ENHANCING THE LIFETIME OF SOFC STACKS FOR COMBINED HEAT AND POWER APPLICATIONS

SOF-CH

WP 1: ENHANCING THE REDOX STABILITY OF NI-BASED ANODES FOR SOFC

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Ausgearbeitet durch

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Zusammenfassung

On the foundation of a general literature survey the fundamental physical phenomena that dominate the degradation of Ni based anodes for solid oxide fuel cells have been identified. Microstructural changes under ideal operating conditions are due to (i) the coarsening of the metal grains in the metal ceramic composite. Because the metallic phase is a three dimensionally percolating network of the metal phase in a 3 D percolating ceramic matrix intermingled with a 3 D percolating pore structure. This system is thermodynamically highly unstable due to its large interfacial area under reducing conditions. The interface between Ni and the ceramic phase is weak due to (ii) bad wetting of metallic Ni on the ceramic. Third factor for degradation under ideal operating conditions is attributed to (iii) the local fuel utilization that might cause surface reactions (carbon deposition), $Ni(OH)_2$ formation or segregation and diffusion of C into the Ni. All this factors lead to a constant decrease in properties of the anode.

Under real operating conditions the disruption of fuel supply due to thermal cycling or system failures can affect the anode`s lifetime and performance drastically. From a thermodynamic point of view a disruption of fuel supply means a strong deviation of system`s equilibrium conditions. Once the anode is exposed to a critical oxygen partial pressure, the oxidation process forms Ni-oxides on the metal surfaces and might change in the case of a nonstoichiometric ceramic matrix its stoichiometry. The process of oxidation of Ni metal to NiO is accompanied by a volume change of 39.9%. This volume change causes additional tensile stresses on the ceramic network and might locally disrupt its mechanical integrity. The similar applies when reducing again the anode back to normal operation status and the resulting thickness of oxide layers.

There are two strategies to improve anodes. On the one side one can try to reduce oxidation by doping the metal part of the composite by alloying. On the other hand during operation under H_2 one can try to extend the catalytic active surface area by lowering the conduction band of ceramic matrix via dopants. This means to introduce a mixed electronic/ionic conducting ceramic phase in the cermet. In this case the transition probability for electrons from the Ni-conduction to the ceramics conduction band should be lowered, so that the active surface is not anymore determined by the triple phase boundary (TPB) line but by an area and its adjacent sites.

Abstract

Degradation problems in long term operation of solid oxide fuel cells (SOFCs) are characterized by a steady decrease of performance of the fuel cell module. The decrease in cells/stacks is to be regarded as a sum of physical effects, in which diffusion, coarsening, interfacial changes play a dominant role. Although the subtle interaction of all this physical phenomena, and their effect on the energy conversion and electrical performance of the anode and the complete solid oxide fuel cell are far from allowing univocal conclusions.

In order to study the degradation of porous anode cermets for solid oxide fuel cells (SOFC) the Ni-cermet anode - respectively Nickel plus Yttrium Zirconia Oxide as the state of art anode material for SOFCs – has been chosen to be analyzed under stringent conditions, for example varying atmospheres and temperatures. On the basis of this research ways and strategies will be elucidated to enhance the stability of the anode.

1. Ausgangslage

The project on "Enhancing the redox stability of Ni-based anodes for SOFC" takes place in the context of a dissertation, started in June 2007, at the Institute for Nonmetallic Inorganic Materials (Professor Gauckler, ETH Zürich).

2. Ziel der Arbeit

Aim of the project is to reveal, in accordance with the experimental analysis of HEXIS Ni-YSZ anodes and alternative anodes, the fundamental physical processes controlling the single steps of anode degradation. Targeted is to propose, on the grounds of a developed model for degradation in Ni based anodes, concepts to overcome or mitigate common degradation effects.

Projektziele

Within the framework of the project started at the 1.June 2007, deliverables, which are subdivided in three working packages (WP), and milestones (M) have been defined. **Fig.1** shows the time scheduling for the different working packages. Consistent with the agenda an extended literature review of redox-stability and degradation of state-of-the-art Ni-YSZ, with special focus on effects for long-term degradation an redox-stability and their improvement, has been performed.
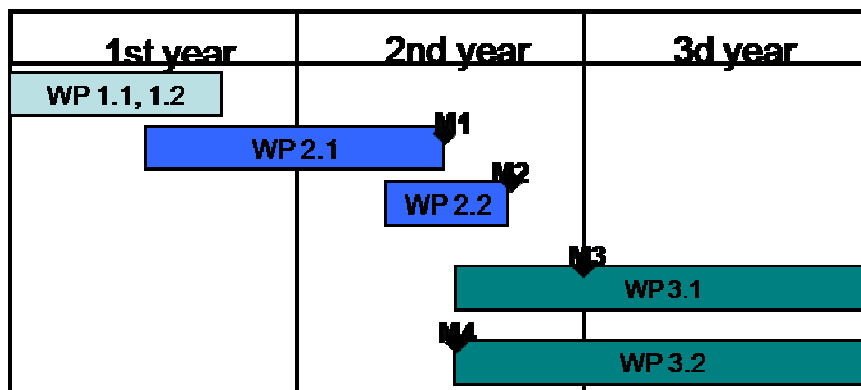
Fig. 1 Roadmap separated in workpackages (WP) and milestones (M)

Work packages (WP):

WP 1: Literature analysis of redox-stability and degradation of state-of-the-art Ni-YSZ anodes:

WP 1.1: Literature study on long-term degradation an redox-stability of Ni-YSZ anode.

WP 1.2: Literature study on improvement of redox-stability of Ni-YSZ anode.

WP 2: Degradation and redox stability of HEXIS Ni-YSZ anodes:

WP 2.1: Microstructure analysis of HEXIS Ni-YSZ anodes prior to redox cycling and post-mortem.

WP 2.2: Model for the redox-degradation of Ni-YSZ anodes is developed.

WP 3: Improved redox stable anodes:

WP 3.1: Experiments on alternative redox stable anodes towards Ni-YSZ.

WP 3.2: Experiments to improve redox-stability of Ni-YSZ anodes

Milestones (M):

M1: Model for the redox-degradation of Ni-YSZ anodes proposed.

M2: Microstructure changes through redoxcycling of Hexis anodes characterized.

M3: Alternative anodes are identified.

M4: Experiments to improve redox-stability of Ni-YSZ anodes are proposed.

3. Ergebnisse

Long-term stability is an important requirement for the application of fuel cell technology, for competing with common energy conversion concepts it is mandatory to guarantee a lifetime span of 40.000h, with a total degradation value below 1%/1.000h. The total degradation of the cell performance is the sum from all components of the solid oxide fuel cell (SOFC) [anode, cathode, electrolyte, current collectors and stacking components] [1]. Typical industrial operating conditions are operating temperatures in an interval [700°C,1000°C] using natural gas, partially reformed in a reformer or under laboratory conditions pure hydrogen or hydrocarbons.

The microstructure of a state of the art anode for SOFCs, typically Ni/ yttrium stabilized zirconia (YSZ) or Ni/ ceria gadolinium oxide (CGO) [2], is characterized by a porous composite "cermet", made of a metallic phase, in general Nickel and a ceramic phase, usually YSZ or CGO. Within this cermet, the metallic phase contributes to the electronic conduction and the ceramic phase to the ionic conduction. The intersections of ceramic metal, and fuel, the so called three-phase boundaries (TPBs), are thought to be the areas where the oxidation of the fuel takes place.

One of the weak points of SOFCs is to maintain chemical and mechanical stability during fabrication, long-term operation and thermal cycling [3]. The main mechanisms for these instabilities are going to be motivated in a compact form in the following sections.

(I)   Degradation effects of Ni based anodes in SOFCs

The predominant microstructural change in anode materials, such as porous Ni/CGO or Ni/YSZ cermets, is the agglomeration and particle coarsening of the metallic Ni. It is widely assumed [4-6] that the ripening of Ni in SOFC anodes, is connected to the weak interface between the metal and ceramic material and to the large surface energy of the Ni.

As consequence of the Ni coarsening changes the distribution of Ni particles in the ceramic matrix from a quasi-uniform linked network to isolated precipitations. This particular changes in microstructure condition a transition in electrical conductivity which can be described by percolation theory. A coarsening leads finally to reduction of electrical path-ways in the cermet and finally to increasing over-potentials and losses of power output. A detailed introduction of the relations of conductivity and percolation properties of metal-insulator composites is given in the monography of M.Sahimi.[7].

As a consequence of Ni coarsening the three-phase-boundary length (TPB) will decrease [8]. To reduce the coarsening it has been suggested to use mixed conducting ceramic to form a cermet with Ni, in order to increase the wetting of the metal on the ceramic. It has been suggested that for example TiO_2-doped YSZ exhibits better interfacial bonding in contact with Ni [9,10] and therefore the agglomeration of the Ni-particles is suppressed. Itoh et al. have studied the effect of mixing fine and coarse YSZ particle on the anode stability [11]. This second phase reduces the mobility of Ni grain boundaries by the Orowan process.

During the literature study no results were found on the well known coarsening suppression due to solute drag. This effect is widely used in metallurgy to hinder recrystallization e.g. in Al and steels. Another option to slow down recrystallization kinetics is lowering the operating temperature, which directs in the world of micro solid oxide fuel cells (µSOFCs) or thin film oxide fuel cells (TFSOFCs) [12].

No other reasonable way has been found, to hinder effectively Ni coarsening in this porous ceramic composite. This is in no way surprising if one takes a look at the physical principle including the necessary boundary conditions of Ostwald ripening.

(I.II) <u>Thermodynamics of Ni coarsening due to Ostwald ripening</u>

Ostwald ripening takes place among precipitates when particles with various sizes are dispersed in a matrix. The growth originates from the concentration gradients around the particles caused by the thermodynamic demand, i.e. the Gibbs-Thomson equation: the concentration at the surface of particles in equilibrium with larger particles is lower than that with smaller particles. Solute atoms are transported through the concentration gradients both from the surface of the smaller particles to matrix and from the matrix to the surface of larger particles. During this process, average radius of the particles increases. This phenomenon can take place in any stage of precipitation. Any system of particles distributed in a medium and possessing certain solubility in it will be thermodynamically unstable due to a large interface area. Its decrease in approaching equilibrium is accompanied by particle coarsening whose solubility depends on their radii and is described by the well known Gibbs-Thomson relation

$$C_r = C_e \cdot \exp\left[\frac{2\gamma \cdot \Omega}{R_B T} \cdot \frac{1}{r}\right] \approx C_e \left[1 + \frac{2\gamma \cdot \Omega}{R_B T} \cdot \frac{1}{r}\right]$$ (1)

where C_e is the solute concentration at a plane interface in the matrix in equilibrium with particle of infinite radius, C_r is the solubility at the surface of a spherical particle with radius r, γ is the specific interfacial energy of the matrix-precipitate particle boundary, Ω is the mean atomic (or molar) volume of the particle, R_B is the Universal gas constant and T is the absolute temperature. The difference between C_r and C_e induces a diffusive flux of atoms from the smaller to the larger particles. Thus the average particle radius increases and the total number of particles decreases with time, as well as the total free surface enthalpy of the system [13].

As the Ni based anodes are open porous structures, a solid solubility is not a mandatory condition for ripening as the atoms have under certain conditions, for example high temperatures, the possibility to recrystallize by surface diffusion, self-diffusion or diffusion over the gas phase [14]. The self-diffusion coefficient for Ni in Ni at 930°C is 6(2)·10^{-13} cm²/s [15]. Applied to a grain with a characteristic medium diameter of 1µm this value corresponds to a diffusion time of approximately 3h.

(II) <u>Mismatch strain and weak metal ceramic interfaces</u>

(a)   **(b)**
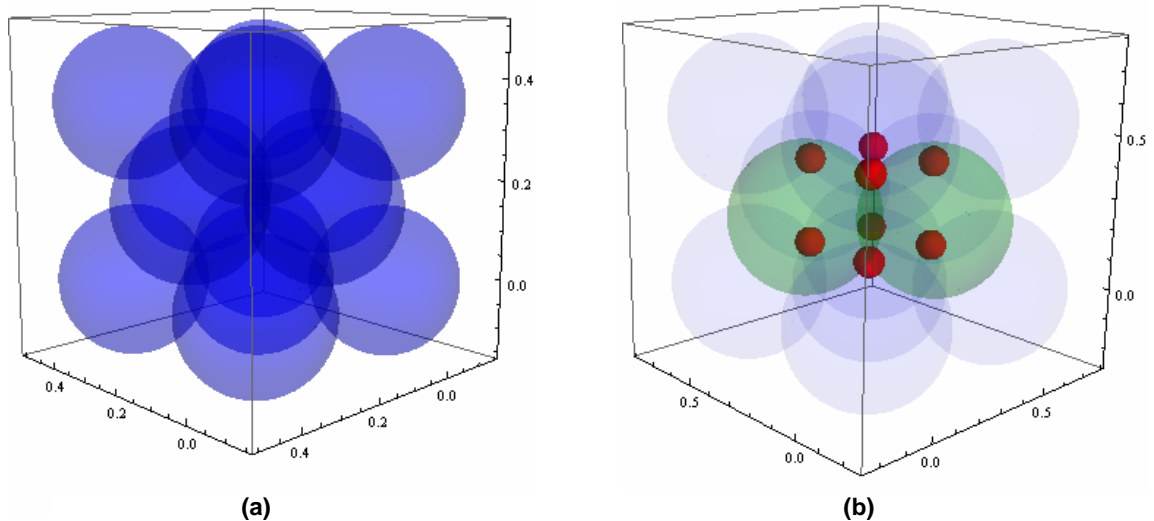
Fig. 2 a Fcc unity cell of nickel, lattice constant a$_{Ni}$=0.352nm **b** Unity Cell of Cerium (light blue)-Gadolinium (green)-Oxide (red) lattice constant a$_{CGO}$=0.542nm.

Deviations of thermal and mechanical properties between ceramics and metals weaken demonstrably ceramic/metal interfaces. In general the thermal expansion coefficients of the metal and ceramic differ so much that small deviations of the joining temperature can cause large residual stresses. The same counts for strains due to lattice mismatches. Therefore an adequate mechanical integrity of metal ceramic composite is intricate [16].

Considering a 10µm thick Ni-film, deposited at 400°C, on a Cerium Gadolinium Oxide (CGO) substrate of the same thickness a rough estimation of the total strain which is taken as linear combination of the mismatch and thermal strain can be made. [17].

$$\varepsilon_{tot} = \varepsilon_{mismacht} + \varepsilon_{thermal} = \frac{a_{Ni} + a_{CGO}}{a_{Ni}} + \left(\alpha_{Ni} - \alpha_{CGO}\right)\Delta T \qquad (2)$$

The stress free lattice parameter of CGO is larger than that of Ni, therefore the Ni is expanded in directions parallel to the interface. The coefficients of thermal expansion (CTE) are $a_{Ni}=13 \cdot 10^{-6}$°C^{-1}[17] and $a_{CGO}=9.14 \cdot 10^{-6}$ °C^{-1} respectively [18].
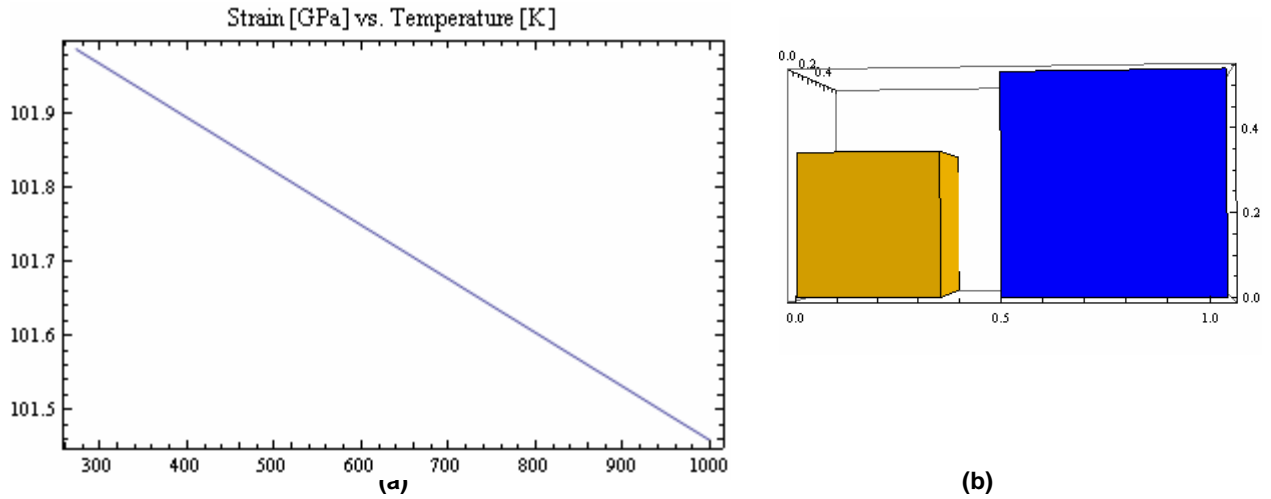
Fig. 3 a Equi-biaxial stress in the Ni Film as function of Temperature **b** Volume of unit cells Ni (yellow), CGO (blue) in comparison.

The equi-biaxial strain in the Ni-film which is the response on the mismatch and thermal stresses can be calculated by $\sigma_m = \varepsilon_{m,tot} \cdot E_{Ni} /(1-\nu)$, where E_{Ni} is the E-Module of Ni and ν is poisson ratio. In Fig 3a is shown the equi-biaxial strain as function of temperature, as the the strain at the interface in this raw-modell exceeds 1GPa it its reasonable to assume that dislocations are needed at the metal ceramic interface.

This effect and it mechanisms is widely studied in literature Beltz and Rice [19] analyzed dislocation nucleation at metal-ceramic interfaces under mixed mode crack tip. Mao and Li analyzed interface crack initiation and growth in layered materials considering dislocation plasticity in the metal layer as decisive factor [20].

(III) Oxidation of metal surfaces and redox stability

Regarding the theory of oxidation for metals by N.Cabrera and Sir Nevill Mott [21] the growth rate of oxidation layers on metal depends on the diffusion coefficient of interstitial atoms and the concentration of vacant cation sites.

$$A = 2D_i\Omega n(0) \qquad (3)$$

Using the common equation for the diffusion of defects in oxides, with *a* representing the interatomic distance, *v* the vibrational frequency and *U* the activation energy necessary for jump between to adjacent defect sites

$$D_i = a^2 v \exp[-U / k_B T] \qquad (4)$$

The growth rate of the oxide layer becomes and simple exponential shape.

$$A = A_0 \cdot \exp[-B / k_B \cdot T] \qquad (5)$$

A detailed description of oxidation processes is given in [21].

It has been found that nickel oxide, showing rock-salt structure, is a metal deficit p-type semiconductor ($Ni_{1-\delta}O$), the predominant defects being cation vacancies and electron holes. However, the nonstoichiometry; in this oxide is very low even at very high temperatures [22]. The growth process of the oxide scale on nickel at high temperatures is governed by the outward diffusion of cations, and the participation of grain boundary diffusion in this reaction may be neglected. Farther, from the pressure dependence of the oxidation rate of nickel and that of the nonstoichiometry of nickel oxide it follows, that the predominant defects in $Ni_{1-\delta}O$ are doubly ionized cation vacancies and electron holes. Thus, some statements in the literature concerning a complex defect structure in nickel oxide have not been confirmed and may result from the influence of impurities in the studied materials, as suggested by Rapp [23] and Kofstad [24].

Atkinson and Taylor [25] postulated that short-circuit diffusion is the dominant transport mechanism in the oxidation of Ni at intermediate temperatures due to short-circuit diffusion of Ni along dislocations.
In several publications it has been shown, that Nickel Oxide modified with reactive elements like Ceria and Yttrium has a lower oxidation rate than pure Nickel Oxide [26-29]. By F.Czerwinski et al it has been suggested that at high temperatures > 700°C, the CeO_2 particles formed initially by oxidation of Ce implants dissolve, acting as a source of Ce^{+4} ions in NiO grain boundaries. It is believed that Ce^{4+} ion segregants impede the Ni^{2+} diffusion, while allowing O^{2-} diffusion to continue; this results in a change of oxide growth mechanism as compared to pure NiO.[28]

4. Schlussfolgerungen

On the basis of this literature study that explored the basic mechanisms of degradation in porous Ni ceramic anodes, promising concepts to enhance the redox stability of Ni based anodes have been elucidated. Beneficial for reducing Ni oxidation seems to be the modification of NiO with reactive elements like ceria or yttrium.

This should hinder the thickness of the oxidation layer in case the anode is cooled down under oxidizing conditions. Another option is to introduce an interlayer between the ceramic and the metal component of the cermet to improve wetting of the metal on the ceramic in order to prevent delamination at the ceramic-metal joints.

5. Ausblick

In a next literature survey we will concentrate onto finding appropriate experimental techniques that provide specific information about the different aging processes. This includes measuring techniques to characterize the interfacial energies between the ceramic and metal (e.g. sessile drop method and others) and to characterize interface structures. In addition a method is searched for the characterization of the oxidation process (when Ni/ceramic anodes become NiO/ceramic anodes) in situ.

These techniques should provide information on the different aging processes independently from each other.

6. Finanzreport

2-71-683-06

Financial period: 01.06.2007-31.12.2007

(CHF)	Salaries & social charges	Durable equipment	Consumables	Travel	Other	Total expenditure	Budget for period of report	Balance
ETHZ-NIM	29'281.00	0.00	0.00	0.00	195.70	**29'476.7**	55.000	**25'523.3**
					Total	**29'476.7**	55.000	**25'523.3**

Repartition by person:

	Name	Position	Period	% on project	Total salaries	Total social charges	TOTAL
ETHZ-NIM	*Henning Galinski*	Ph.D. student	01.06.2007-31.12.2007	100%	25'668.35	3'612.65	29'281.00

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