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On Degradation Mechanisms of Ni-YSZ Fuel Electrodes in Solid Oxide Cells

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This is a continuation of a series of articles by the principal author on degradation of Ni-YSZ cermet electrodes. This one gives a brief listing of the main aspects and in particular of the disagreements in literature on the long term degradation mechanisms of Ni-YSZ electrodes at high current density. Two main hypotheses are presented, and the weaknesses and strengths are briefly discussed. Recommendations for alleviation of the degradation are given as well as for needed experiments in the future.

Introduction

The solid oxide cell (SOC) is reversible and operates well in both electrolysis cell mode (SOEC) and in fuel cell mode (SOFC). This high temperature (600 - 900 °C) cell type has many advantages compared to low temperature cells (1, 2). Despite this, the relative fast degradation of the Ni-YSZ cermet fuel electrode at high electrolysis current densities ($> 0.5 \text{ A cm}^{-2}$) is still a problem for a broad commercialization of the SOEC. In SOFC mode, the durability is considerably better (3).

Therefore, there is for the time being, a high research activity with the aim of figuring out the mechanism of this type of SOEC degradation. It is associated with a characteristic migration of Ni particles out of the thin (ca. 5 μm) electrochemically active layer of a mixture of ca. 0.2 – 1 μm Ni and YSZ particles, i.e. Ni migration away from the bulk electrolyte towards the coarse structured Ni-YSZ cermet support. After long life time test (9,000 h) two to three layers of the Ni nanoparticles in the active electrode layer next to the electrolyte may have been totally removed as shown in Figure 3 in (4). Also, it has been observed that during the first 100 – 1000 h a lot of contact area between Ni and YSZ particles was lost, and the electrical contact between Ni particles was lost within large regions of the cermet, see Figure 4 in (4). The interconnection between YSZ particles, and of YSZ particles to the bulk YSZ electrolyte seems very stable. Note, [that \(4\) is a new article from 2021.](#)

An important piece of background information is that the essential property of the Ni-YSZ electrode is the length of the three phase boundary (3pb) between the three phases of Ni electron conductor, YSZ oxide ion conductor, and reactant gases, which have electronic contact to the main Ni electrode, ionic contact to the bulk YSZ electrolyte, and access to the main gas atmosphere, respectively. The gas atmosphere may consist of $\text{H}_2 + \text{H}_2\text{O}$ or $\text{CO} + \text{CO}_2$ or a mixture of all 4 gases.

In spite of the fact that there is general agreement about the above mentioned observations, there are serious disagreements between the hypotheses for the mechanisms

of the degradation processes, which may be divided in two main types: One type in which the common assumption is that the Ni migration is driven by Ni-YSZ Interface Energy Gradients (IEG), see e.g. (5,6,7), and another type in which the basic assumption is that the Ni migration is directly driven by Electrochemical Potential Gradients in the Ni-YSZ cermet electrode (EPG). Thus, it is also agreed that the degradation is driven by the electrochemical polarization of the Ni-YSZ electrode (1), but the assumed mechanisms are basically different. A review of more Ni-YSZ electrode literature than just that of YSZ cermets between 700 and 850 °C points out that the IEG hypothesis cannot explain several reported clear experimental results, whereas the present EPG hypothesis is based on released Ni⁺ ions from Ni particles without electrochemical contact that migrate across the YSZ surface to new 3pb active Ni particles 3 – 5 μm away from the YSZ bulk electrolyte. We, the present authors, favor the EPG hypothesis of (4,8,9) with small changes. More details than previously published are described below, where the two hypotheses are discussed further.

It should also be noted that at temperatures above 900 °C it is well proven that Ni migration takes place by gaseous species in steam, probably as NiOH in vapor phase (4).

Experimental Observations

The observations behind the two hypotheses are briefly outlined hereunder.

The IEG Hypothesis

The IEG hypothesis is mainly based on post mortem scanning electron microscopy investigations of Ni-YSZ cermet SOC negative electrodes long term tested in the temperature range of 700 – 850 °C over several hundreds and often many thousands of hours (10). Apparently, a Ni migration away from the very negative polarized 3pbs next to the bulk electrolyte towards the Ni-YSZ support takes place in SOEC. This is, not surprisingly, interpreted as if Ni migrates from very negative polarized Ni-YSZ to less polarized YSZ away from the YSZ bulk electrolyte. This seems also supported by the picture seen in SOFC mode. The Ni migration direction is from the low polarized YSZ next to the support towards to most positive (least negative) polarized 3pbs next to the bulk electrolyte in SOFC (6). The driving force is assumed to be a gradient in the polarization dependent Ni-YSZ interfacial energy.

This is, however, in contrast to many other observations of polarized Ni-YSZ. As explained further below in this manuscript, the main problem with the IEG hypothesis is that the processes taking place during the very long testing time, in particular the loss of contact between Ni and YSZ particles and between Ni particles and the consequences of this, are not taken into account.

The EPG Hypothesis

The EPG hypothesis in its present form has not been published previously, whereas the IEG has been extensively published see (7 and references therein). Therefore, we give a much more detailed description of the EPG hypothesis here.

The Loss of Ni Contact. As mentioned, there is a tendency that the Ni loses both its contact to active 3pbs and electrical contact to other polarized Ni particles. If a Ni particle in a Ni-YSZ cermet does not have an active three-phase boundary (3pb) to other Ni particles, then it is electrochemically isolated. This does not prevent the Ni particle from having good mechanical-physical contact with YSZ particles. Long 3pb pieces are blocked by glassy SiO₂ and perhaps by other impurities (11,12). Furthermore, the Ni-YSZ phase interface (2pb) may also be electrically blocked by silica glass or other impurities in a "monolayer". Furthermore, such "monolayers" between the NiO and YSZ particles (in the precursor for the active Ni-YSZ electrode) may also contain Ni²⁺ ions. When strong reduction takes during high current density electrolysis, the reduction of SiO₂ may in some areas make the Ni and YSZ detach from each other within a relatively short time. Also, it has been indicated that the Ni-YSZ may detach from each other at very high negative overpotentials because the interface energy becomes zero (7 and references therein). We will in the following call the electrochemically separated Ni particles for "separated" only.

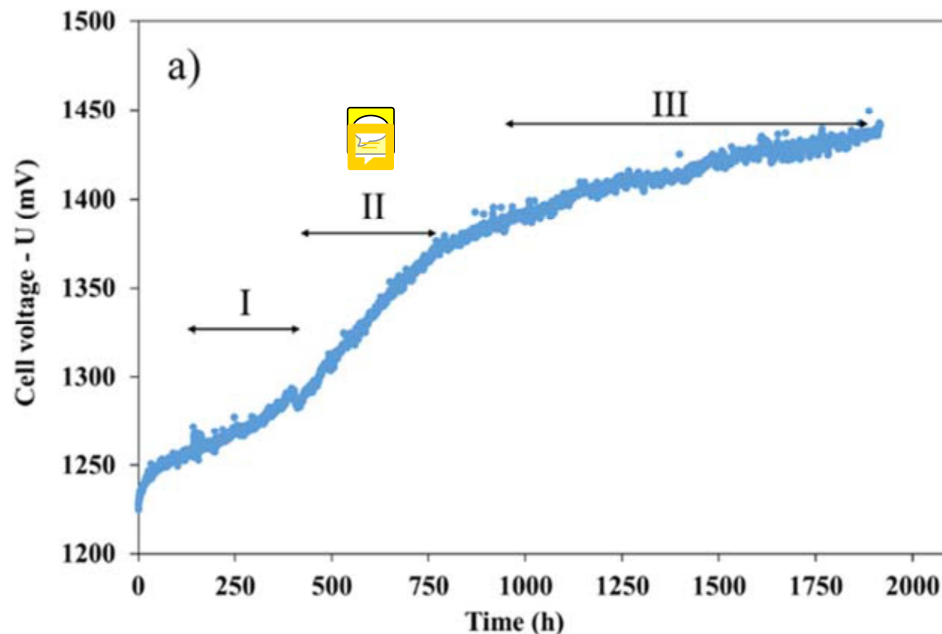


Figure 1. Cell voltage as a function of time at 750 °C in galvanostatic electrolysis mode, -1 A cm^{-2} , $\text{pH}_2/\text{pH}_2\text{O} = 0.1/0.9$, $12 \text{ Nml cm}^{-2} \text{ min}^{-1}$ and steam conversion 64%. After L. Rorato et al. (7).

This kind of processes forming separate Ni particles is our explanation of the fast degradation during the early (50 – 500 h) stage of long term tests. In the work of L. Rorato et al. (7) shown in Figure 1, they have marked 3 periods, which they model, while the first 70 h before period I they call “a short transient period” of ≈ 70 h. However, the increase in cell voltage during this “short transient” period is ca. 35 mV, corresponding to 500 mV/1000 h! We attribute this to the process of forming separate Ni particles, or in other words – destruction of many 3pbs. Further we assume that not until after this very first period of time does the Ni migration process really take off, and it is only the separate Ni that migrates. This Ni migration is from positive (less negative) electrochemical potential (ca. OCV) towards the imposed negative Ni-YSZ electrode

potential at the new 3pbs in the region in which the Ni particles are still in electrochemical contact as further explained below.

Mechanism of Ni Migration. Previously, we assumed that the migrating Ni-species were NiOH entities on the YSZ surface (9). Later, it has been shown experimentally that a very similar process happens in dry CO-CO₂ atmosphere. Thus, the migrating species cannot contain OH. Therefore, we revise our hypothesis. The essential change is simply to assume that it is Ni⁺-ion that migrates on the YSZ-surface layer as either Ni⁺ + OH⁻ in case of steam electrolysis, or as Ni⁺ ions balanced with CO₃⁻ radical ions in case of CO₂ electrolysis. “Ni₂CO₃” on a YSZ surface is not assumed to be any kind of crystalline Ni₂CO₃, but rather a layer of adsorbed Ni⁺ and CO₃⁻ in which CO₃²⁻ has one of its oxygen atoms incorporated into the crystalline YSZ surface which is formed by reaction between CO₂ molecule, a Ni atom, and an unsaturated surface oxygen with one electron (O⁻) in similarity to CO₂ reduction on ceria (13). The process is sketched in Figure 2 and 3, and the reaction equations are given in eqs. 1 - 3.

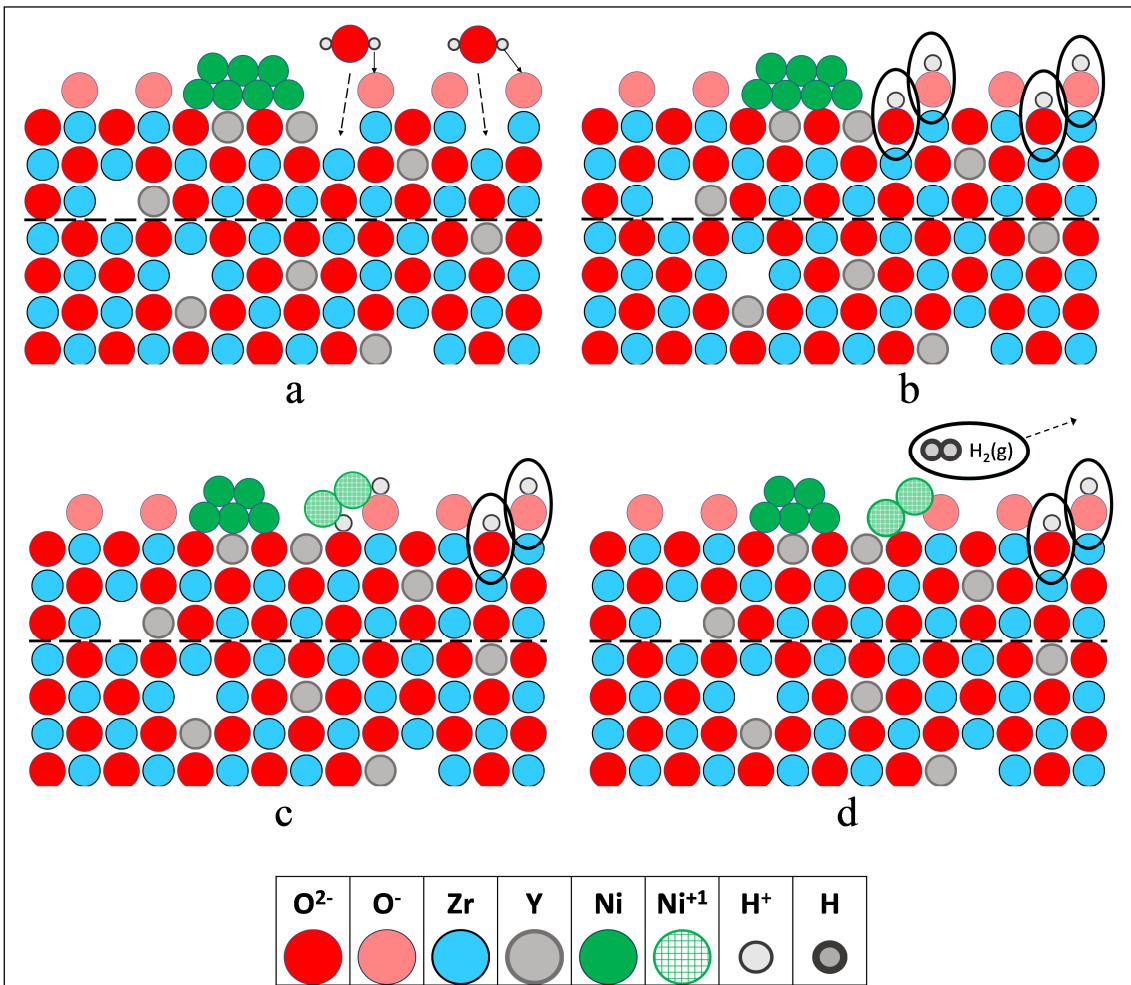
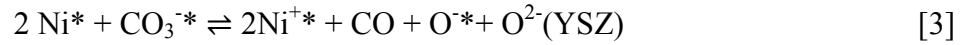
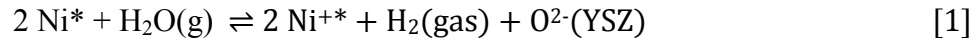


Figure 2. Sketch of $\text{H}_2\text{O} + 2 \text{Ni} \rightarrow \text{H}_2 + 2 \text{Ni}^+$ mechanism on a YSZ surface layer (above the dashed line) in the vicinity of Ni (3pb). The balls represent atoms and ions as given in the legend. a) the starting situation with O⁻ and O-vacancies at the YSZ surface; b) the dissociative adsorption of H₂O with help of vacancies; c) formation of Ni⁺ on YSZ, d) evolution of H₂ gas.

The assumed reactions on the YSZ surface are



Eq. 1 is for H₂O-H₂ and eqs. 2 and 3 are for CO₂-CO. The asterisk indicate adsorbed species.

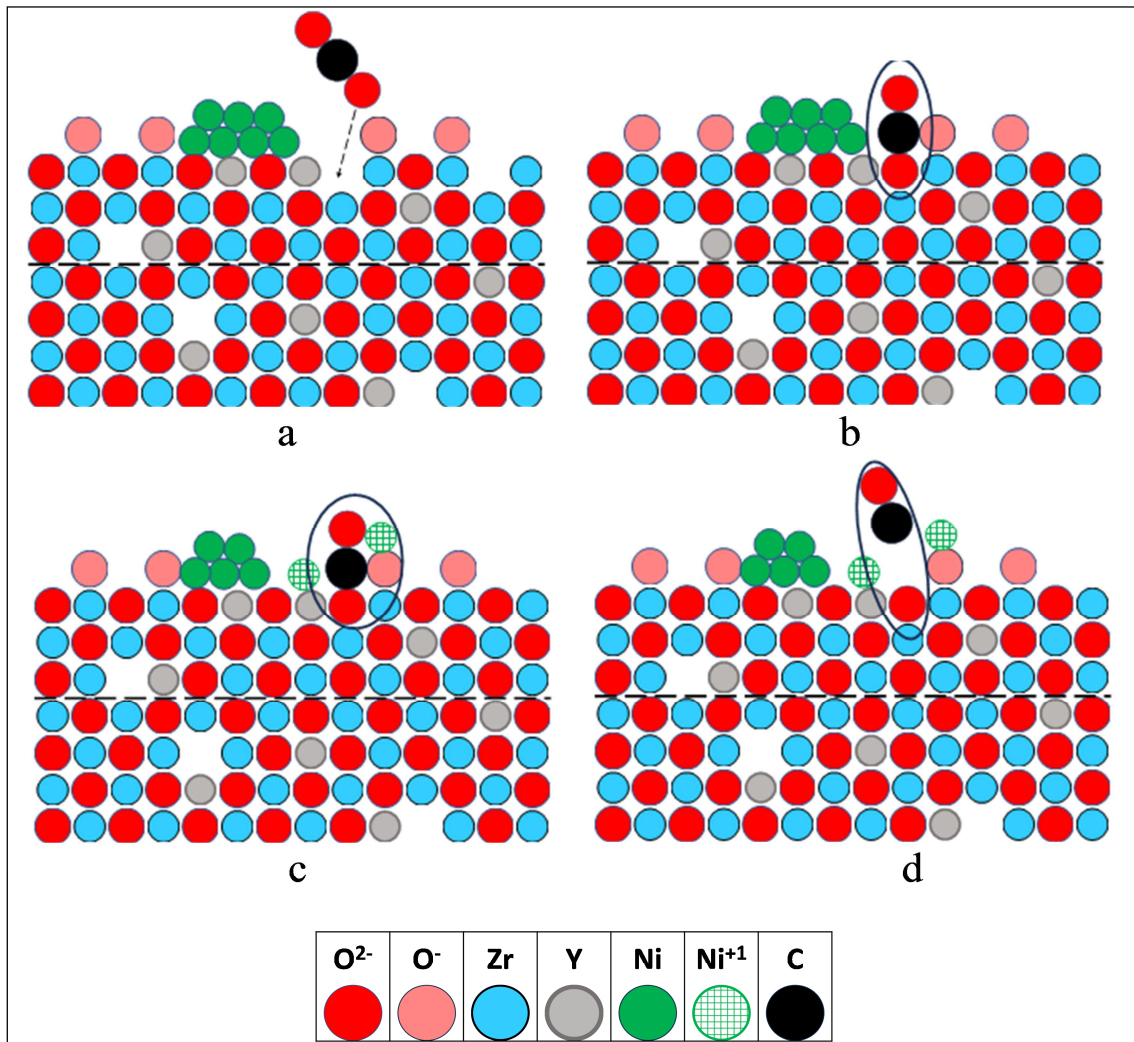
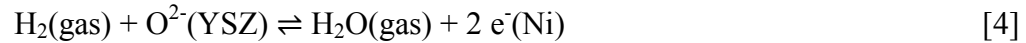


Figure 3. Sketch of CO₂ + 2 Ni to CO + 2 Ni⁺ mechanism on a YSZ surface layer (above the dashed line) in the vicinity of Ni (3pb). The balls represent atoms and ions as given in the legend. a) the starting situation with O⁻ and O-vacancies at the YSZ surface; b) the adsorption of CO₂ with help of vacancies; c) formation of Ni⁺ on YSZ, d) evolution of CO gas.

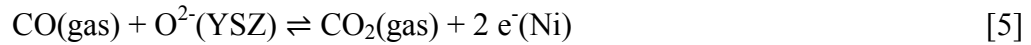
Note, that all reactions are reversible. This means that the processes may also take place in Ni-YSZ SOFC electrode as actually observed experimentally in Ni-YSZ cermets and Ni-YSZ model electrodes (3,4).

Next, let us imagine how the process develops over time on the particle level. A separated Ni particle cannot feel the electrode potential imposed by the current density. It will instead take the potential determined by the ratio of the partial pressures p_{H_2O}/p_{H_2} or p_{CO}/p_{CO_2} through the electrochemical reaction with oxide ions, O^{2-} , and this must be the case as separated Ni must have mechanical support by YSZ or oxide impurities as it cannot exist in a cermet without any support.

Thus, separated Ni has the potential determined by the equations



Or



Near the steam inlet in an SOEC p_{H_2O}/H_2 will be similar in the gas channel and in the electrochemical reaction layer in the cermet next to the bulk electrolyte. This means that the potential of separate Ni will be similar to the active Ni potential at OCV. In other words, the potential of separate Ni near the electrolyte is similar to that at OCV (overpotential $\eta \approx 0$). Thus, the potential difference between the potential of separate Ni and the new 3pb region is approximately equal to the imposed electrode overpotential. The imposed Ni-YSZ overpotential at -1 A cm^{-2} may be in the range of -100 mV or more. This means that the potential gradient of about $3 \text{ }\mu\text{m}$ becomes $-30 \text{ mV }\mu\text{m}^{-1}$. This is the kind of driving force for moving the Ni^{+*} ions away from separate Ni near the electrolyte to the new 3pb region. Furthermore, the surface concentration of Ni^{+*} on YSZ near the separate Ni with the relative positive potential will be much higher than the Ni^{+*} on YSZ in the negative polarized new 3pb region.

Again, it should be noted that all the processes are reversible, so the the processes and migration direction may be opposite in Ni-YSZ SOFC electrodes, in case of a formation of similar separate Ni regions. However, it is well known that the impurities like SiO_2 behave very different in SOEC and SOFC. Further, the Ni-YSZ interface energy is potential dependent, and therefore different for SOEC and SOFC.

In case of simple polarization of Ni on the EPG hypothesis predicts that in case of little loss of electrochemical contact to the Ni particles, the Ni particles will via Ni^{+*} migrate towards negative polarized Ni and away from positive polarized Ni. There are several examples of this in the literature (4 and refs. therein).

Development over Time

Figure 4 is a sketch of a possible development in the active part of an SOEC Ni-YSZ electrode under galvanostatic load. The top picture represents the beginning of a test when only a few μm next to the YSZ electrolyte will constitute an active 3pb region. The middle picture indicates that after a few hours (50 – 100 h) some separate Ni particles

have been formed, and the most active 3pb region has moved a little away from the bulk electrolyte.

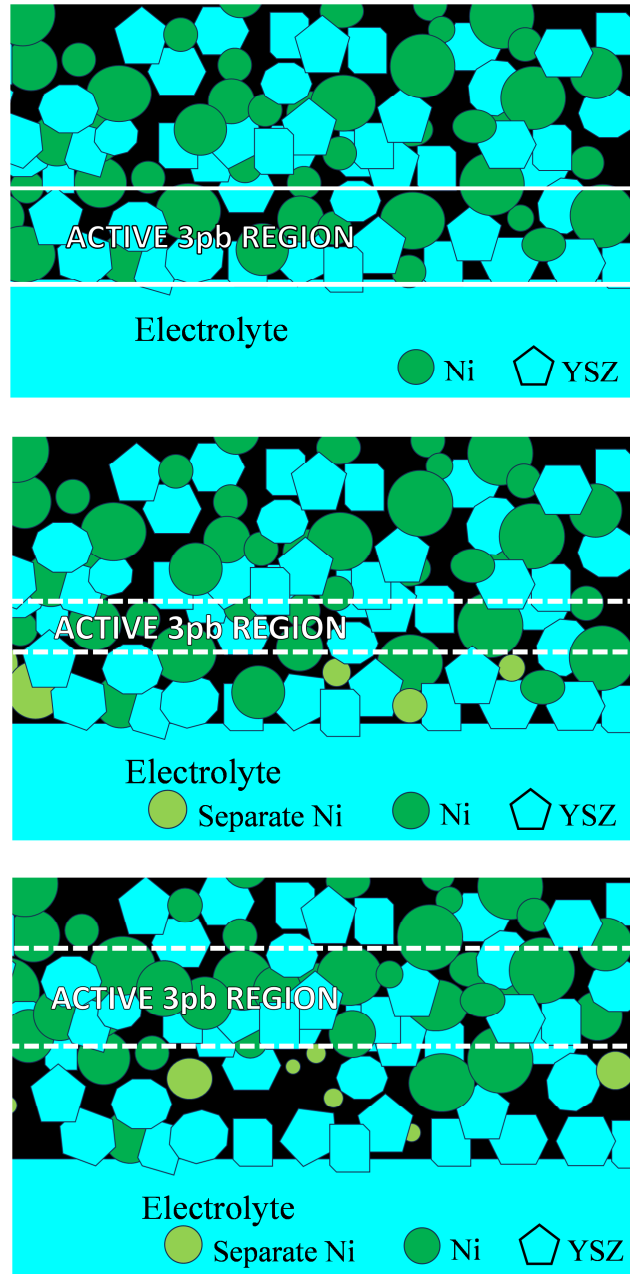


Figure 4. A sketch of a possible development in the active part of an SOEC Ni-YSZ fine structured ($0.5 - 1 \mu\text{m}$ particles) electrode under galvanostatic load in a long term test at highly negative current density of -1 A cm^{-2} or above. The top picture represents the beginning of the test with the active 3pb region next to the YSZ electrolyte as marked. The middle picture is the situation after 50 – 100 h, and the bottom picture sketches the situation with a layer of YSZ particles with only few active Ni particles next to the electrolyte.

The bottom picture depicts the situation after long time of 1000+ h.

A characteristic of the migration of Ni is that after 1000 h or so, the movement of the 3pb region seems to stop. This is probably due to an overpotential threshold below which the Ni particles do not get electrochemically separated (4) probably because below this threshold the Ni-YSZ interface energy is sufficient to avoid the loss of adherence. As the Ni-YSZ cermet degrades, the practical electrolyte thickness thickens with the porous YSZ layer between the bulk electrolyte and the new 3pb region. This YSZ layer has a bad O^{2-} due to the high porosity. This naturally causes a gradual redistribution of overvoltage and current density. The initial high values at the steam-hydrogen inlet change gradually to lower values, and the initial low overvoltage and current density at the outlet are increased. The consequence is that for a long time until the Ni migration has degraded the cermet significantly all the way out to the steam-hydrogen outlet, the degradation rate looks relatively low (period I in Figure 1). After this, the cell voltage starts to increase faster again and the overpotential at the inlet gets above the degradation threshold once more, and the picture is repeated with fast degradation in period II and slower again in period III. Possibly, another repetition would have happened if the test had been continued. Our prediction is that this will happen until the negative overvoltage becomes high enough to induce significant electron conductivity in the YSZ electrolyte and from there this will dominate the cell behaviour.

It is the impression that the reproducibility of these galvanostatic long term tests with high current density are not very reproducible, probably because the development is very dependent on the detailed electrode structure, on the detailed procedure of the initial reduction of NiO, and on the types and concentrations of impurities. Much more research on this is needed.

Weaknesses and Strengths of the IEG and EPG Mechanisms.

IEG. A clear weakness of the IEG is that it is directly against a number of reliable experimental results from several sources. This is actually also accepted by the advocates of the IEG mechanism (7). Further, IEG has no clear migrating species apart from just mentioning Ni, but we think that migration of neutral Ni atoms across an metal oxide surface is dubious. Furthermore, surface diffusion coefficient of Ni on YSZ is not known to us.

A strength of the IEG is the quantitative mathematical modeling, but as it can only model selected Ni migration data, it is not very strong.

EPG. A weakness is that one step in the process, the electrochemical separation, is not well described even though there is some proposal for the mechanism.

The clear strength of the EPG hypothesis is that it covers all known Ni-migration data in SOC. Also it can explain the observed effect of increasing growth rate of Ni coarsening with increasing pH_2O , and this is a clear consequence of eq. [1]. Finally, the PEG gives some understanding of the observed potential threshold for the degradation.

How to Stop the Degradation and the Ni Migration

A simple way to alleviate the migration is to stay below the overpotential threshold, to keep the impurity level low, and to handle the impurities in a proper manner. Further, optimization of the Ni-YSZ electrode structure to as small particles as possible by means producing the NiO-YSZ precursor as dense as at all possible. Finally, addition of surface active species that increase the adherence between Ni and YSZ may help (4).

Concluding Remarks

It is recommended to do more well-designed experiments in order to clear up the disagreements. In particular, it is recommended to do potentiostatic experiments as the EPG hypothesis predicts that we will find a clear overpotential threshold and much less destruction over time. Furthermore, most experimental publications in the area are based on tests of a single or very few tests. There is a strong need for careful reproducibility tests.

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