel Jørgensen, UiO, for ideas and help.

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Figure 1. SEM image of continuous Ni network with open YSZ surface in holes, formed by Ni contraction at high temperature.

Figure 2. Charge transfer resistance vs three phase boundary length at 1173 K and p(H₂)=120 Pa, p(H₂O)=630 Pa.