Preparation and electrochemical characterisation of supporting SOFC–Ni–YZT anodes

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Abstract

Symmetrical cells consisting of Ni–$Y_{0.20}Ti_{0.18}Zr_{0.62}O_{1.90}$ (Ni–YZT) cermet electrodes on a Ni–YSZ support have been investigated with respect to the hydrogen/water partial pressures. Impedance spectra at open circuit potential were obtained as function of temperature and analysed in terms of a fractal finite length Gerischer Impedance. For fine and coarse microstructures of the Ni–YZT electrodes, a consistent set of model parameters could be obtained. The results indicate that surface diffusion rather than bulk diffusion plays a role in the hydrogen/water reaction but also that a fine-grained fraction in the mixed conducting YZT phase is advantageous for the overall electrode performance and the surface exchange reaction.
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1. Introduction

Solid oxide fuel cells are still receiving an increasing interest as future energy conversion systems. The concept of a supported electrolyte (mostly yttria-stabilised zirconia is used) allows thin electrolyte layers and thus operating temperatures of around 800–850 °C with acceptable ohmic losses. However, in this cell design, electrochemical characterisation is usually limited to full cell tests, since the thin electrolyte does not allow the use of reference electrodes without imposing the risk of significant errors in the measurements due to misalignment problems [1].

Although the Ni–YSZ cermet electrode is the most frequently used fuel electrode in solid oxide fuel cells, there is a significant interest in investigating alternative SOFC anode materials. For the use of carbon containing fuels such as methane and higher hydrocarbons, mixed electronic–oxygen ion conducting ceramics are promising candidate materials with or without a metallic current collector [2,3]. Among them, $Y_{0.20}Ti_{0.18}Zr_{0.62}O_{1.90}$ (YZT) is of interest because of matching properties with the YSZ

electrolyte and increased stability of the electrochemical performance compared to Ni–YSZ [4]. The electrochemical performance of Ni–YZT cermet electrodes was shown to be lower than for Ni–YSZ anodes, which was attributed to the lower ionic conductivity of YZT.

In order to characterise the single anode performance of Ni–YZT anodes in more detail, and in an anode supported SOFC symmetrical cells have been prepared consisting of two nominally identical electrodes (including the support). This symmetrical cell concept has also been demonstrated for Ni–YSZ and Ni–CGO cermet electrodes to give reliable results [5]. In this work we present the electrode preparation and temperature dependence of the hydrogen water reaction on these Ni–YZT cermet electrodes. An electrochemical model based on the partial pressure dependence of the hydrogen/water reaction on these electrodes is described in Boukamp et al. [6].

2. Experimental

The supporting electrode substrates have been fabricated by cold die pressing of NiO$Zr_{0.85}Y_{0.15}O_{1.93}$ (NiO–YSZ). Polymer bounded NiO–YSZ granules with 50 w% NiO (Cerac) and 50 w%

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Table 1
Structural modifications in Ni–YZT cermet anodes and electrode performance at 800 °C, 97% H_2, 3% H_2O

Anode ID	Mean particle size YZT, D_{50} (μm)		Fraction of "fine" YZT (%)	Initial performance, $R_{p,av}$ (Ω cm^2)	Stabilised performance, $R_{p,av}$ (Ω cm^2)	E_{act} (kJ/mol)
	"Fine"	"Coarse"				
AI11a	0.8		100	2.9	5.9	113
AI12	0.8	2.2	50	3.9	7.9	113
AI13	0.8	2.2	30	4	7.1	113
AI11		1.8	0	5.5	10	102

YSZ (8 mol% yttria, (Tosoh, GTV)) have been prepared by spray drying. The NiO–YSZ granules were pressed to pellets of 14 mm diameter and a thickness of 0.8 mm.

$Y_{0.20}Ti_{0.18}Zr_{0.62}O_{1.90}$ (YZT) powders have been synthesized by the solid state route using a calcinations temperature of 1450 °C for 33 h. The as prepared powder showed a mean particle size, D_{50} of 1.8–2.2 μm (denoted as "coarse"). By subsequent milling a finer fraction ($D_{50} = 0.8$ μm) could be obtained (denoted as "fine").

The electrode layer was deposited by air spraying a low viscous water based slurry containing NiO and YZT. Different NiO–$Y_{0.20}Ti_{0.18}Zr_{0.62}O_{1.90}$ (Ni–YZT) electrode layers were prepared by varying the amount of the YZT fine and coarse fraction (details see Table 1). All electrodes contain 40 vol.% nickel after reduction. The electrodes were subsequently coated with a $Zr_{0.85}Y_{0.15}O_{1.93}$ (Unitec) electrolyte layer by air spraying. Two nominally identically prepared half-cells were then pressed together and fired at 1430 °C for 2 h in air to form the symmetrical electrode supported cells. The principal structure of the symmetrical cells is shown in Fig. 1a.

The as prepared symmetrical cells have been electrochemically characterized in the test set-up in Fig. 1b. In order to ensure an optimal electrical contact to the Ni–YSZ supports in the symmetrical cells were first contacted with Ni-meshes and subsequently sandwiched between two Pt-meshes connected to the current and potential probes.

Impedance spectra (50 kHz to 10 MHz) have been taken between 600 °C and 800 °C as a function of temperature in 97% H_2 and 3% H_2O. The validity of the impedance data has been checked by performing a Kramers–Kronig transformation. The EQUIVCRT software was used to first analyse the high frequency part of the impedance spectra, while the remaining contribution
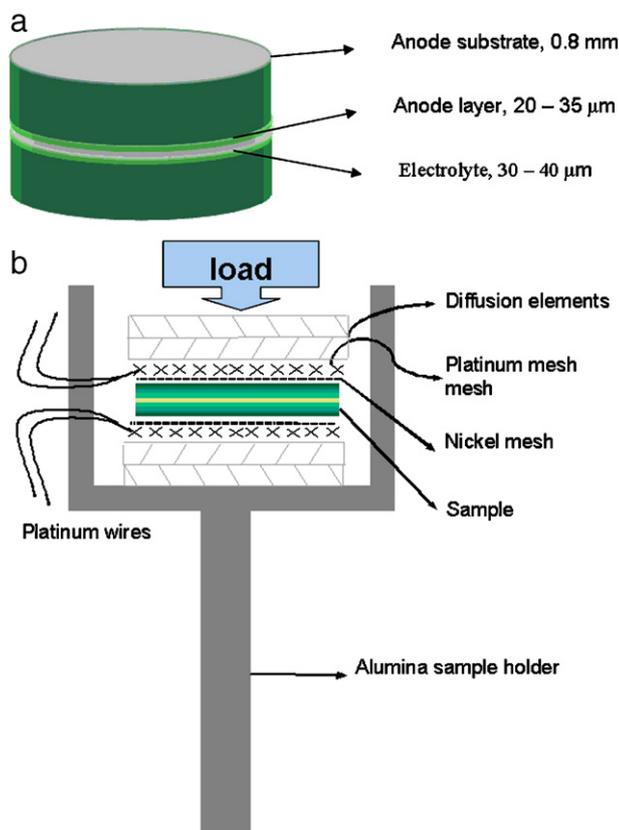

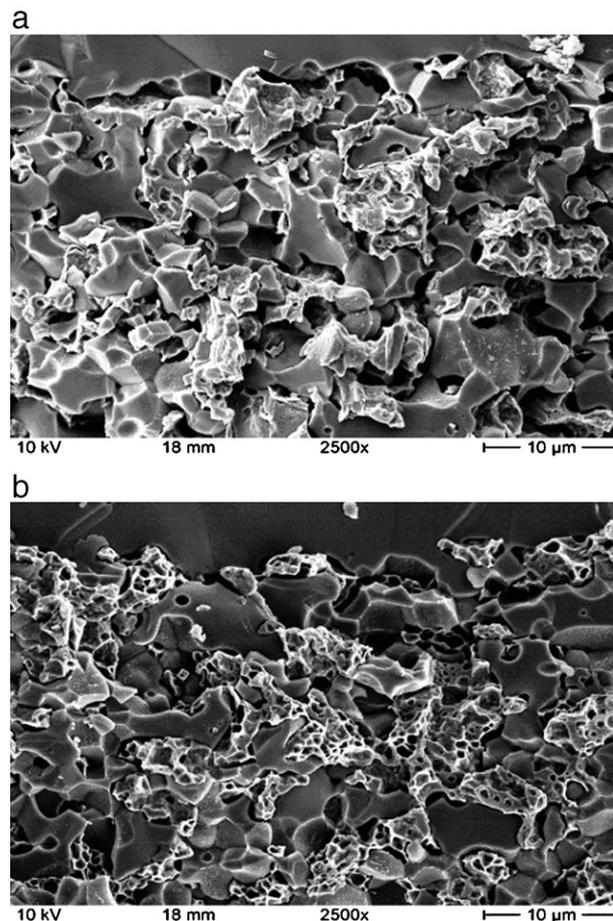Fig. 1. Symmetrical (a) cell construction and (b) test arrangement.

Fig. 2. Typical microstructure of the Ni–YZT electrodes reduced, non-tested (a) and after 120 h (b) of electrochemical testing.
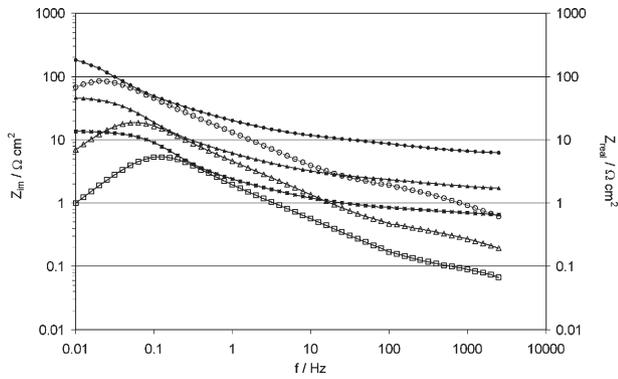
Fig. 3. Impedance spectra as a function of temperature in 97% H_2, 3% H_2O, solid symbols real part, open symbols imaginary part of the impedance: square, 800 °C; triangles, 700 °C; spheres, 600 °C.

was further analysed in an Excel spreadsheet. From this analysis the ohmic losses in the test cell as well as the average Faradaic impedance of a single electrode can be obtained [5,7].

3. Results and discussion

A typical microstructure of the Ni–YZT electrodes is shown in Fig. 2a and b reduced but not tested and after the electrochemical testing, respectively. The only change appears in the bright particles which are attributed to the Ni-phase in the Ni–YZT cermet showing an increased porosity after the electrochemical tests.

This structural change might be related to the time dependence of the electrochemical impedance for Ni–YZT electrodes. During an initial period of 24 h–50 h at 800 °C and 97% H_2/3% water, the Faradaic electrode resistance $R_{p,av}$, increases by a factor of 2 as shown in Table 1 for all samples investigated. For longer measurement times the electrode performance was stable, allowing for systematic investigations of the temperature dependence of the hydrogen water reaction.

The change to more fluffy, porous Ni-particles, without any visible particle growth during the test period, is different from the frequently observed Ni-coarsening in conventional Ni–$Zr_{0.85}Y_{0.15}O_{1.93}$ cermets. At present the origin for this structural change is not clear. However, since during non-measurement periods the oxygen content in the hydrogen backup gas could not be controlled precisely, we cannot exclude a slight, partial re-oxidation of the Ni-cermet in non-measurement periods e.g. overnight. That under such conditions the overall Ni grain size remains stable is tentatively attributed to an increased bonding between Ni and YZT compared to YSZ as discussed in [4], which may prevent Ni agglomeration.
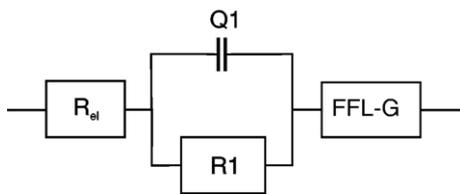

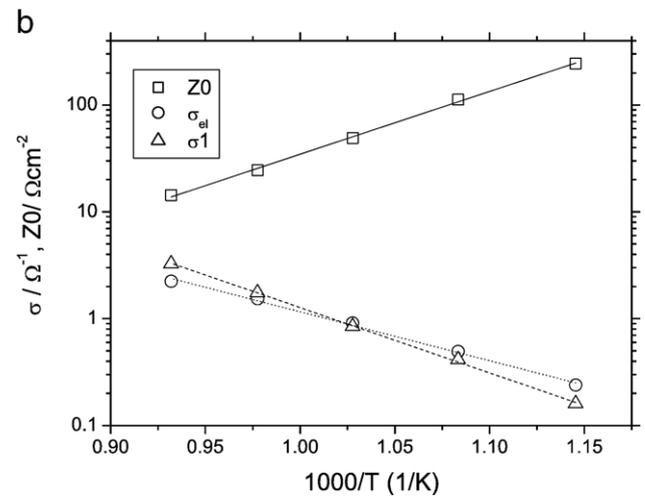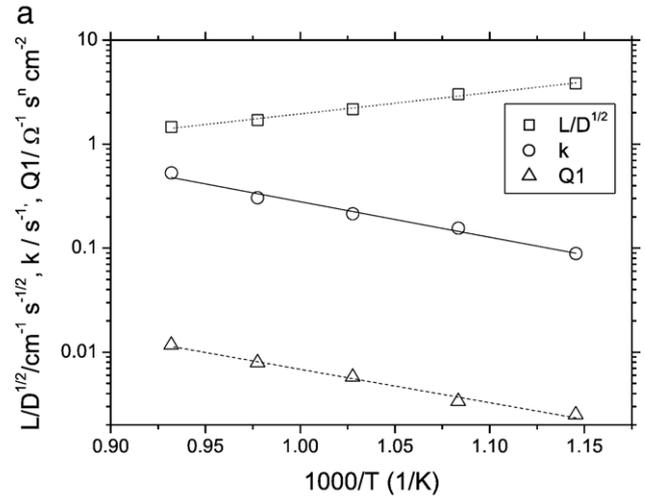Fig. 4. Equivalent circuit describing the Ni–YZT impedance.

Fig. 5. Impedance parameters from Fig. 4 as a function of temperature: (a) $L/D^{1/2}$, k, Q1; (b) σ_{el}: $1/R_{el}$, σ_1: $1/R_1$ $Z_0/D^{1/2}$.

Modifying the YZT mean particle size (D_{50}) from 0.8 mm to 1.8 mm increases the overall Faradaic electrode resistance, $R_{p,av}$, from 5.9 to 10 Ω cm^2. Replacing 30 wt.% and 50 wt.% of the coarse YZT by a finer fraction does not affect the initially measured $R_{p,av}$, however, the degradation during the first 50 h is less severe for 30% fine YZT leading to a lower $R_{p,av}$ even at higher coarse YZT fraction.

The temperature dependence of the impedance is shown in Fig. 3. The impedance consists of a minor high frequency contribution and a dominant low frequency part, which both are activated by the temperature.

Table 2
Activation energies (kJ/mol) for the model parameters (see Fig. 4) describing the impedance of Ni–YZT electrodes

Anode	Amount of "fine" YZT (%)	σ_{el}	σ_1	Q1 ($n=0.5$)	$L/D^{1/2}$	$Z_0/D^{1/2}$	k
AI11a	100	92	117	63	−34	−112	47
AI12	50	81	122	35	−35	−110	57
AI13	30	88	117	62	−39	−112	65
AI11	0	89	123	50	−31	−105	72

The impedance can be described by the equivalent circuit given in Fig. 4. Therein, the minor high frequency contribution is described by a resistor in parallel to a constant phase element (R1Q1), while the dominating impedance contribution is modelled by a fractal finite length Gerischer impedance (FFL-G) according to Eq. (1):

$$Z(\omega) = Z_0 \frac{\tanh\left[L\left((k + (j\omega)^{\alpha})/\tilde{D}\right)^n\right]}{(k + (j\omega)^{\alpha})^n} \qquad (1)$$

The FFL-G is discussed in detail in Boukamp et al. [6] and can be related to surface diffusion of adsorbed oxygen species (or bulk oxygen ion diffusion), in competition with (bulk) oxygen uptake/release through a surface exchange reaction at the YZT surface. Following this mechanism L represents the diffusion length, D the diffusion coefficient for oxygen, and k the rate constant of the oxygen uptake/release.

The temperature dependence of the circuit parameters is shown in Fig. 5. All adjustable parameters show an apparent Arrhenius behaviour indicating that they can be related to single parameters as discussed below. The corresponding activation energies are summarised in Table 2 for the various samples investigated.

The activation energy of the electrolyte conductivity, σ_{el} of 90 kJ/mol is in agreement with the ionic conductivity of YSZ, while the activation energies of 110–120 kJ would correspond to an electrochemical reaction step in the hydrogen/water reaction on Ni–YZT electrodes. It should be noted that the temperature dependence of both σ_{el} and of the capacitance Q1 attributed to the capacitance of the electrochemical reaction are lower for AI12 (50% fine YZT fraction) than for all other samples. The reason for this is not fully understood but might be related to a particular microstructure at the electrode/electrolyte interface resulting from the 50:50 coarse/fine YZT fraction.

As indicated in the impedance, the electrochemical reaction is apparently not the rate-determining step and more of interest is the understanding of the dominating fractal finite length Gerischer impedance. The temperature dependences of the adjustable parameters $Z_0/D^{1/2}$, $L/D^{1/2}$, and k show an apparent Arrhenius behaviour. The negative slopes of $Z_0/D^{1/2}$ and $L/D^{1/2}$ indicate an activation of the diffusion coefficient D with increasing temperature. Presuming the diffusion length L independent of temperature, this corresponds to an activation energy for D of 70–80 kJ/mol. This value is lower than the activation energy for the oxygen ion conductivity in YZT which is 110 kJ/mol [8] and thus might indicate that surface rather than bulk oxygen diffusion is involved in the hydrogen water reaction.

Increasing the fine fraction of YZT in the cermet decreases the activation energy of the surface exchange reaction as expressed in the rate constant k. This implies that the use of smaller Ni–YZT particles prepared by ball milling accelerates the oxygen uptake–release and thus is advantageous for the overall performance of the Ni–YZT electrodes in hydrogen water atmospheres.

4. Conclusions

The performance of Ni–YZT cermet electrodes for the hydrogen/water reaction was investigated on symmetrical cells in an anode supported SOFC configuration. The impedance can be analysed in terms of a fractal finite length Gerischer model, which gave a consistent set of model parameters as a function of temperature. The surface exchange reaction plays an important role in the hydrogen/water reaction on these electrodes.

Acknowledgements

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