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Published in:
ECS Transactions

Link to article, DOI:
[10.1149/09101.0613ecst](https://doi.org/10.1149/09101.0613ecst)

Publication date:
2019

Document Version
Peer reviewed version

[Link back to DTU Orbit](#)

Citation (APA):

Mogensen, M. B., Chen, M., Frandsen, H. L., Graves, C. R., Hauch, A., Jacobsen, T., Jensen, S. H., Skaftø, T. L., & Sun, X. (2019). Comprehensive Hypotheses for Degradation Mechanisms in Ni-Stabilized Zirconia Electrodes. *ECS Transactions*, 91(1), 613-620. <https://doi.org/10.1149/09101.0613ecst>

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Comprehensive Hypotheses for Degradation Mechanisms in Ni-Stabilized Zirconia Electrodes

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Degradation of nickel-stabilized zirconia (Ni-SZ) electrodes is predominantly due to four features 1) high mobility of Ni, 2) fragile nature of SZ ceramics, 3) narrow three phase boundary (3PB), and 4) effects of impurities: i) in blocking (poisoning of 3PB), and ii) on mobility of Ni. Impurities may be contaminants in reactant gases and influenced by the reactants H₂O, CO₂ and CO, or impurities in cell and stack materials. Examples of important degradation types and hypotheses of the degradation mechanisms are described. Examples are: a) loss of electrochemical contact between Ni and YSZ (yttria stabilized zirconia) particles and loss of contact between Ni-Ni particles followed by Ni-migration away from the YSZ electrolyte - one reason is hypothesized being a result of huge potential and thermal gradients at the 3PB; b) growth of Ni-particles; c) redoxing; d) blocking of 3PB and reaction sites by impurities like Si and S. Mitigation methods are discussed.

Introduction

Degradation of Ni-SZ electrodes is one of the main obstacles for a fast commercialization of reversible solid oxide cells (RSOC), which can operate well in both electrolysis (SOEC) mode and in fuel cell (SOFC) mode. Ni-SZ means a composite of Ni-metal and zirconia stabilized with other oxides such as yttria, scandia, ceria or mixtures of these. In the present paper, we try to analyze available knowledge with the aim to make interrelated hypotheses.

Brief literature overview of Ni-SZ degradation phenomena

The degradation of Ni-SZ composite electrodes in solid oxide cells can be described by the thermoelectrochemical interaction between Ni and SZ interfaces under the influence of impurities and gaseous reactants and products. Figure 1 presents a summary of most of the reported degradation phenomena (1), and Figure 2 summarizes the Ni migration types observed (2,3). At low electrode polarization and current density (typically < ca. 1 A cm⁻² in both electrolysis and fuel cell modes) the unavoidable S and Si based impurities that accumulate on the surfaces of Ni and SZ and at the three phase boundaries (3PBs) may cause a complex set of degradation processes in particular in the

early cell life of less than 1000 h. At high electrode polarization and current density (more than $\pm 1 \text{ A cm}^{-2}$ at $800 \text{ }^\circ\text{C}$) different degradation processes take place. Loss of contact between Ni and YSZ particles, and between Ni-particles are observed at electrolysis current densities higher than 1 A cm^{-2} together with severe migration of Ni out of the active RSOC fuel electrode layer has been observed (3). Another degradation process is the Ni particle growth, which is strongly influenced by gas phase composition and temperature. The growth rate of Ni-particles increases with both partial pressure of H_2O ($p\text{H}_2\text{O}$) and temperature.

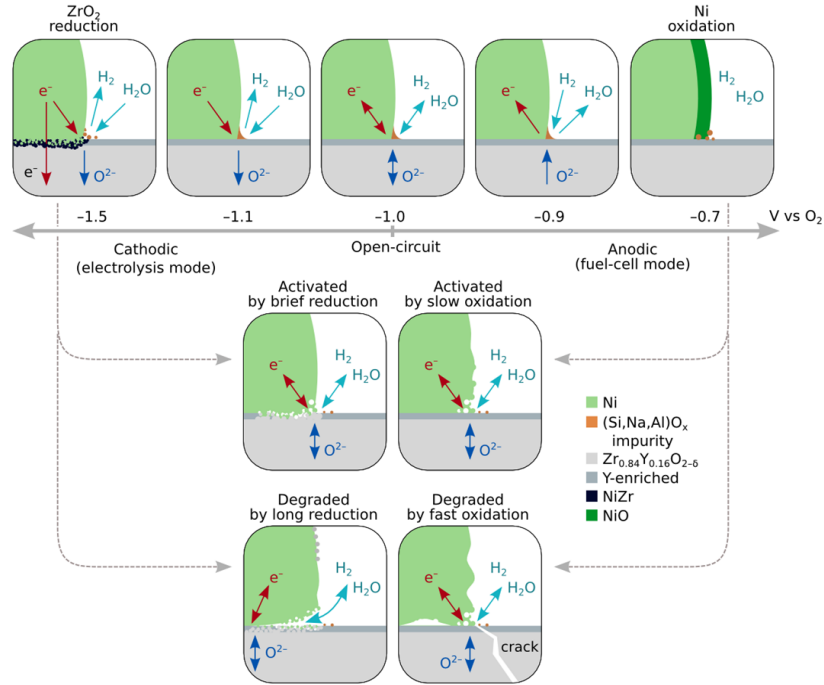
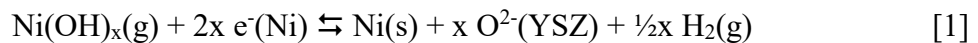


Figure 1. Commonly seen Ni-YSZ fuel electrode-potential-driven activation and degradation phenomena that affect the Ni/YSZ/ $\text{H}_2, \text{H}_2\text{O}$ or CO/CO_2 three-phase-boundary (3PB). From (1).

The growth of Ni-particles and the migration of Ni in or out of the active Ni-YSZ electrode layer have been explained by the formation of surface or gas phase species of $\text{Ni}(\text{OH})_x$, $x = 1$ or 2 .



Under relative oxidizing conditions (SOFC mode) x may be 2 and under more reducing conditions (SOEC mode) x may be 1 .

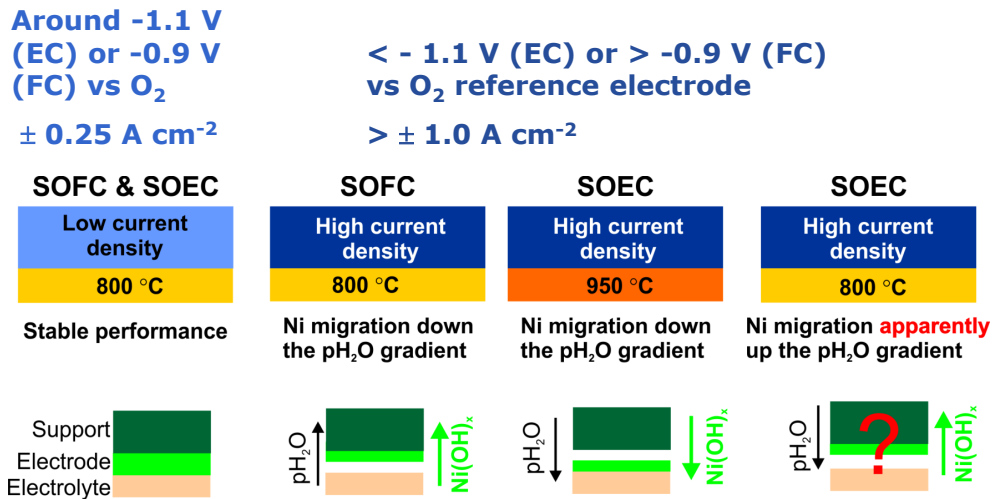


Figure 2. Summary illustration of observed migration of Ni in Ni-YSZ in SOEC and SOFC based on (2,3). The behavior has been explained by eq. [1], but apparently observations are not explainable by this equation alone, see text.

Apparent discrepancies in literature

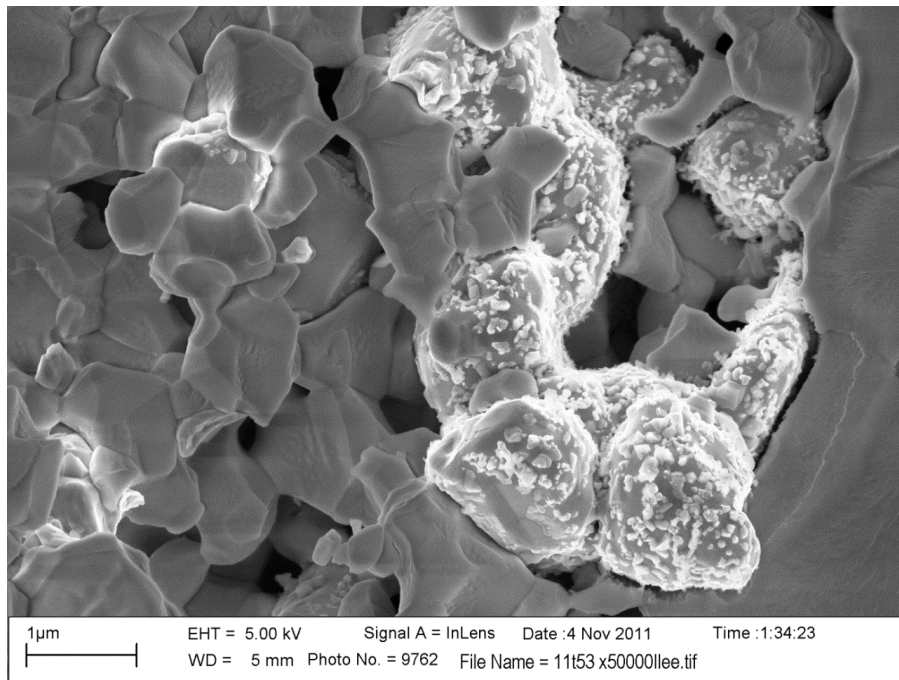


Figure 3. SEM of Ni-YSZ cermet electrode after a 1200 h SOEC galvanostatic test. 850 °C, 10 % H₂ + 45 % H₂O + 45 % CO₂, -1 A/cm², cell voltage: start 1130 mV, end 1290 mV, reactant conversion degree 62 %, showing that detrimental nano-particles of YSZ are formed on interfaces between Ni- and YSZ particles breaking the electrochemical contact between them (5).

The migration of Ni away from the YSZ|Ni-YSZ electrolyte|electrode interface was explained as caused by loss of contact between Ni- and YSZ-particles in the volume of the Ni-YSZ cermet next to the electrolyte followed by NiOH migration in the resulting

potential gradient towards new 3PB of lowest electrochemical potential formed outside the layer with loss of particle contact (3). However, we previously had difficulties in explaining the loss of Ni-YSZ contact and the observed high rates of Ni migration. The calculated concentrations of surface activity or partial pressure of Ni(OH)_x are very low and will require exorbitant high diffusion rates in order to explain the observed migrations rates (4).

An explanation of the loss of contact between Ni- and YSZ-particles might be formation of YSZ nanoparticles at the interface between Ni and YSZ as shown in Figure 3. This was proposed to be caused by reduction of ZrO_2 (in YSZ) to Zr metal and reoxidation of the metal to zirconia. However, the cell voltage at start of the test was only 1.13 V and 1.29 V at the end of the test. This means that the potential of the Ni-electrode particles at all times was well above -1290 mV versus pure oxygen at the same temperature. This is about 1 V more positive than the reduction potential of ZrO_2 to Zr metal (5,6), and thus this cannot be the full, correct explanation.

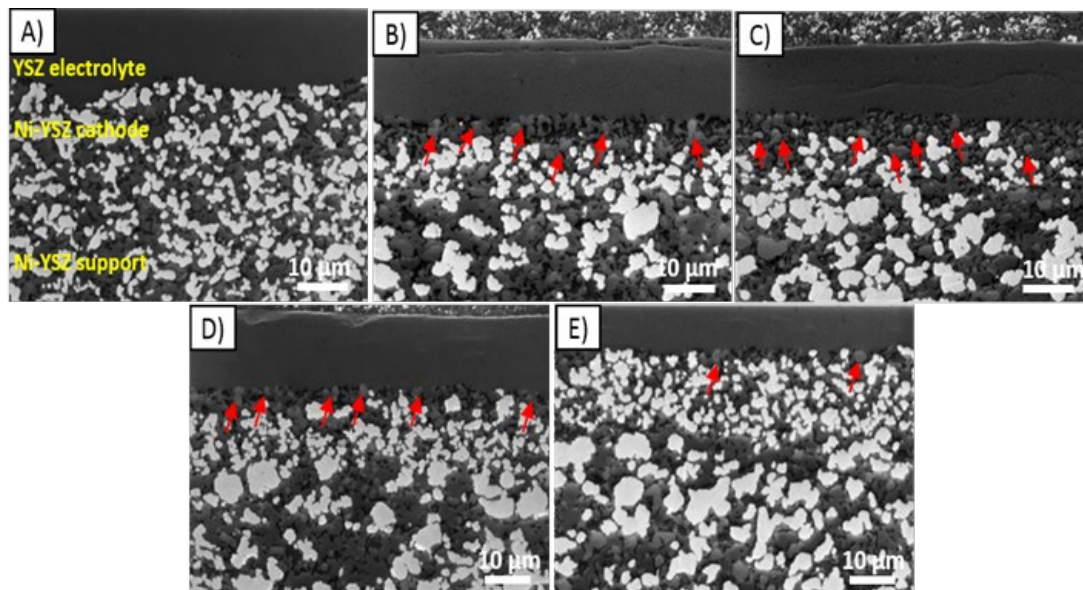


Figure 4. Low-voltage SEM micrographs of fine-structured Ni-8YSZ active electrode between the coarse 3YSZ support and the 8YSZ electrolyte. A) not tested, and B) to E) after galvanostatic test at -2.0 A cm^{-2} , 60 % (steam + CO_2) conversion. B) $\text{H}_2\text{O-H}_2$ inlet and C) outlet tested 678 h, D) inlet and E) outlet tested 138 h. Bright: interconnected Ni; light grey: non-connecting Ni; dark grey: YSZ; black: pores. Red arrows point to uncontacted Ni. Temperature: 865 °C increasing to 875 °C. Inlet gas: 45 % H_2O + 45 % CO_2 + 10 % H_2 . The cell voltage of the 678 h test was below 2.0 V and the 138 h test below 1.8 V (7).

Figure 4 shows a series of SEM micrographs of non-tested and long-term tested Ni-8YSZ active electrodes from SOECs. YSZ nanoparticles in similarity to Figure 3 were found in the tested electrodes (7), and Figure 4 shows that the phenomenon of Ni-migration away from the electrolyte is much more pronounced at the steam inlet than at the outlet for both the 138 h and the 678 h test. As the voltage across the cell is uniform over the whole cell this difference in degradation rate from inlet to out cannot not be related to any difference in reduction potential of the Ni-YSZ electrode, but seems rather

related to the high overvoltage and current density at the H₂O + CO₂ inlet compared to the H₂ + CO outlet.

Improved Hypotheses

Discussion of elements of hypotheses

We realize that we need to improve our previous hypotheses for degradation of Ni-YSZ electrodes in steam electrolysis mode at high overvoltage. We still hypothesize that migration of Ni at high overvoltage in SOEC mode is not the basic cause of the degradation and that the degradation is initiated by loss of contact between Ni and YSZ. Furthermore, we now assume that loss of Ni-to-YSZ contact is associated with the formation of YSZ nanoparticles at the Ni-YSZ interface, because observations point to simultaneous occurrence of YSZ nanoparticle formation and Ni-migration away from the electrolyte in case of steam electrolysis with or without concomitant CO₂ electrolysis. We have found that YSZ nanoparticle formation seems not associated with electrochemical reduction of zirconia to zirconium metal but rather associated with high overpotential and high current density. A qualitative explanation may be as follows.

Figure 5 shows an illustration of our understanding of the detailed mechanism of the H₂/H₂O/Ni/YSZ electrode in electrolysis direction. The simple reversible reaction is



The fully reversible mechanism has been described previously (8,9), but now some of the effects at high overvoltage of each step in this mechanism will be considered.

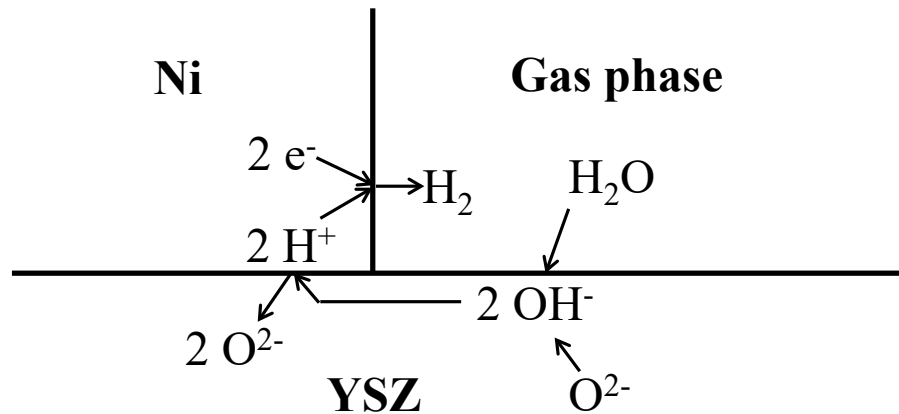


Figure 5. Illustration of our hypothesis for the reaction mechanism for steam electrolysis process, $\text{H}_2\text{O} + 2 e^- \rightarrow \text{H}_2 + \text{O}^{2-}$, at a clean 3PB. The whole figure is meant as a cross-section of a 3PB. The dimensions of the active 3PB zone are assumed to be in the range of 1 - 10 nm in the shown plane.

The first step is the dissociative adsorption reaction of H₂O onto YSZ



Transferring H₂O gas molecules into solid state YSZ involve a big change in entropy. As the entropy of OH⁻ and O²⁻ in solid state is assumed to be negligible compared to the entropy of H₂O gas then the change in entropy, ΔS_{YSZ} , at the YSZ surface in 3PB zone is equal to the total entropy content in H₂O gas, i.e. 233 J K⁻¹ mol⁻¹ of H₂O reacted. This further implies heat input at 850 °C = 1123 K onto the YSZ of $-T\Delta S_{\text{YSZ}} = 1123 \cdot 233$ J mol⁻¹ = 261.7 kJ mol⁻¹ of H₂O reacted. When 3PB length is known, local heat input at a given current density can be estimated.

The second process is the conduction of protons (OH⁻ is perceived as a proton in the YSZ matrix) through the top part of YSZ to Ni at the 3PB. This will dissipate Joule heat, but we do not know the length of the conduction path and the proton conductivity. The length will depend on the amount of impurities at the 3PB. We always find some kind of segregation of impurities and yttria to the YSZ surface, and in particular to the 3PB region (10).

The third process is the transfer of protons to the near surface region of the Ni at the 3PB. Probably, this resistance is small compared to the resistance of the proton conduction through the YSZ 3PB zone to the Ni. However, we are able to estimate the total line specific polarization resistance, $\text{LSR}_{\text{p,3PB}}$, of the 3PB, i.e. the sum of the electrical resistances of the second and third step, based on extensive impedance measurements and 3D reconstruction of the Ni-YSZ electrode structure using FIB-SEM. An example is a value of ca. 200 Ω cm at 850 °C for a DTU Ni-YSZ electrode (11).

The fourth and final step is the hydrogen evolution on the Ni surface next to 3PB. This involves a consumption of electrons and evolution of the H₂ into gas phase. This requires input of entropy in the form of heat. The need for input of entropy to the Ni at the 3PB is estimated to -155 J K⁻¹ mol⁻¹ of H₂ evolved. This means a heat consumption of $-155 \cdot 1123$ J mol⁻¹ = 174 kJ mol⁻¹ of H₂ evolved.

Such strong heating at the YSZ side and strong cooling at the Ni side of 3PB indicate that rather steep thermal gradients will exist in YSZ next to the Ni at high current density. Quantitative estimates are not available yet because calculation of a temperature gradient requires a heat transfer number across the Ni-YSZ two-phase-boundary (2PB) near 3PB. Anyway we hypothesize that steep temperature gradients will be formed in the YSZ within the narrow 3PB zone due to low heat conductivity of the YSZ. Besides this there will be a steep electric potential gradient across the 2PB with an electrochemical double layer. This will modify the composition of the YSZ surface the more the higher the overpotential of the Ni-electrode is. Finally, it should be noted that strong polarization of an interface will change the interface energy. All in all, we assume that these temperature and potential gradients together with changes in interface composition and energy destabilize the YSZ so that nanoparticles are formed at the Ni-YSZ interface and the Ni-YSZ contact is broken.

As mentioned we have found that the Ni migration both in SOEC and SOFC mode are faster than we can explain by Ni(OH)_x species. Therefore, we assume Ni to be oxidized by impurities like sulfur or phosphor into volatile compounds, such as NiSH or NiPH₂. This means that we have a modified Figure compared to our previous one (3) to explain the migration away from the bulk YSZ electrolyte. This is illustrated in Figure 6 in which we have denoted the migrating Ni-species NiX as other species than NiSH or

NiPH₂ may take part. We imagine that NiX will migrate away from the non-polarized Ni-particles in the "lost contact" layer and reduced again at the TPBs of the strongly negative polarized Ni-particles in the "intact layer" that are in contact with YSZ, which is in ionic contact with the electrolyte.

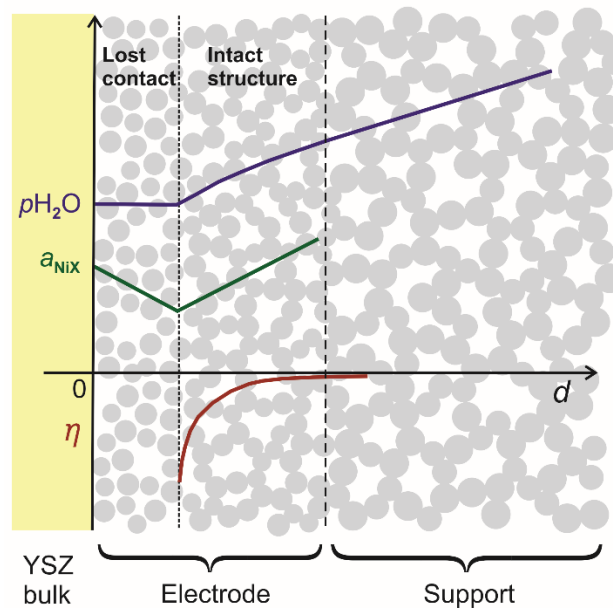


Figure 6. Sketch of qualitative variation of three important parameters away from the surface of the bulk electrolyte ($d = 0$) through the two zones of the as-fabricated SOEC active cathode (Electrode), which has been separated into a zone with partially lost contact between Ni and YSZ particles and a zone with intact structure. d is the distance from the bulk YSZ electrolyte, η is the local overvoltage of Ni particles, a_{NiX} is the activity of NiX species, which has its minimum at the lowest potential at the inner points of active 3PB, and p_{H_2O} is steam partial pressure, which is indicative of the redox potential.

Alleviation of the degradation

Apart from cleaning as much as profitable the reactant gases and cell and stack materials, other ways to circumvent the degradation problems are: 1) replace the Ni with another good electrocatalytic electron conducting material than Ni, or 2) add a mixed ion and electron conductor like Gd₂O₃ doped CeO₂ (CGO), which is mixed conducting in reducing atmosphere, as nanoparticles to the Ni-SZ-composite, or 3) totally substitute YSZ with CGO in the active fuel electrode, i.e. use a Ni-CGO composite. 2) and 3) will broaden the 3PB and decrease all temperature and potential gradients. However, during operation the latter has the disadvantages of a mechanical weaker and a less sintering stable active electrode layer. A better way may be to find a zirconia dopant that turns SZ into a mixed conductor.

Summary

This short paper describes the state of our on-going efforts to understand in depth the long term degradation of Ni-YSZ cermet electrodes. We have a fair understanding of most or the known types of degradation but even more detailed knowledge is necessary in

order to make a quantitative modeling. The paper also describes in some detail the type of new knowledge that we need to acquire in order to be able to do this modeling. Finally, some measures to mitigate the degradation problems are listed.

Acknowledgments

We acknowledge the financial support from the project “Maturing SOEC” (Energy Technology Development and Demonstration program, EUDP, project no 64015-0523), and we are grateful to Dr. Gurli Mogensen for her help in proof reading this paper.

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