H$_2$S IN NATURAL GAS FUEL REDUCES MECHANICAL STRESS
IN SOLID OXIDE FUEL CELLS

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ABSTRACT

Simulations indicate that the mechanical stress caused by temperature differences within a SOFC stack is significantly reduced when 25ppm H$_2$S is present in the natural gas. The Sulphur adsorbs on the Ni surface in the nickel-zirconia anode material. The Sulphur thus blocks sites and slows down the methane reforming reaction. Thereby the cooling effect of the endothermic reforming reaction is distributed more evenly in the stack. Simulations also shows that simultaneously is the lattice expansion of Sr, Ca-doped lanthanum chromite (interconnect material) reduced in the fuel inlet section.

INTRODUCTION

The tensile stresses introduced in Sr, Ca-doped lanthanum chromite SOFC interconnect plates are very high compared to reported material strength. The stress is induced by lattice expansion in reducing atmosphere and stress caused by temperature differences within the SOFC stack. The mismatch between introduced stress and material strength may be lowered by improved material strength, SOFC design optimisation, and optimization of operational conditions. In this paper we address how the mechanical stress in the SOFC interconnect material is influenced by H$_2$S in the natural gas fuel. The study is based on theoretical models on electrochemical reactions, sulphur impact on steam reforming reactions and FEM stress analysis.

The detrimental effect of sulphur on the electrochemical reactions is however modelled on the basis of limited experimental information. The SOFC material stability in H$_2$S environment is only briefly discussed in the paper.

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THEORY

SOFC electrochemical model

The mathematical model has been presented in earlier papers\(^{(5,6)}\). In the model, the cell stack is cast into finite difference elements, each of which represents a unit cell modelled as a CSTR (Continuously Stirred Electrochemical Tank Reactor). The unit cell consist of air and fuel chambers enveloped by the interconnect material except in the direction of gas flow and separated by the triple layer consisting of the electrodes and electrolyte. The solid, air and fuel phases have different temperatures, but the temperature of each phase is assumed to be uniform inside the unit cell element. The Statoil cell concept has internal manifold with counter-flow in the main part of the cell. In the model the Statoil cell is cast into 20x23 unit cells.

For the methane steam reforming we have used Statoils own reforming equation based on experimental works\(^{(9)}\).

\[
 r_{CH_4} = 6300 \exp\left(\frac{-8000}{RT}\right) \left(P_{CH_4}\right)^{1.20}
\]

[1]

In this equation the temperature is in Kelvin and the partial pressure of methane in atm. The Statoil equation has a reforming rate about 10 times faster than reported by Lee\(^{(10)}\) and about 10 times slower than reported by Parsons and Randall\(^{(11)}\).

Influence of Sulphur on Steam reforming

Most of the material presented in this subchapter is based on the work of Rostrup-Nielsen\(^{(7)}\). It is common practice to desulfurize the fuel when natural gas is used as fuel in SOFC. This practice probably originate from the fact that H\(_2\)S is known as a poison to most catalysts, i.e. deactivation of the catalyst. Thus the fuel gas supplied to SOFC with internal catalytic reforming of methane often contain H\(_2\)S levels below 10 ppb. However, small amounts of H\(_2\)S in the fuel provide only partial deactivation of the catalysts and thus a reduction of the reforming reaction rate. H\(_2\)S chemisorbs on nickel\(^{(7)}\) according to:

\[
 H_2S + * = S + \ast + H_2
\]

[2]

Below a certain \(p_{H_2S}/p_{H_2}\) ratio the Ni surface is not saturated with sulphur and the equilibrium coverage is dependent on the \(p_{H_2S}/p_{H_2}\) ratio and the temperature. The sulphur coverage (\(\theta_s\)) may be described with a Temkin-like isotherm\(^{(12)}\).

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\[ Y = \exp(-\Delta H_0^0(1-a\theta_s)/RT-\Delta S^0/R) \quad [3] \]

\[ Y = \frac{p_{H2S}}{p_{H2}} \quad [4] \]

Rostrup-Nielsen\(^{(13)}\) fitted eq. 3 to experimental data. \(-\Delta H_0^0 = 280 kJ/mol^{-1}\), \(\Delta S^0 = -19 J/mol^{-1}\), and \(a=0.69\) fits the experimental data well\(^{(7)}\) at typical SOFC temperatures and with moderate Sulphur coverage. Thus:

\[ \theta_s = 1.45 - 9.53 \times 10^{-5}T + 4.17 \times 10^{-5}T\ln(Y) \quad [5] \]

The reference reaction rate \((r_0^0)\) without \(H_2S\)\(^{(12)}\) is decreased with a the factor \((1-\theta_s)^3\)

\[ r_i = \frac{r_0^0}{(1-\theta_s)^3} \quad [6] \]

Eq. [6] is verified with experiments\(^{(7)}\) and explained with 3 active nickel atoms in the reforming reaction. Eq. [5] and [6] are included in the previously presented electrochemical model.

**Lattice expansion of Sr, Ca doped lanthanum chromite**

Lattice expansion of Sr and Ca doped lanthanum chromite in reducing atmosphere is reported to be a common reason for mechanical failure in SOFC stacks\(^{(1)}\). The lanthanum chromite lattice loose oxygen at high temperature when the partial pressure of oxygen on the fuel side of the interconnect is sufficiently low. Thus the lattice expand on the fuel side of the interconnect and not on the air side, and this causes high stress levels in the interconnect. The mechanism of lattice induced stress is well understood and reliable models exits\(^{(1)}\). The present article do not model the lattice induced stress in detail. However, the lattice expansion in fuel side conditions as a function of temperature and oxygen partial pressure is calculated for different \(H_2S\) levels. The expansion is the driving force of the lattice induced stress and thus an indication of the stress level introduced. The lattice expansion is calculated on the basis of experimental data on \(La_{0.8}Ca_{0.2}CrO_3\) (LCC 20)\(^{(2)}\). The expansion data \(\varepsilon\) is correlated to \(p_{O2}\) and temperature (T) with the following simple correlation:

\[ \varepsilon = 0.0292((T-1073)/50-\log(p_{O2})-15.0) \quad (\varepsilon \geq 0) \quad [7] \]

\[ \varepsilon = 0 \quad \text{(otherwise)} \]
Sr doped lanthanum chromite (LSC) show the same expanding tendencies as LCC in respect to temperature and $p_{O_2}^{2(5)}$. Thus the analysis and the conclusions made for LCC in this article is similar for LSC interconnect material.

**SOFC function with $H_2S$ in fuel gas**

**Electrochemical reactions.** The electrochemical reaction [eq.8,9] take place in the gas exposed part of the Nickel/ Zirconia interchange layer. The reduction in active Ni sites in $H_2S$ atmosphere may affect these reactions. Westinghouse(8) did some experiments with up to 50 ppm $H_2S$ in the fuel. From this information we have increased the SOFC activation overpotential with 10% when 25ppm $H_2S$ is present in the fuel gas.

\[
H_2 + O^{2-} \rightarrow H_2O + 2e^- \quad [8]
\]
\[
CO + O^{2-} \rightarrow CO_2 + 2e^- \quad [9]
\]

**Material stability.** Investigations\(^{(12,14)}\) indicate that the isosteric heat of adsorption is approximately 155 kJ mol\(^{-1}\) at moderate surface coverage. The heat of formation of bulk sulfide (Ni\(_3S_2\)) is 75kJ mol\(^{-1}\) of S. Thus the adsorbed Sulphur is strongly bound to the surface, and the "two dimensional sulfide" is stable at conditions when bulk Ni\(_3S_2\) is not stable\(^{(7)}\). The SOFC operational conditions represented with the partial pressure of oxygen ($p_{O_2}$) and sulphur ($p_{S_2}$) must be in a region where Ni is stable in order to avoid sulfidation of the Ni phase in the Nickel-Zirconia cermet. $p_{O_2}$ and $p_{S_2}$ could be calculated from equation [10] and [11] if equilibrium conditions are assumed.

\[
2H_2S = S_2 + 2H_2 \quad [10]
\]
\[
2H_2O = O_2 + 2H_2 \quad [11]
\]

The fuel inlet section of the cell has the "worst case" operation condition in respect to Ni stability i.e. low temperature. As indicated in Figure 1, Ni phase remain stable when 25ppm $H_2S$ is present in the fuel gas. It is assumed that the stability diagram in Figure 1 is unaffected of the small electrical potential in the SOFC. The actual partial pressures are marked with a dot in Figure 1. Long term sintering effects because of sulphur induced surface tensions and possible destruction of the anodic pore structure must be investigated with experiments. The other SOFC materials are regarded to be oxides with no practical solubility towards sulphur.
FEM stress analysis

The calculations in the present article are done on a Statoil designed counter flow SOFC geometry with internal gas distribution manifolds (Figure 2). The four holes in the interconnect are used for the fuel and air supply and exhaust. As a result of a large SOFC research program initiated by Statoil\(^{15}\) comprehensive models have been made in order to simulate different SOFC designs in respect to stress and operation. Vik et al.\(^{16}\) have made the following models:

- Stack model for thermal/fluid analysis (FIDAP 7.0)
- Stack model for thermo-elastic analysis (NASTRAN 68)
- Cell models for fluid flow analysis (FIDAP 7.0)
- Cell models for thermo-elastic and creep analysis
- Cell models for O\(^2\)\ diffusion analysis

Unfortunately we were not able to complete a full FEM stress analysis in respect to both lattice expansion and temperature gradients in due time to the SOFC-V conference. Thus the present FEM stress is restricted to stress due to temperature gradients in a cell plate. The thermo-mechanical stress analysis in this article are performed using the NASTRAN 68 finite element program. The grid model used in the NASTRAN simulation is shown in Figure 2. The temperature distribution grid from the electrochemical simulations is adopted to the finer NASTRAN grid with a simple interpolation.

RESULTS AND DISCUSSION

Electrochemical simulations

Some operational constraints, mechanical properties and physical properties used in the simulations are listed below:

| Operational constraints:                  | Mechanical Prop LCC (1000 °C):   |
|------------------------------------------|----------------------------------|
| Electrical effect: (100x100 mm cell plate)| 16W Youngs Modulus 80 Gpa       |
|                                          | Electrical potential >0.6 V      |
| Fuel type (SOFC input): (25 % pre-reformation) | NG Thermal expansion: 9.7E-6 (1/K) |
| Fuel inlet temp.: 950 °C Conversion: 65%| Char. strength: 76 MPa          |
| Air: 6 stoic. (ref. to converted fuel)   | Physical prop. LCC (1000 °C):  |
| Air outlet temperature: 1040°C          | Density: 4200 kg/m\(^3\)        |
|                                          | Conductivity: 110E-2 W/mK       |
|                                          | Specific heat: 1000 J/kgK       |
The demand for electrical effect, methane conversion and air outlet temperature are met by manipulating the fuel flow rate, air inlet temperature and the electrical potential. Two simulations with respectively 5 ppb and 25 ppm H$_2$S in the fuel are simulated. 5ppb H$_2$S is chosen for desulphurized natural gas.

Figure 3 shows the temperature distributions in the cell plate. The figure illustrates the cooling effect of the fast reforming reaction [Eq.1]. The fuel inlet section of the cell becomes approximately 100°C cooler when desulfurized gas is used as fuel. 25 ppm H$_2$S slows down the reforming reaction and the difference between maximum and minimum temperature in the cell plate become approximately 100°C smaller than in the desulfurized case. However, the maximum temperature is approximately 10°C higher when H$_2$S is present in the fuel. This could be explained with the increased overpotential due to the sulphur coverage of Ni sites.

Figure 4 shows the sulphur coverage [Eq.5] for 5 ppb and 25ppm H$_2$S. An interesting point in respect to material stability and electrochemical functionality is that even desulfurized fuel gas (5ppb H$_2$S) cover app. 35% of the Ni surface with Sulphur. The Sulphur coverage is increased to app. 85% with 25 ppm H$_2$S.

**FEM stress calculations**

Unrestrained (free) and restrained (kept flat) interconnect are simulated. In reality the interconnect will be partly restrained and the stress distribution will be between the two cases. Calculated max. stress for 5 ppb and 25 ppm H$_2$S is given in Table 1. The maximum stress level due to temperature gradients appears near the fuel inlet on the fuel side of the interconnect (see Figure 6). Figure 6 shows the stress distribution of a flat interconnect with 25 ppm H$_2$S in the fuel. A small area of very high stress levels (53- 62 E6 N/m$^2$) is seen in connection with the fuel inlet hole. Vik et al.\(^{(16)}\) do not consider this as relevant stress levels, but rather as numerical noise due to coarse grid (Figure 2). Thus the values in Table 1 is corrected for this error.

Hendriksen et al.\(^{(1)}\) have reported that lattice expansion of Lanthanum Chromite in reducing atmosphere is a common reason for mechanical failure of SOFC. However comparing the values in Table 1 (typical 60 MPa) with the strength of the interconnect (76 MPa) it appears that the stress induced by temperature gradients may also play a role. Vik et al.\(^{(16)}\) however do point out that the lattice induced stress and temperature gradient induced stress in SOFC may to a certain degree counteract each other. The simulated lattice expansions are shown in Figure 5. The lattice expansion is slightly reduced in the fuel inlet section of the cell plate when 25 ppm H$_2$S is present in the fuel.
This indicates that the stress induced by lattice expansion is also slightly reduced with 25 ppm of sulphur in the fuel.

Table 1 Max. stress in LCC interconnect due to temperature gradients.

|                  | 5 ppb H₂S   | 25 ppm H₂S |
|------------------|-------------|------------|
| Free interconnect| 60 E6 N/m²  | 44 E6 N/m² |
| Flat interconnect| 63 E6 N/m²  | 53 E6 N/m² |

CONCLUSION

Mechanical stress in Lanthanum Chromite SOFC interconnect materials caused by temperature gradients is significantly reduced when 25 ppm of H₂S is present in the natural gas fuel. Most probably the Sulphur also reduces the overall mechanical stress in the interconnect.

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Figure 1: Stability diagram of the Ni-S-O system at 870 °C.

Figure 2: 100x100mm Counter Flow SOFC Geometry (Statoil design) (NASTRAN grid)

Figure 3: Spatial temperature distribution. SOFC with natural gas fuel with 5 ppb and 25 ppm H$_2$S.
Figure 4: Sulphur coverage (5 ppb and 25 ppm H₂S).

Figure 5: LCC lattice expansion (5 ppb and 25 ppm H₂S).
Figure 6: Stress distribution of a flat interconnect with 25 ppm H₂S in the fuel.