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Understanding the Electrocatalytic Activity of Transition Metal Nanoparticles for Solid Oxide Cell Fuel Electrodes

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Abstract

In this work, we utilized the concept of decoupling the electrocatalytic activity from the current conducting phase of solid oxide cell fuel electrodes to investigate the electrochemical performance of three different transition metals, namely Ni, Co, and Fe. It was found that the nickel and cobalt infiltrated cells had comparable performances in both 4% H₂O/H₂ and 50% H₂O/H₂. Furthermore, iron nanoparticles were found to be the better electrocatalyst at low pO₂ values, however at higher pO₂ values the iron infiltration became the inferior catalyst. Investigating the temperature dependence of the polarization resistance in terms of activation energy and pre-exponential factor showed interesting differences between the metal catalysts and a dependence on the gas atmosphere. The results were analyzed by developing a model based on the harmonic oscillator, the model allows for correlating changes in activation energy and pre-exponential factor with kinetic parameters of the electrode reaction. The model indicates that at higher pO₂ values, iron

nanoparticles experience a surface blockade, i.e. strong bonding of the reactants to the catalytic sites. For the nickel electrocatalyst, an increase in steam content according to the model leads to an increase in the turnover frequency, which is in good agreement with earlier reports in literature.

Keywords

Solid Oxide Cells, Infiltration, Electrocatalytic Activity, Model for Adsorption of Species, Nanoparticles, Fuel Electrodes.

1. Introduction

Solid oxide cells (SOCs) are high-temperature electrochemical cells that offer a highly efficient conversion of chemically stored energy into electrical energy and reverse. The current state of the art (SoA) SOC use a nickel-YSZ composite fuel electrode for H_2/H_2O and CO/CO_2 reactions [1]. However, the Ni-YSZ composite electrodes experience significant degradation during unintended redox cycles, are prone to carbon deposition and even small amounts of often seen impurities in the fuel, like sulphur, will inhibit the fuel electrode functionality [2-6]. These challenges with the Ni/YSZ cermet electrodes can be circumvented by adding different external system components to the balance of plant, however, this will result in a more complicated system design and increase the system cost. Furthermore, enhanced stability of the fuel electrode is still needed since nickel particles tends to grow at the operating temperatures of the SOC, resulting in degradation in cell performance over time, due to loss of nickel percolation and loss of electrocatalytic active surface area [7]. Thus, alternatives to Ni- cermet electrodes and especially Ni-free fuel electrodes are still receiving considerable interest.

One strategy to overcome some of the challenges with the Ni/YSZ electrodes is to decouple the functionalities of the fuel electrode, by separating the electronically conductive phase from the

electrocatalytic phase. This can increase the redox stability of the electrode, by designing a redox stable porous backbone that can be infiltrated with the electrocatalytic active material. This decoupling could be obtained by using donor-doped SrTiO_3 (ST) compositions as backbone material, since these compositions are tolerant to oxygen, carbon, and sulphur containing atmospheres, have a high electronic conductivity and are highly redox stable [8-12]. It has already been found that the redox stability of the Nb-doped strontium titanate (STN) based SOC fuel electrodes is significantly enhanced compared to the conventional fuel electrode Ni/YSZ materials, even if the infiltrated electrocatalyst is nickel nanoparticles [13]. This is due to the fact, that the electronic conductivity in the infiltrated STN electrode is independent of the electrocatalyst. Nevertheless, new challenges arise with infiltrated STN electrodes, since the infiltrated nanoparticles will experience growth, which will decrease the triple phase boundary [14], just as the low ionic conductivity of the STN backbones makes co-infiltration with an ionic conductive phase advantageous.

In previous work performed by T. Ramos et al., it was found that co-infiltrating a $\text{Sr}_{0.94}\text{Ti}_{0.9}\text{Nb}_{0.1}\text{O}_3$ (STN94)/YSZ cell with metals (Ni, Pd, and Ru) and gadolinium doped cerium oxide (CGO) increased the performance and stability of the SOC fuel electrode compared to the conventional Ni/YSZ [15-16]. However, both ruthenium and palladium are precious metals and therefore not suited for commercial use, due to their cost. Hence, it is of interest to explore the electrocatalytic activity of different, non-precious, transition metals which are infiltrated into the STN backbone structure. It is found in the literature that transition metals like nickel, cobalt, and iron will have comparable electrocatalytic behavior [16-17], but still shows interesting similarities and differences in electrocatalytic activity [18].

In the present work these three transition metals were infiltrated into STN94/YSZ symmetrical cells. In order to investigate the electrocatalytic activity of the transition metals alone, it was chosen to perform the infiltration without co-infiltration of CGO. The scope of the current work is to use electrochemical impedance spectroscopy to investigate and understand the electrocatalytic properties of nickel, cobalt, and iron nanoparticles. Furthermore, for analyzing the kinetics of the electrochemical reactions a model based on the harmonic oscillator is derived and applied on the experimental results.

2. Experimental

2.1 Symmetrical cell fabrication

The electrochemical characterization of the infiltrated electrocatalysts was made using symmetrical cells. For fabrication of the cells, STN94 ink was spray deposited onto a pre-sintered $240 \pm 10 \text{ }\mu\text{m}$ thick Sc_2O_3 , Y_2O_3 co-stabilized ZrO_2 (Sc-YSZ) electrolyte. After deposition, the electrodes were sintered at 1200°C , 8h in air, resulting in electrode thicknesses between 20 and 40 μm . A detailed description of the fabrication procedure of the symmetrical cells can be found elsewhere [9]. After sintering, the cells were laser cut into smaller pieces of $0.6 \text{ cm} \times 0.6 \text{ cm}$.

The infiltration solutions were prepared by dissolving the respective metal nitrates in water along with a surfactant. Metal concentration in the solution was kept to 1M. Prior to infiltration, the symmetrical STN94/YSZ cells were weighed and the infiltration was then performed using the following infiltration procedure: A drop of infiltrate solution was placed upon the surface of the cell where the capillary forces are expected to ensure an equal distribution through the porous structure down to the electrode-electrolyte interface. The drop was left on the surface for one minute, and then dried off using an absorbent laboratory tissue. Both sides of the symmetric cell

were subjected to this procedure before the cell was heated to 350°C for 30 minutes. After heat treatment the cells were wiped off, using a laboratory tissue, to remove residues from the surface, and then infiltrated again. This infiltration procedure was repeated three times in total, with the last heat-treatment step at 350°C prolonged to two hours. After the prolonged heat-treatment, the infiltrated cells were weighed again in order to determine the catalyst load. Emphasis should be made on the handling of the cells after being infiltrated since nanoparticles were now present inside the electrode backbone. These nanoparticles were attached to the surface, but even so, the cells had to be handled following safety guidance for handling of nanoparticles.

2.2 Microstructural Characterization

The microstructure of the cells was investigated from a fractured cross-section, without any pretreatment of the samples, using scanning electron microscopy (SEM) (ZEISS Merlin, Carl Zeiss, Germany). The microstructure of the samples was investigated directly a) after infiltration, b) after being heated to 850°C and reduced for 24 hours in humidified hydrogen, and c) after the whole test protocol had been performed. In order to analyze the catalyst distribution through the electrodes, all of them were investigated on five to seven different points between the electrode surface and the electrode-electrolyte interface,

2.3 Electrochemical characterization

Prior to the electrochemical characterization, the infiltrated cells were hand-painted with a Pt-paste current collection layer. Following this, the cells were mounted in an experimental setup allowing for simultaneous testing of four symmetrical cells per test. A detailed description of the setup can be found elsewhere [20]. All tested samples were exposed to the test protocol described below, and 4-5 cells were tested for each type of catalyst infiltration.

The test protocol performed on each cell in this work is schematically represented in figure 1 and included the following steps: Heating up to 850°C in air followed by a 30 minutes reduction of the cells in 4% H₂O/H₂. After the cells had been reduced a first reference EIS measurement was performed at the reference conditions; 4% H₂O/H₂ at 850°C, marked with #1 in figure 1, followed by impedance measurements at every 50°C down to 450°C in 4% H₂O/H₂. Afterwards the temperature was raised back to 850°C for reference measurement #2. Then the steam content was increased to 50% and EIS measurements were performed at every 50°C from 850°C down to 650°C. Afterwards the temperature was raised again and the reference measurement #3 was performed. The 4% H₂O/H₂ atmosphere was then changed to 50% CO₂/CO and EIS measurements were performed at every 50°C down to 650°C followed by reference measurement #4 at 850°C. Following the reference measurement, a short 48 hours stability test at 650°C in 50% CO₂/CO was performed, to investigate the tolerance of the electrodes to carbon containing fuels. Finally, after the short stability test, the final reference measurement #5 was performed before cooling down to room temperature in air.

[Figure 1 about here]

The electrochemical impedance spectroscopy was performed at OCV using a Gamry Reference 600 potentiostat. Impedance spectra were recorded between 0.01Hz-1MHz with 10 points/decade applying a 50 mV amplitude.

Analysis of the impedance data was performed using impedance transforms in the Python-based software RAVDAV developed at DTU Energy [19]. The series resistances (R_s) observed in the impedance data were not corrected for ohmic contributions arising from the Pt leads in the

experimental setup, as the lead resistance based on previous experiments is estimated to be less than 5% of the measured R_s .

3. Results and Discussion

3.1 Electrode microstructure and electrocatalyst load

Figure 2 shows the microstructure of the different infiltrated cells right after the infiltration procedure had been performed. The different metal infiltrations resulted in different types of nanostructures of sizes 5-10 nm. It was found that the infiltration procedure had resulted in a uniform distribution of the infiltrate throughout the electrode, since no variations in the catalyst distribution were found between the five to seven different points investigated on each electrode. The cobalt and iron infiltrated cells had spherical nanostructures (figure 2a and b), while the nickel infiltrated samples showed a nano-needle structure (figure 2c).

[Figure 2 about here]

The average weight gain per square centimeter of each type of electrode after finishing the infiltration procedure can be seen in table 1. The increase in mass indicates the amount of metal catalyst introduced into the STN backbone. Notably, the weight gain of the nickel- and iron-oxide infiltrated are almost identical while the cobalt-oxide infiltrated samples is smaller.

[Table 1 about here]

The final morphology of the infiltrated cells after the entire test protocol can be seen in figure 3. It can here be observed that independent of the initial morphology, the final morphology of the nanostructures is the same, namely spherical nanostructures with a diameter of 100-200 nm. This evidences that the particles have agglomerated into larger particles due to the high temperatures.

In addition, it was found from the SEM investigation that this morphology is already obtained after 25 hours at 850°C. The observed growth of the nanoparticles, which has also been reported elsewhere in the literature [14], ultimately reduces the triple phase boundary and the amount of the active reaction sites, which in return will decrease the performance for these cells.

[Figure 3 about here]

3.2 Electrochemical characterization

3.2.1 Impedance analysis

The characteristic impedance spectra of Co, Fe, and Ni infiltrated STN backbones at 850°C in 4% H₂O/H₂ are shown in figure 4. A single arc with a characteristic frequency between 15 and 35 Hz can be observed in the impedance spectra. Additionally, a small ohmic contribution to the impedance can be observed at the low frequencies. This latter contribution is suspected to be a result of a non-stationary system, which could be caused by a small degree of nanoparticle agglomeration. As a consequence of this drift, the fit was limited to 0.1 Hz. Constant phase elements in combination with resistances are used for the fitting of the impedance spectra, a physical interpretation of the individual impedance contributions is not within the scope of the current work. The equivalent circuit used for the fitting of impedance spectra was L-R-R₁Q₁-R₂Q₂ (where Q is a constant phase element, R is the resistance and L is the inductance). Notably, the equivalent circuit contains two constant phase elements, which is necessary in order to obtain a decent fit. The high frequency constant phase element used in the fitting, makes up less than 4% of the total polarization resistance, meaning that the other arc completely dominates the impedance spectra. The equivalent circuit model was used for parameterization of the spectra to derive the ohmic and polarization resistance R_p as the sum of R₁ and R₂ (R₁+R₂), without any further analysis

of the underlying reaction mechanism. Examples of this fitting are also shown in figure 4. Notably, the polarization resistance, R_p , is the resistance arising from the voltage loss related to the faradaic current in the electrode.

[Figure 4 about here]

3.2.2 Reproducibility of electrode performance

The reproducibility of the electrode performance of nominally identically prepared electrodes is shown in figure 5 for nickel infiltrated STN electrodes in the temperature range from 650 to 850°C. The polarization resistance R_p of all cells shows an Arrhenius behavior with similar slopes, indicating an identical activation energy. The parallel shift observed in figure 5 indicates that the differences observed in the polarization resistance is a consequence of the differences in the microstructure of the electrode, in accordance with the pre-exponential factor of the Arrhenius equation, which will be described in detail in section 3.2.4. Notably, the cell with the lowest pre-exponential factor (i.e. the lowest interception in the Arrhenius plot), is the cell with the highest Ni load (Ni#2: 0.72 mg·cm⁻²), and the cell with the second highest pre-exponential factor, is the cell with the lowest Ni load (Ni#3: 0.54 mg·cm⁻²), see table 2. An explanation for this could be found in the agglomeration of the nanoparticles, since a higher loading could lead to larger agglomerates, which results in less independent nanoparticles and lower TPB. On the contrary, lower loading, would lead to less agglomeration and thus a higher degree of independent nanoparticles. In conclusion, the parallel shift observed in figure 5 is considered a consequence of differences in the infiltrate structure caused by difference in infiltrate load, however, differences in the electrode backbone cannot be excluded.

[Figure 5 about here]

[Table 2 about here]

3.2.3 Influence of gas atmosphere on electrode performance and stability

Figure 6 gives an overview of the electrode materials performance and degradation throughout the experiment, as determined from the reference measurements. The polarization resistance of the pure STN backbone increased after being exposed to high pO_2 , which is also observed for the cobalt and nickel infiltrated samples. In contrast, the iron infiltrated cells show a decrease in polarization resistance after being exposed to high pO_2 containing atmospheres. The increase in the polarization resistance of the STN backbone can be related to the defect chemistry decreasing the electronic conductivity with higher pO_2 . Moreover, it can in figure 6 be observed that infiltrating the electrode backbone, with either cobalt, nickel or iron, gives rise to a much lower polarization resistance, when compared to pure STN. This shows the good electrocatalytic properties of these three metals. However, their stability seems to be affected by the oxygen partial pressure, which has to be taken into account when analyzing the electrode performance in various atmospheres.

[Figure 6 about here]

As stated earlier, several cells of each infiltration have been tested in this work, and all the reported values have been averaged over 4-5 cells. The average polarization resistance as a function of atmospheres is shown in figure 7 for the cobalt, nickel, and iron infiltrations.

[Figure 7 about here]

From figure 7 it can be seen that the cobalt and nickel infiltrated cells obtain a lower polarization resistance in both 50% H₂O/H₂ and in 50% CO₂/CO when compared to the 4% H₂O/H₂. However, from the reference measurements in figure 6, it was also clear that the initial performance in 4% H₂O/H₂ was never obtained again, suggesting irreversible changes of the electrode. A decrease in polarization resistance has been observed for the Ni-cermet electrodes as well and has been ascribed to the OCV conditions. When the cell is held at OCV the polarization resistance will be determined by the hydrogen evolution reaction and the hydrogen oxidation reaction. When increasing the steam content, the concentration of reactants for the hydrogen evolution reaction is increased and the overall polarization resistance decreases. On the contrary, it can be seen that in the humidified hydrogen atmosphere, containing 4% steam, the iron infiltrated cells have the lowest polarization resistance, which is in good agreement with previous results using single-phase iron fuel electrodes for SOCs [21]. However, the polarization resistance of the iron infiltrated cells rises dramatically in both 50% H₂O/H₂ and even further in 50% CO₂/CO and iron becomes the worst performing electrocatalyst of the three metals (figure 7). However, it can be seen in figure 6 that the reference polarization resistance for the iron infiltrated cells is decreasing with time. This suggests that any changes observed in the polarization resistance in figure 7 are related to changes in the gas atmosphere, since the overall instability of the cells can be regarded as minor changes, when compared to the changes observed in figure 7. Overall, figure 6 and figure 7 suggests that the iron catalyst interacts differently with the gas atmospheres, than the nickel and cobalt, which will be investigated further using the model presented in section 3.2.4.

3.2.4 Temperature dependence

Understanding the interactions between the gas atmosphere and the individual catalysts is important for further optimization of the electrode performance. Hence, in order to obtain a deeper

understanding of the kinetics in the electrochemical reactions, one approach is to look at the temperature dependence of the polarization resistances, as can be seen in figure 8 for the cobalt, iron and nickel infiltrations. The polarization resistance of all the infiltrated cells shows an Arrhenius behavior, from which the activation energy E_a and the pre-exponential factor, A , can be derived (equation 1).

$$\ln(R_p) = \ln(A) - \frac{E_a}{RT} \quad (1)$$

[Figure 8 about here]

The averaged activation energy for the different infiltrations in the different atmospheres can be seen in table 3. When the atmosphere is changed from 4% H_2O/H_2 to 50% H_2O/H_2 , the corresponding increase in pO_2 is accompanied by an increase in the activation energy. This increase in activation energy could be related to oxidation of the metal catalyst, for which reason the chemical stability of the metal towards oxidation was estimated from Ellingham diagrams [22]. The maximum pO_2 tolerance of the metals found from the Ellingham diagrams are stated in table 4 together with the pO_2 present in the three tested atmospheres.

[Table 3 about here]

From table 4 it is clear that the nickel and cobalt nanoparticles are stable as metals at all test conditions. In contrast, the oxygen partial pressure in both 50% H_2O/H_2 and 50% CO_2/CO is close to the maximum tolerance of the iron nanoparticles. Hence, a partial or even full re-oxidation of

the iron nanoparticles is likely in both 50% H₂O/H₂ and 50% CO₂/CO, which could also be reflected in a stronger interaction between iron and oxygen.

[Table 4 about here]

Because of the absence of information, a comparison with literature values for the activation energy of the transition metal nanoparticles is not possible. However, the activation energies for SoA Ni-YSZ SOC fuel electrodes could be found ranging from 1.01 eV and up to 1.47 eV for the hydrogen-water reaction, depending on the fabrication method, steam content and test conditions [23-24, 26-28]. In table 3 one can observe similarities between the change in activation energy with atmosphere, between the nickel cermet and the nickel infiltrated samples. This correlation indicates that even though the nickel has been infiltrated as nanoparticles, the activation energy is not affected significantly by the Ni morphology, indicating that the reaction mechanism is not affected by the morphology of the catalyst. Moreover, it can be observed in table 3 that when the steam content is increased from 4% to 50%, the activation energy of the cobalt, nickel, and iron infiltrated cells increases by approximately 50%, 14%, and 25%, respectively. But, when the atmosphere is changed from 50% H₂O/H₂ to 50% CO₂/CO the activation energy of cobalt and iron infiltrated cells decreases by 13% and 17%, respectively, while the activation energy of the nickel infiltrated cells increases even further by 11%. This indicates that the changes in the reaction mechanisms following changes in the different atmospheres, are diverse and a deeper analysis is therefore necessary. This can be done by analyzing the activation energy and the pre-exponential factor of the Arrhenius equation in more detail.

In order to complement the above observations the pre-exponential factor, A, in each atmosphere for the different infiltrations was calculated and presented in table 3. An analysis of the pre-

exponential factor can give further knowledge of the kinetics of the reaction, since the pre-exponential factor describes, amongst others, the kinetics of the electrochemical reaction [29]. The pre-exponential factor, A , in the Arrhenius equation is a combination of a precursor equilibrium constant, $K_{P,O}$, representing the ratio of the reactant concentration in the reactive position, a transmission coefficient, κ_{el} , related to the probability of the reaction, and a frequency factor, ν_n , which represents the frequency of attempts on the energy barrier E_a . The pre-exponential factor, A , can, therefore, be described as [30]:

$$A = K_{P,O} \cdot \kappa_{el} \cdot \nu_n \quad (2)$$

The approach followed in this work is to develop a model that allows for analyzing the kinetics of the electrochemical reaction by correlating the activation energy with the pre-exponential factor. The model used for the analysis is described further in the following section.

3.2.5 Model description

In order to better understand the electrode processes, a theoretical model was deduced based on four assumptions and the harmonic oscillator, for which the restoring force is described by Hooke's law (equation 3).

$$F = k \cdot x \quad (3)$$

Where F is the force, k is the force constant and x is the bond length. The harmonic oscillator is applied to describe the bond between the adsorbed reactant and the metal-catalyst, an approach which has been confirmed to be valid at low overpotentials up to 0.2 V [31]. In the following, the four assumptions used in deducing the model are described in more detail.

Firstly, it is assumed that the electrode potential for a given atmosphere is identical for the individual cells and not influenced by the electrocatalyst at OCV conditions. This follows from the electrode potential being determined by the activity of the oxygen ions in the electrolyte and the oxygen in the atmosphere, which is independent of the electrocatalyst [32].

Secondly, it is assumed that the force term in the harmonic oscillator is proportional to the binding energy of the adsorbed species and that this binding energy is directly proportional to the activation energy of the transition state (equation 4) [33]. This assumption is reasonable, since the energy needed to overcome the activation barrier, the activation energy, must be translated into another form of energy, namely binding energy between the adsorbent and the catalytic site. Furthermore the attractive force which the adsorbed molecule feels towards the catalytic site must also be proportional to the energy stored in that bond, if the bond length is fixed.

$$F \propto E_{\text{binding}} \propto E_a \quad (4)$$

Hence, higher activation energy would give rise to an increase in the force, F , which would result in a change in either the bond length x or the force constant k in accordance to Hooke's law.

Thirdly, it is assumed that the bond length, x , between the adsorbent and the metal is fixed. This is reasonable since it is a chemical adsorption process and the adsorbent and the metal surface are as close together as they can be. The model is thus analyzing the intermediate regime between the adsorption and the electrocatalytic reaction. A change in activation energy can therefore only give rise to a change in the force constant, k [34]. This force constant can be expressed as a function of the period of the harmonic motion and the mass of the adsorbed reactant, (equation 5).

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$$k = \frac{4\pi^2 \cdot m}{T^2} \xrightarrow{f=\frac{1}{T}} k = 4\pi^2 \cdot m \cdot f^2$$

not

defined.(5)

Where k is the force-constant, T is the period, m is the mass of the adsorbed reactant and f is the oscillating frequency. Notably, in equation 5 it can be seen that a change in the mass will result in a one to one increase in the force-constant, while an increase in the oscillating frequency will result in a power-law increase of the force-constant [34].

In order to correlate equation 5, with the pre-exponential factor from the Arrhenius equation (equation 1) a new variable, ϕ , must be introduced instead of the mass term in equation 5. The variable ϕ is proportionally dependent on the precursor equilibrium constant, $K_{P,O}$, and hence describes the nature of the reactant and reaction sites. Furthermore, since the harmonic oscillation is happening in the region between the molecule getting adsorbed and the reaction taking place, it is reasonable to imagine that an increase in the oscillation frequency would result in an increase in the attempts on reaction, namely the frequency factor of the pre-exponential factor. The oscillating frequency can therefore be replaced by the turnover frequency, which is proportional to the frequency factor of the pre-exponential factor: $f_{\text{turnover}} \equiv \kappa_{\text{el}} \cdot \nu_n$, where κ_{el} is the transmission coefficient and ν_n is the frequency factor.

$$k \propto 4\pi^2 \cdot \phi \cdot f_{\text{turnover}}^2$$

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The fourth and final assumption of the model is that there is a linear correlation between the pre-exponential factor and the force-constant of the harmonic oscillator (equation 7). This assumption is reasonable since the pre-exponential factor and the force-constant both describes the kinetics of the electrochemical reaction and the harmonic motion, respectively. The model utilizes the parallel between an adsorption bond and the harmonic oscillator to describe the kinetics of a reaction involving adsorption to the catalyst surface. A linear correlation between the force-constant of the harmonic oscillator and the pre-exponential factor is hence reasonable for the purpose of the model.

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$$\ln(A) = c_1 \cdot k + c_2$$

Where c_1 and c_2 are constants.

Combining the four assumptions yields equation 8, which describes the pre-exponential factor as a function of two constants, a variable, φ , which is proportionally dependent on the precursor equilibrium constant and finally a frequency term, which is dependent on the transmission coefficient and the frequency factor.

$$\ln(A) \propto 4\pi^2 \cdot c_1 \cdot \varphi \cdot f_{\text{turnover}}^2 + c_2$$

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defined.(8)

In total, according to equation 8, equation 3, equation 4, and by combining all constant terms into one constant, that is absorbed into proportionality, a general expression for the model can be obtained (equation 9).

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$$E_a \propto (4\pi^2 \cdot c_1 \cdot \varphi \cdot f_{\text{turnover}}^2 + c_2) \cdot x$$

not

defined.(9)

According to equation 9, if the change in the natural logarithm of the pre-exponential factor diverges from the change in the activation energy, it can only be due to a change in the frequency term, since this is to the power of two. While if the change in the natural logarithm of the pre-exponential factor does not diverge from the change in the activation energy, it can only be a result of changes in the linear term, φ . Therefore, a power law correlation between the percentage change in $\Delta\% \ln(A)$ and $\Delta\% E_a$, is a direct result of a change in the turnover frequency, f_{turnover} . On the other hand, if a one to one correlation is observed between the percentage change in $\Delta\% \ln(A)$ and $\Delta\% E_a$, it indicates a change in φ which can be correlated to a change the precursor equilibrium constant. Notably, due to the standard deviations observed in table 3, and due to a small divergence between a linear and power-law expression at smaller values, the correlation is defined to be power-law correlated if and only if $|\Delta\% \ln(A)| - |\Delta\% E_a| > 6\%$ else, it is considered as a one to one correlation. Notably, a change in the turnover frequency does not exclude a minor change in the nature of the reaction.

In short, a one to one correlation between the change in activation energy and the change in the pre-exponential factor indicates a change in the adsorbed molecules or the number of active reaction sites. On the other hand, a power law correlation indicates a change in the frequency of attempts on the energy barrier in the electrochemical reaction, and thus the turnover frequency. For the purpose of analyzing the results with this model, the percentage change in the logarithm of the pre-exponential factor and the percentage change in the activation energy was calculated (table 5). The difference between these two values was also calculated and is also presented in table 5.

[Table 5 about here]

An increase in activation energy is followed by an increase in the pre-exponential factor for the nickel and the cobalt infiltrations, when the atmosphere is changed from 4% H₂O/H₂ to 50% H₂O/H₂ (table 5). Furthermore, the change in the pre-exponential factor exceeds the change in activation energy. The iron infiltrations also experience an increase in both activation energy and in the pre-exponential factor when the steam content is increased, however, the increase in activation energy exceeds the change in the pre-exponential factor. Also, when the atmosphere is changed from 50% H₂O/H₂ to 50% CO₂/CO the activation energy and the pre-exponential factor for the nickel infiltrated cells increases by a similar amount. Meanwhile, the cobalt and iron infiltrated cells both experience a decrease in activation energy and pre-exponential factor of a similar size. In short, the differences observed between the different infiltrated cells suggest differences in the underlying electrode processes.

The correlations observed between the change in activation energy and the change in the logarithm of the pre-exponential factor are furthermore summarized in table 5. It can here be seen that the

cobalt and nickel infiltrated samples behave similarly in regard to the correlation, namely that they both experiences a power law increase when the steam content is raised from 4% to 50% indicating a higher turnover frequency. Notable, this does not exclude a minor change in the reactant concentration, reactive position, and transmission coefficient, since a minor one to one increase would be overshadowed by the power law increase. However, when the atmosphere is changed from 50% H₂O/H₂ to 50% CO₂/CO both the nickel and cobalt infiltrated cells experience a one to one correlation, indicating a change in the nature of the adsorbent, the nature of the adsorption bond, or a change in the amount of active reaction sites, which is logical. However, the iron infiltrated cells behave differently than the other two infiltrations since they experience an inverse power-law correlation when the steam content is increased to 50%. This is quite interesting and indicates several things, which will be discussed shortly. Furthermore, when the atmosphere is changed to 50% CO₂/CO the iron infiltrated cells experience a negative power-law correlation that indicates a decrease in the turnover frequency.

The inverse power-law correlation observed for the iron infiltrated cells when the steam content is increased to 50% suggests several things. Firstly, the increase in the activation energy describes an increase in the binding energy of the transition state. Secondly, the inverse power-law correlation indicates, amongst others, a change in the turnover frequency, but due to the inverse correlation, it is not a simple decrease in the turnover frequency, but rather a decrease in the turnover frequency combined with an increase in the reactant concentration in the reactive position. A combination of these two points suggests that the adsorbed reactant in the reaction is changed, meanwhile, the turnover frequency for the adsorption process is decreased. Thus, once adsorbed to the surface, the reactant does not desorb again. However, this blockade does not simply reduce the amount of catalytic sites, but rather changes the reaction mechanism. After the blockade

of catalytic sites, the reaction will take place, but now through the adsorbed specie. In short, the model suggests that the iron nanoparticles experience partial surface blockade in the 50% H₂O/H₂ atmosphere, which is also in good agreement with the oxygen partial pressures given in table 4. There exist three possibilities for the blockade of the catalytic sites, which are schematically presented in figure 9. All three start with the formation of the adsorption bond between the water molecule and the catalytic site on the iron nanoparticle. Thereafter, there are three possible reaction mechanisms. (I): One hydrogen atom is dissociated from the water molecule and the now OH adsorption bond is too strong to be broken and the reaction must go through the OH-bond. (II): The water molecule remains adsorbed with an adsorption bond too strong to be broken, and the reaction must go through the water molecule. (III): The water molecule dissociates both hydrogen atoms, and the oxygen remains firmly adsorbed, resulting in an oxygen blockade of the nanoparticles. Ultimately, all three reaction mechanisms result in a blockade of the catalytic sites and the reactions now need to go through these adsorbed species. The correct reaction mechanism could be identified by near ambient pressure X-ray photon spectroscopy (NAP-XPS) which can distinguish between the adsorbed species [35].

[Figure 9 about here]

4. Conclusion

In this work, the electrocatalytic activity of three transition metals, namely nickel, cobalt and iron has been investigated as catalysts for fuel electrodes in solid oxide cells. Infiltration of the metals as nanoparticles into a porous STN backbone was found to be a viable route to compare the electrocatalytic activity of the electrocatalysts. The Ni and Co infiltrated electrodes showed similar performance in carbon containing atmospheres, indicating a good carbon tolerance of these

electrode materials. In 50% H₂O/H₂ at 850°C, polarization resistances of 0.51 and 0.52 Ωcm² were observed for the nickel and cobalt infiltrated cells, respectively, while significantly higher polarization resistances of the iron infiltrated cells indicated a problem with iron at high oxygen partial pressures. In order to gain further insight into the interplay between the gas composition and electrochemical reaction mechanism, a model was derived based on the harmonic oscillator. The model allows for the correlation of changes in the atmosphere with changes in the turnover frequency or changes in the nature of the electrochemical reactants. To the authors' knowledge, a model like this has not previously been presented in literature. By using the model, it was determined that increasing the steam content from 4% H₂O/H₂ to 50% H₂O/H₂ on the iron infiltrated electrode introduces a surface blockade of the catalytic sites, which forces the reaction mechanism to change. On the contrary, the same increase in steam content enhances the turnover frequency on both the cobalt and nickel infiltrated electrodes, without changing the reaction mechanism. The model derived in this work is not restricted to a specific cell design, but can be applied to any temperature dependent electrochemical system, where molecules are adsorbed to the surface of the electrocatalyst.

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Table 1: Average weight gain from the infiltration procedure for each electrode in $\text{mg}\cdot\text{cm}^{-2}$ and percentage relative to the entire mass of the cell.

Infiltration	Weight gain ($\text{mg}\cdot\text{cm}^{-2}$)	Weight gain (%)
CoO	0.54 ± 0.08	0.71
FeO	0.69 ± 0.08	0.94
NiO	0.68 ± 0.06	0.86

Table 2: The slope of the linear fit alongside with the interception and weight gain in $\text{mg}\cdot\text{cm}^{-2}$, of the individual nickel infiltrated samples seen in figure 5

Cell	Slope	Interception	Weight gain / $\text{mg}\cdot\text{cm}^{-2}$
Ni#1	13.6	-11.70	0.57
Ni#2	13.2	-10.66	0.72
Ni#3	13.5	-11.27	0.54
Ni#4	13.2	-11.10	0.61
Ni#5	14.1	-11.90	0.69

Table 3: Calculated averaged activation energy in eV and the natural logarithm of the pre-exponential factor of the different metal infiltrations in the different atmospheres.

Infiltration	Averaged activation energy (eV)		
	4% $\text{H}_2\text{O}/\text{H}_2$	50% $\text{H}_2\text{O}/\text{H}_2$	50% CO_2/CO
Co	0.96 ± 0.02	1.48 ± 0.06	1.29 ± 0.05
Ni	1.17 ± 0.03	1.33 ± 0.06	1.48 ± 0.02
Fe	1.52 ± 0.11	1.89 ± 0.05	1.57 ± 0.05
Pure STN94	1.06 ± 0.04	1.27 ± 0.01	1.25 ± 0.02
SoA Ni cermet	1.01-1.3 [22]	1.47 [23]	1.63-1.70 [24]
Infiltration	Averaged natural logarithm of the pre-exponential factor		
	4% $\text{H}_2\text{O}/\text{H}_2$	50% $\text{H}_2\text{O}/\text{H}_2$	50% CO_2/CO
Co	9.1 ± 0.3	16.0 ± 0.5	13.0 ± 0.2
Ni	11.3 ± 0.5	14.4 ± 0.8	15.7 ± 0.5
Fe	16.3 ± 0.6	17.7 ± 0.7	12.8 ± 0.5
Pure STN94	7.36 ± 0.2	10.0 ± 0.3	6.7 ± 0.3

Table 4: The tolerance of pO₂ for the different infiltrations and the estimated pO₂ in the different test atmospheres.

Infiltration	Temp. (°C)	Maximum pO ₂ tolerance [21]	pO ₂ for 4% H ₂ O/H ₂	pO ₂ for 50% H ₂ O/H ₂	pO ₂ for 50% CO ₂ /CO
Fe+O	600 / 800	10 ⁻²⁴ / 10 ⁻¹⁸	10 ⁻²⁷ / 10 ⁻²²	10 ⁻²⁴ / 10 ⁻¹⁹	10 ⁻²⁵ / 10 ⁻¹⁹
Ni+O	600 / 800	10 ⁻²⁰ / 10 ⁻¹⁴			
Co+O	600 / 800	10 ⁻²¹ / 10 ⁻¹⁵			

Table 5: Overview of the change in the activation energy, the change in the natural logarithm of the pre-exponential factor, and the difference between these two parameters, for the different infiltrates when changing from one atmosphere to another. Furthermore, the correlation in accordance to equation 3 and 8 is also summarized here.

4% H ₂ O/H ₂ →50% H ₂ O/H ₂	Ni	Co	Fe
$\Delta_{\%} E_A$	14%	53%	25%
$\Delta_{\%} \ln(A)$	27%	76%	9%
Difference ($ \Delta_{\%} \ln(A) - \Delta_{\%} E_A $)	13%	23%	-16%
Correlation according to equation 3 and 8	Power-law	Power-law	Invers power-law
50% H ₂ O/H ₂ →50% CO ₂ /CO	Ni	Co	Fe
$\Delta_{\%} E_A$	12%	-13%	-17%
$\Delta_{\%} \ln(A)$	9%	-19%	-28%
Difference ($ \Delta_{\%} \ln(A) - \Delta_{\%} E_A $)	-3%	6%	11%
Correlation according to equation 3 and 8	One to one	One to one	Power law

Figure 1: Schematic representation of the test protocol used for all cells in the present work. Black dots mark electrochemical impedance measurements performed during the test, and numbers with black diamonds state reference impedance measurements.

Figure 2: Infiltrated STN94 right after the infiltration procedure a) cobalt infiltrated sample with a spherical nanostructure b) iron infiltrated sample with a spherical nanostructure c) nickel infiltrated sample with a nanoneedle structure. Notice, examples of the infiltration structures are indicated with red arrows.

Figure 3: Infiltrated STN94 after the test procedure a) cobalt infiltrated sample b) iron infiltrated sample c) nickel infiltrated sample. Notice, that examples of the infiltration structures are indicated with red arrows.

Figure 4: EIS data plot from a) cobalt, b) iron, and c) nickel infiltrated STN94 measured at 850°C in 4% H₂O/H₂, fitted with the equivalent circuit L-R-R₁Q₁-R₂Q₂.

Figure 5: Temperature dependence of the polarization resistance for all nickel infiltrated samples measured in 4% $\text{H}_2\text{O}/\text{H}_2$. The lowest nickel content is found in Ni#3 (green) with $0.54 \text{ mg}\cdot\text{cm}^{-2}$ and the highest nickel content observed was for NiO#2, with $0.72 \text{ mg}\cdot\text{cm}^{-2}$ (red).

Figure 6: Polarization resistance measured in $\Omega\cdot\text{cm}^2$ for the reference measurements conducted throughout the test

Figure 7: Polarization resistance measured in $\Omega \cdot \text{cm}^2$ as a function of the atmosphere at 850°C for the different infiltrations.

Figure 8: The highest (x) and lowest slope (o) values for the temperature dependence of the polarization resistance of a) cobalt infiltrations, b) iron infiltrations and c) nickel infiltrations in 4% H₂O/H₂ (blue), 50% H₂O/H₂ (red) and 50% CO₂/CO (black).

Figure 9: Schematic representation of three possible reaction mechanism for the blockade of catalytic sites on the iron nanoparticles. The green spheres represent the iron nanoparticle, the light blue represent oxygen atoms, and the red spheres represent hydrogen atoms