ADVANCED CHARACTERISATION TECHNIQUES FOR NICKEL-YSZ CERMET ELECTRODES USED IN SOLID OXIDE FUEL CELLS

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ABSTRACT

The functioning of a complex system such as the Nickel-Yttria stabilised Zirconia cermet electrode for solid oxide fuel cells can only be investigated by using a broad range of tools. Theoretical calculations on ageing of Ni/YSZ-cermet anodes show a large influence of the ceramic structure on the rate of sintering. Depending on the conditions this sintering may be catastrophic for the activity of the electrode or even increase the electrode activity. Accurately determined microstructural parameters for a cermet anode allow the use of a newly developed theory linking the reaction resistance of an anode to the porosity and mean pore radius. Electrochemical measurements of a model system of Au on YSZ single crystals show a complex behaviour. Analysis of this system results in a better understanding of the charge distribution at the electrode-electrolyte interface. Kinetic studies on a screen printed Ni/YSZ-cermet anode result in a reaction model for the anodic reaction. Information obtained from impedance spectroscopy is corroborating a proposed reaction model based on data from current-voltage experiments. Infrared spectroscopy at elevated temperatures on a model cermet anode gives first results of the interaction between the anode material and carbon monoxide.

INTRODUCTION

The study of electrodes for high temperature applications has developed into an important field in electrochemistry. Even for simple electrochemical systems complex reaction mechanisms are observed. This means that the traditional methods used in electrochemistry are no longer sufficient to elucidate a reaction mechanism. This holds especially for complex systems such as porous mixed conducting electrodes or porous cermet electrodes. Using mainly the porous Nickel-Yttria stabilised Zirconia (Ni/YSZ) cermet electrode as example, a number of different approaches to the problem of analysing the electrode processes are presented.
One of the problems in SOFC is the ageing of electrodes, especially of the anode. It is widely accepted that sintering of nickel is playing an important role\(^1\). A theoretical approach to this problem will be presented. The influence of the microstructure on the electrochemical properties is evident. A direct relation between these two properties is proposed. The study of the electrochemical kinetics of a reaction needs reference values of model systems to enable interpretation of the data. Data from such a model system are presented. The use of these reference data for a cermet-anode contributes to the interpretation of electrochemical data for such an anode. When a SOFC is used in power generation the fuel will probably be based on some form of hydrocarbons. This means that the influence of carbon on the electrochemistry must also be studied. This can be done by performing optical spectroscopy during operation. A development in this directions is presented.

**INFLUENCE OF THE MICROSTRUCTURE ON THE ELECTROCHEMICAL PERFORMANCE.**

Theoretical calculations of percolation systems and ageing phenomena.

One problem of Nickel-cermet electrodes is ageing. The performance of the electrode will decrease in time. It is widely assumed that this is caused by sintering of the nickel particles in the cermet structure. In order to study this problem, calculations on a fcc lattice whose lattice positions are randomly filled with nickel particles, YSZ particles or pores are performed. In these calculations, a nickel particle is assumed to be able to sinter to a neighbouring nickel particle depending on the number of YSZ particles occupying the four lattice positions surrounding the nickel-nickel 'bond'. Sintering may only be blocked when all four neighbouring sites are occupied by YSZ particles (weak constraint) or the particles will not sinter with one or more YSZ particles on neighbouring sites (heavy constraint). Depending on the amount of sintering the particle may just lose contact to its other neighbours (weak sintering) reducing the number of active contact points. Additionally a pore may be created behind the sintering particle (hard sintering) increasing the porosity of the anode. The activity of the electrode as function of the sintering is calculated in real time by determining the number of active contact points between a nickel particle a YSZ particle and a pore. The contact point is active when: the nickel particle is part of a nickel cluster that is in contact with the current collector, The YSZ particle is part of a cluster of YSZ particles connected to the electrolyte, and the pore is part of a pore system in open contact with the gas atmosphere. The details of these *dynamically correlated percolation model* calculations are presented elsewhere\(^2\).

Examples of results from calculations with different types of sintering and different types of constraints are presented in figure 1 and figure 2. The results of these calculations can be summarised as:
The active three phase boundary in a nickel cermet electrode degrades with sintering of the nickel. This degradation will stop when all possibilities for sintering are exhausted.

The degradation may lead to almost complete inactivity if the initial concentration of one of the species comprising the electrode is close to the percolation threshold.

The degradation is depending on the constraints placed on the sintering by the YSZ structure. If these constraints are hard the number of active contact points will change little with time (see fig.2) or may even increase.

From these results it is obvious that in order to produce a cermet electrodes showing little ageing, it is necessary to develop electrode structures that put high constraints on the mobility of the nickel.

**Microstructure analysis of Ni/YSZ-cermet electrodes anode structure**

The electrochemical properties of an Ni/YSZ-cermet electrode are a function of the microstructure. The connection between microstructure and the electrochemical properties was only qualitatively understood. A detailed analysis of the microstructure of a Ni/YSZ-cermet anode was made in order to link microscopic properties as porosity (ε) and average pore radius (rp) to the reaction resistance (Rm) measured for these samples.

The microstructure of the electrodes was investigated by means of a novel porosimetry method suitable for accurately measuring the porosity of thin supported layers (MSP) (3). Based on these investigations, a model of the electrode structure was developed (Fig.3). As shown in this figure, the structure of the SOFC anode cermet consists of single nickel particles, nickel agglomerates as well as small ceramic particles, sintered together to bigger grains without any agglomerate structure. Volume I consists of single nickel particles, the volume II is characterised by the nickel agglomerates, in which some residual internal porosity can still exist. The sum of the volumes I and II forms the volume of nickel, the envelop of which is at least partially in direct contact to the ceramic electrolyte.

As the dependency of the volume changes on the pore radius can be calculated from the porosimetry results, the corresponding integral envelop surface Si can be estimated using to the formula (4):

\[
S_i = k \int_{r_1}^{r_2} \frac{1}{r} \frac{dV}{dr} \, dr
\]

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The value of the integral $S_v$ representing the surface enveloping some pore volume $v$, is dependent on the pore geometry. From the comparison of MSP data to mercury porosimetry data for a number of reference samples, a value of $k = 2$ is derived.

The values of $S_v$ calculated from the porosity data obtained by MSP are presented in Fig. 4. It can be shown that the surface integral curves in their increasing branch (Fig.4) follow the empirical formula:

$$S_i = \frac{1 - \varepsilon}{r_p} \sqrt{4 \varepsilon \pi^2}$$  \hspace{1cm} \text{[2]}

Applying the general theory of porous electrodes as used at low temperatures (5), a relation between the apparent reaction resistance $R_m$ and $S_i$ is found:

$$R_m = \sqrt{\frac{R_w}{\sigma \cdot S_i}}$$  \hspace{1cm} \text{[3]}

In equation 3 $\sigma$ represents the conductivity of YSZ corrected for the porosity. The value $R_w$ represents the microstructure independent reaction resistance for the hydrogen oxidation at a Ni/YSZ contact point at a given temperature and hydrogen partial pressure.

For three samples both the microstructural data and the electrochemical data at 950°C and $p(H_2)=20$ kPa were obtained. The values are presented in table 1. Using these data the value of $R_w$ can be calculated. These values are presented in the same table.

The values for $R_w$ range from 27.3 $\Omega \cdot cm^2$ to 37.2 $\Omega \cdot cm^2$ with a mean value of 32.2 $\Omega \cdot cm^2$. Whether this value for $R_w$ is valid for all electrodes, independent of production method, remains to be checked by further experiments.

**ELECTROCHEMICAL PROPERTIES**

**Interfacial properties of the model system Gold / YSZ-(100,110,111)-single crystal**

An important parameter, which determines the kinetics of the electrode reactions, is the charge distribution at the electrode/electrolyte interface. Besides a pseudo capacitance of adsorbed species on the electrode or the electrolyte, different types of
double layer capacitance of the electrode-electrolyte interface have been proposed in the literature, such as surface capacitance due to intrinsic disorder (6), inner and outer Helmholtz capacitance (7) and space charge capacitance (8).

In a first approach, we have investigated the model system Au/YSZ-single crystal. The advantages of this system compared to the Ni/YSZ system are the chemical stability of gold and the possibility to prepare defined and reproducible interfaces by melting the gold onto the single crystal surface. We have measured the interfacial capacitance of the system Au/YSZ-single crystal by impedance spectroscopy and galvanostatic double pulse experiments in dependence of the potential, the temperature, the oxygen partial pressure, the size of the gold droplet, the aggregate state of the gold electrode (solid ↔ liquid) and the orientation of the YSZ-single crystal.

A fit of the impedance data using the EQUIVCRT programme (9) was performed with the equivalent circuit of Fig 5a, which contains two capacitive elements in parallel, i.e. a capacitance C and a constant phase element Q (n ≈ 0.9). The capacitance C, which occurs in the three phase boundary Au/YSZ/gas phase, can be interpreted as a double layer capacitance. It is independent of oxygen partial pressure and is significantly dependent of the crystallographic orientation of the YSZ-single crystal. It decreases in the order (111) > (110) > (100), which can be correlated with a decreasing density of oxygen ions in the surface layer. The constant phase element Q, which can approximately be regarded as a capacitance, is located in the area of interface Au/YSZ and is nearly independent of oxygen partial pressure. A certain correlation of the capacitance C and the constant phase element Q with e.g. a Helmholtz capacitance, a space charge capacitance or a surface capacitance is not possible in the present state of investigation. The dependencies of C and Q on the experimental parameters are presented in table 2.

Electrochemical properties of a screen printed nickel-cermet anode.

Information on the fundamental electrochemistry of the Ni/YSZ cermet-anode can be obtained from steady state current-voltage measurements and impedance spectroscopy as function of temperature and hydrogen partial pressure.

For a screen printed electrode these measurements were performed. The results of the steady-state current-voltage measurements were previously reported (10). Two temperature domains with different kinetics were reported. In the temperature domain below 840°C the charge transfer reaction of atomic hydrogen adsorbed on nickel is assumed to be rate limiting. At temperatures above 840°C no single rate limiting process can be distinguished due to the mutual influence of the different elementary reaction steps. High fractional surface coverage (θ → 1) at high temperatures is assumed to lead to a hydrogen partial pressure independence of the current at higher overvoltages.

Analysis of the impedance data at open cell voltage showed three time constants. For a charge transfer controlled reaction involving adsorbed species an equivalent
circuit as in figure 5b can be assumed (11). As this equivalent circuit only possesses two time constants an extra contribution is necessary. The impedance data show that the high frequency time constant is associated with a diffusion process. The equivalent circuit was therefore augmented with a parallel branch containing a Warburg impedance in series with a resistance (fig 5c) resulting in a similar equivalent circuit as used for the analysis of the YSZ/Au model system data. The results of the analysis of the impedance data with the programme EQUIVCRT (9) using this equivalent circuit are presented in figure 5 for the resistances \( R_{ct}, R_p \) and \( R_w \) and figure 6 for the capacitive elements \( C_d, Q_p \) and \( W \). The ohmic resistance \( R_q \) does not belong to the electrode reaction and is therefore not discussed. Comparing the data for \( R_{ct} \) with the activation enthalpy of 145 kJ/mol obtained for the charge transfer process from the DC-experiments show a close resemblance. The values of \( R_{ct} \) and \( R_p \) for high temperatures are of the same order of magnitude. The CPE connected to the surface coverage \( Q_p \) is becoming temperature independent above 840°C. This would agree with the assumption that at high temperatures there is no single rate limiting reaction and a high fractional surface coverage as assumed from the steady state results. The double layer capacitance \( C_d \) has an order of magnitude that agrees with the data from the model experiments mentioned in the previous paragraph.

The branch of the equivalent circuit containing the Warburg element may be the contribution of the cathodic reaction to the impedance spectrum at open cell voltage. From the DC-experiments it is evident that the cathodic reaction mechanism differs from the anodic reaction mechanism. It is therefore to be expected that the cathodic contribution to the impedance spectrum at open cell voltage will be expressed by a parallel branch in the equivalent circuit. It is therefore likely that Warburg containing branch of the equivalent circuit of figure 5c is caused by the cathodic reaction.

INFRARED SPECTROSCOPY

In order to understand the kinetics and the mechanisms of the processes on SOFC electrodes, a detailed knowledge of the adsorbed species involved in the electrochemical reactions is necessary. With infrared spectroscopy, it is possible to obtain information about the identity of adsorbed species, strength of interactions and type of bonding under operating conditions.

In our work, we have used the techniques of infrared emission spectroscopy (IRES) and diffuse reflectance FTIR spectroscopy (DRIFTS) to investigate the adsorption of CO onto model anodes made of a powder mixture of a metal catalyst (Ni, Pd, Pt, Ru) and 8 mol% yttria stabilised zirconia. The amount of metal catalyst was either 0.1 or 1 wt.%. The measurements were carried out as a function of temperature (130 - 700°C) and CO partial pressure (0.1-10^5 Pa) under non-electrochemical conditions.
As an example, the infrared spectra of CO on Ni/YSZ show three vibration bands. The positions, intensities and relative intensities of the bands are dependent on the CO partial pressure and the temperature. By increasing the temperature from 250 to 650°C and the CO partial pressure from 30 to 480 Pa, the vibration frequencies shift from 2025 to 1996 cm⁻¹ (singly bonded), from 1921 to 1890 cm⁻¹ (doubly bonded) and from 1836 to 1811 cm⁻¹ (triply bonded).

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Table 1. Microstructurcal and electrochemical data for three different Ni/YSZ-cermet electrodes produced by wet powder spraying (WPS)™
(The values for R_w are calculated for T=950°C and p(H_2)= 20 kPa.)

|     | ε  | r_p | S_i | R_m | R_w |
|-----|----|-----|-----|-----|-----|
| A   | 0.47 | 0.29 | 0.98-10^4 | 0.34 | 29.4 |
| B   | 0.45 | 0.23 | 1.24-10^4 | 0.34 | 37.2 |
| C   | 0.35 | 0.25 | 1.01-10^4 | 0.30 | 27.3 |

Table 2. Interface YSZ single crystal/Au droplet: C and Q in dependence on crystal orientation, oxygen partial pressure (p(O_2)= 3 kPa - 100 kPa, T = 1040°C, YSZ-110), temperature (900°C ≤ T ≤ 1040°C, p(O_2) = 100 kPa, YSZ-110) and covered surface by the gold (T = 1000°C, p(O_2) = 100 kPa, YSZ-110)

| order of single crystal orientation | reaction order | activation energy E_a / kJ mol⁻¹ | exponent n (Å⁻⁴) |
|-----------------------------------|---------------|-------------------------------|----------------|
| capacitance C                     | 100 > 110 > 111 | 0                             | 29             | 0.43 |
| CPE Q                             | 111 > 100 > 110 | 0.04                          | 5              | 1.06 |
Figure 1. The number of active points as a function of time for strong sintering with weak constraints.

Figure 2. The number of active points as a function of time for strong sintering with hard constraints.
Figure 3. Example of particle forms in a Ni/YSZ cermet-anode (dark Ni, light YSZ).

Figure 4. Integral envelope surface as a function of pore radius for three different samples.

Figure 5. The equivalent circuits for the model experiments (a), a Langmuir-Hinschelwood mechanism (b) and the analysis of the Ni/YSZ cermet data (c).
Figure 6. Arrhenius plot of the resistive elements calculated using the equivalent circuit of Fig 5c. The line represents an activation enthalpy of 145 kJ/mol.

Figure 7. Plot of the values of the capacitive elements calculated using the equivalent circuit of Fig 5c.

Figure 9. IRES spectra of CO adsorption on Ni/YSZ at a temperature of 450°C, p(CO) = 30, 60 and 120 Pa, p(H₂) = 1100 Pa.