

# The influence of the solid electrolyte on the impedance of hydrogen oxidation at patterned Ni electrodes

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## ARTICLE INFO

### Article history:

Received 13 October 2009

Received in revised form 9 June 2010

Accepted 14 June 2010

### Keywords:

Impedance spectroscopy

Ni electrodes

YSZ

LSGM

Electrode kinetics

## ABSTRACT

In order to investigate the role played by the solid electrolyte in the H<sub>2</sub> oxidation reaction, patterned Ni electrodes on YSZ (yttria stabilized zirconia) single crystals with different crystallographic orientations, on polycrystalline YSZ and on polycrystalline LSGM ((La,Sr)(Ga,Mg)O<sub>3-x</sub>) were studied in H<sub>2</sub> + H<sub>2</sub>O gas as a function of partial pressure of H<sub>2</sub>O in the temperature range of 673–823 K. Symmetrical cells using YSZ single crystals exhibit a single almost perfect electrode semicircle in the Nyquist plot. The corresponding polarisation resistance (R<sub>p</sub>) depends on the surface orientation of the YSZ single crystals with a maximum of R<sub>p</sub> for <110> and a minimum for <100>. The capacitance obtained from the impedance arc is almost temperature independent but different for the three surfaces. In the case of polycrystalline YSZ a depressed impedance arc results with the capacitance being between the extreme values measured for single crystals of different orientation. A modified situation is found for patterned Ni electrode on LSGM: the capacitance of the single arc depends on temperature and is much larger than in the case of YSZ cells. The polarisation resistance on polycrystalline LSGM is much smaller than on polycrystalline YSZ while activation energies of the polarization resistance are still similar. Capacitances and resistances are discussed in terms of possible mechanisms.

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## 1. Introduction

Solid oxide fuel cells offer environmental friendly and efficient means of conversion of chemical to electrical energy [1,2]. Understanding the mechanisms of electrochemical reactions occurring in these fuel cells is crucial for an enhancement of their performance and for the development of new materials. An improved exploitation of different kinds of gaseous fuels also requires knowledge on the reaction kinetics at the fuel electrode, i.e. at the anode. Numerous studies to understand the mechanism of hydrogen oxidation at Ni-YSZ (yttria stabilized zirconia) cermets and patterned Ni model electrodes have been reported in literature (see e.g. [3–9]). The complex microstructure of porous Ni-YSZ cermets often leads to highly complex situations with spatially varying reaction rates and thus to difficulties in interpreting the experimental data in terms of mechanisms. Primdahl et al., for example, reported studies of the oxidation kinetics of hydrogen at Ni-YSZ cermet anodes by impedance spectroscopy in the high temperature regime from 850 °C to 1000 °C [3] and discussed the impedance data in terms of at least

three rate-limiting processes: a high frequency relaxation process has been attributed to charge transfer while two low-frequency processes have not unambiguously been interpreted. Holtappels et al. [4,5] investigated Ni-YSZ cermet electrodes in a temperature range of 725 °C–950 °C and reported that at temperatures below 845 °C the real part of the Faradaic impedance was charge transfer controlled. At temperatures above 890 °C charge transfer and adsorption are suggested to determine the rate of the overall reaction. Jiang et al. [6] studied the reaction mechanism in dry and moist H<sub>2</sub> atmosphere. In dry H<sub>2</sub> the rate controlling step was supposed to be dissociative adsorption/diffusion of hydrogen on the surface of the metal electrode. For moist H<sub>2</sub> both Ni and electrolyte surfaces were suggested to contribute to the H<sub>2</sub> oxidation reaction.

Investigations of the kinetics by means of well defined patterned nickel anodes avoid many complexities associated with porous cermet electrodes [7–9]. In an earlier study with patterned Ni electrodes in H<sub>2</sub>-H<sub>2</sub>O atmospheres Mizusaki et al [7] suggested dissociative adsorption of reactants or surface diffusion of the adsorbed species on the nickel surface as the rate limiting step. They assumed exclusively the Ni surface to be electrochemically active. Boer et al. [8] also studied the H<sub>2</sub> oxidation reaction mechanism at patterned Ni electrodes on YSZ by impedance spectroscopy. The spectra revealed three arcs and the dominating process was ascribed to a charge transfer step. The exact nature of all

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processes could not unambiguously be clarified. In a recent study Bieberle et al [9] reported further impedance data of patterned Ni electrodes. The measured impedance arc was concluded to be due to a single elementary process and attributed either to adsorption/desorption reaction of  $H_2$  on Ni or to removal of  $O^{2-}$  from the electrolyte.

From this incomplete overview on some studies it already becomes clear that the elementary reaction mechanism of  $H_2$  oxidation on solid electrolytes is still controversially discussed and only partly understood. Neither the rate limiting step nor its location is clarified unambiguously. It was also shown that water has a catalytic effect on the reaction kinetics but its role in enhancing the electrode performance is not clearly understood; a new model has been presented in Ref. [10]. In all studies it is assumed that the so-called triple phase boundary (TPB) between electrode, electrolyte and gas phase plays a crucial role in the reaction mechanism. However, very little information is available on the dependence of anodic polarization resistances on the type and surface orientation of the electrolyte.

In this work we present data illustrating the role of the electrolyte in the polarization of patterned Ni electrodes with a defined triple phase boundary length. The polarization resistance of nominally identical Ni-patterns on YSZ single crystals of different orientations, on polycrystalline YSZ and on LSGM ( $(La,Sr)(Ga,Mg)O_{3-x}$ ) was investigated in different  $H_2 + H_2O$  atmosphere and for varying temperature. Impedance spectroscopy was used to analyse resistive and capacitive contributions of the corresponding hydrogen oxidation reaction kinetics.

## 2. Experimental

### 2.1. Preparation of LSGM and YSZ

YSZ ( $ZrO_2 + 9.5 \text{ mol\% } Y_2O_3$ ) single crystals of  $10 \times 10 \times 1 \text{ mm}^3$  size with three different orientations ( $\langle 100 \rangle$ ,  $\langle 110 \rangle$  and  $\langle 111 \rangle$ ) were obtained from Crystec, Germany. Powders of LSGM ( $La_{0.8}Sr_{0.2}Ga_{0.83}Mg_{0.17}O_{2.815}$ ) and YSZ ( $ZrO_2 + 8 \text{ mol\% } Y_2O_3$ ) were prepared by the mixed oxide route.  $La_2O_3$ ,  $Ga_2O_3$ ,  $SrCO_3$  and  $MgO$  were taken as starting materials for the preparation of LSGM.  $MgO$  was calcined at  $1000^\circ C$  for 6 h before mixing the starting materials in a ball mill for 12 h. Subsequently the mixture was calcined twice at  $1000^\circ C$  with an intermediate ball milling step. The calcined powder was compacted in a cold isostatic press and the obtained compacts were annealed twice at  $1500^\circ C$  for 6 h with intermediate grinding and ball milling. In XRD only a single phase (LSGM) could be detected after a single annealing step at  $1500^\circ C$  for 10 h. However, SEM examination of the as-prepared LSGM samples showed a very small quantity of  $SrLaGa_3O_7$  impurity ( $<3 \text{ vol\%}$ ). For the preparation of YSZ, the starting powders of  $ZrO_2$  and  $Y_2O_3$  were mixed in a ball mill, compacted and then annealed at  $1600^\circ C$  for 15 h. Single phase YSZ was obtained after annealing. The samples of polycrystalline YSZ and LSGM with  $\sim 11.5 \text{ mm}$  diameter and  $1.4 \text{ mm}$  thickness were fine polished with  $1/4 \mu m$  diamond paste.

### 2.2. Photolithographic preparation of patterned Ni electrodes

Photoresist was applied onto the clean surface of the samples and subjected to prebaking. Using a circular mask of  $9.5 \text{ mm}$  diameter with a mesh size of  $70 \mu m \times 70 \mu m$  the photoresist was selectively exposed to UV light and developed. A thin layer of Ni ( $200 \text{ nm}$ ) was deposited by physical vapour deposition onto the polycrystalline YSZ and LSGM and by magnetron sputtering onto the YSZ single crystals. Vapour deposition of Ni was done by an electron-gun with  $10 \text{ kV}$  and  $100\text{--}125 \text{ mA}$ . The deposition rate under these conditions was  $0.8^\circ A/s$ . The triple phase boundary length of the resulting Ni pattern (see Fig. 1) is  $1.43 \text{ m/cm}^2$  on a

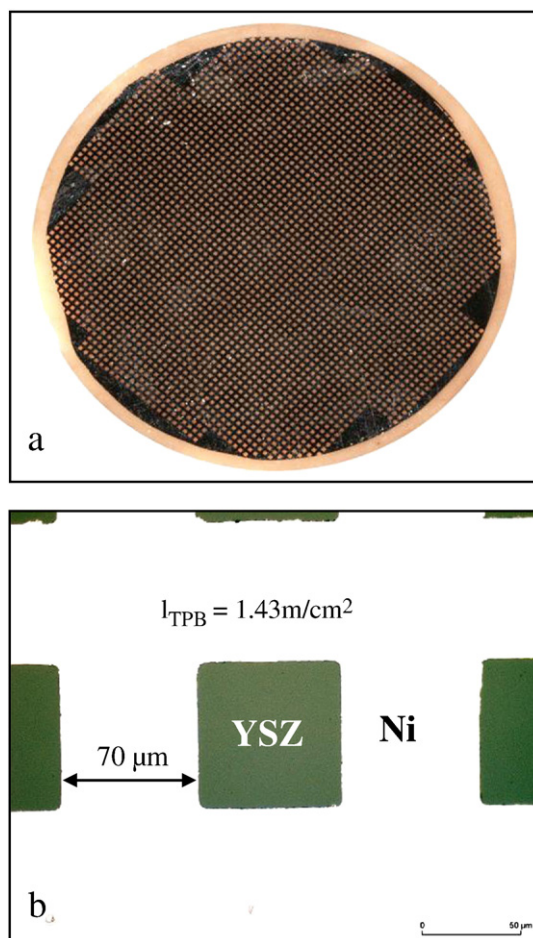


Fig. 1. The design of the Ni-pattern used as electrodes (a) in an overview and (b) in an optical microscope.

Ni-covered area of  $0.52 \text{ cm}^2$ . The same electrodes were symmetrically deposited on both sides of each sample. The stability of the Ni patterns as a function of temperature was studied using Scanning Electron Microscope (SEM) and Optical microscopes and it was found that Ni patterns are not stable above ca.  $550^\circ C$ . At  $800^\circ C$  the patterns were completely disintegrated and formed agglomerates. At temperatures  $\leq 550^\circ C$  the Ni-patterns are completely stable and hence all impedance measurements were performed in the temperature range  $400\text{--}550^\circ C$ .

### 2.3. Impedance measurements

Fig. 2 shows the schematic of the impedance cell and symmetrical cell of the Ni-patterned electrolytes. The impedance cell was spring loaded and positioned in the uniform temperature zone of an inductively heated furnace. A thermocouple which is placed very close to the sample is used to control the temperature of the sample precisely. The samples with symmetric Ni-electrodes were contacted with Pt-meshes on both sides. Ribbed alumina disks (Fig. 2b) which are placed over the Pt-mesh on either side of the sample are then pressed against the sample by the spring-loaded cell. Impedance measurements of two YSZ single crystal sample series (each including  $\langle 100 \rangle$ ,  $\langle 111 \rangle$ , and  $\langle 110 \rangle$  surface orientation), polycrystalline YSZ and polycrystalline LSGM samples were carried out at various temperatures and  $H_2 + H_2O$  gas compositions using a ZAHNER, IM6 impedance analyser. The experimental parameters are listed in Table 1. The data were analyzed by means of the ZAHNER equivalent circuit fitting routine.

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