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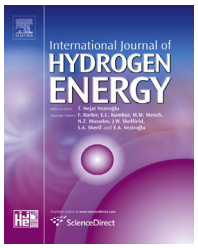

# Study of Methane Steam Reforming kinetics in operating Solid Oxide Fuel Cells: Influence of current density

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ABSTRACT

In literature, little is reported on the experimental studies of Methane Steam Reforming (MSR) kinetics in Solid Oxide Fuel Cells (SOFCs) when a current is drawn. This work investigates MSR reaction kinetics in a complete SOFC with a $Ni-Gd_{0.1}Ce_{0.9}O_{2-\delta}$ (Ni–GDC) anode under varying gas compositions, operating temperatures and current densities in order to obtain reliable experimental data for Computational Fluid Dynamics (CFD) modeling studies. Consistent with previous work, the methane conversion $X_{CH_4}$ decreases as the temperature decreases. A slight increase in the MSR reaction rate is observed when a current is drawn. A positive dependency of the MSR reaction rate on methane concentration was found. Current has an insignificant influence on the methane reaction order. Under open-circuit working condition, steam concentration has a slightly positive influence at higher temperature and a slightly negative influence at lower temperature on the MSR reaction rate. The influence of steam concentration on the reaction rate becomes more negative when a current is drawn. It is probably due to the blockage of reaction sites by the adsorbed oxygen/water molecules/ions.



## Introduction

Solid Oxide Fuel Cells (SOFCs) are fuel flexible. Under certain conditions, natural gas or biosyngas containing $CH_4$ can be internally reformed in SOFC anodes due to the presence of a catalyst, usually nickel, for the Methane Steam Reforming (MSR) reaction [1–6]. Although the steam reforming reaction is a highly endothermic process, the electrochemical oxidation is overwhelmingly exothermic [7–9]; thus, the electrochemical reaction is sufficient to support the internal MSR reaction in many cases. The overall MSR reaction is:

$$CH_4 + H_2O \leftrightarrow CO + 3H_2, \quad \Delta H_{298} = +206\ kJ/mol \tag{1}$$

and the Water Gas Shift (WGS) is:

$$CO + H_2O \leftrightarrow CO_2 + H_2, \quad \Delta H_{298} = -41\ kJ/mol \tag{2}$$

Modeling studies of the cell performance have been previously reported in our group [10,11]. The MSR kinetics plays an important role in determining the gas compositions and the temperature distributions in SOFCs [12]. In order to accurately predict methane fueled cell performance with Computational Fluid Dynamics (CFD) model, it is important to obtain reliable MSR kinetic data. The kinetic data used in modeling

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studies is generally obtained with experiments performed using catalyst beds in test reactors or with SOFC anodes under open-circuit working conditions [1,7–9,13–18]. Whether kinetic parameters obtained by these experiments can be used to model operating SOFCs has seldom been reported. Dicks et al. has stated that oxygen ions might have an influence on the reforming reaction rate [16]. Similarly, current production will bring down the hydrogen concentration and increase the steam concentration. Both may affect the reforming reactions as well. Therefore, the influence of current on the reforming reaction should be investigated.

Previous studies of MSR kinetics on both industrial catalysts and SOFC anode materials show a wide distribution in kinetic parameters [1,7–9,13–18], as shown in Table 1. This could be attributed to different nickel contents, morphologies, particle sizes, distributions of nickel in the anode and rate expressions used in the studies [1,7–9,14,16–25]. Generally, the reported activation energies with *Ni–GDC* anodes are lower than those with *Ni–YSZ* anodes [7–9,13–15,18,19,26]. It has been suggested that the doped ceria in the anode promotes the catalytic activity [27]. H. Timmermann et al. [13] has conducted experiments with *Ni–GDC* anodes operated at steam to carbon ratios from 0 to 3 and temperatures from 1073 *K* to 1223 *K*. N. Nakagawa et al. [14] reported that the catalytic activity deteriorated with a current density as high as 6000 $A/m^2$. The results from G. Brus et al. [18] indicate the importance of combined numerical and experimental studies in the design of SOFC reformers. The process of reforming biogas on a *Ni–YSZ* and *Ni* supported on Samarium-doped Ceria (*Ni–SDC*) catalyst has been numerically and experimentally investigated. In these measurements different thermal boundary conditions, steam to carbon ratios and several different fuel compositions were used. The results of the numerical computation were compared with the experimental data and good agreement was found.

In spite the large efforts in experimental investigations into *MSR* reaction as aforementioned, the influence of the electrochemical reaction on the reforming reaction needs further investigation. In this work, experiments were conducted to study the effect of current density on the *MSR* kinetics in *Ni–GDC* anode in an operating SOFC. The *MSR* reaction was investigated under both open-circuit (open cell voltage with no current) and closed-circuit (with current in the circuit) working conditions. The results obtained in this study enable a more comprehensive understanding of the influence of current on the *MSR* reaction [3,12,18,23,28–32]. The kinetic parameters obtained in this study can be used in CFD models to more precisely investigate the effect of the *MSR* kinetics on the cell performance.

**Table 1 – The MSR kinetics from literature.**

| Ref | Test materials | $E_a$(kJ/mol) | $k_0$ | $\alpha_{CH_4}$ | $\alpha_{H_2O}$ | T (K) | SC | Current ($A/m^2$) |
|---|---|---|---|---|---|---|---|---|
| N. Nakagawa et al. [14] | Ni–YSZ–$CeO_2$ | 18 | – | 1 | −1–0 | 973–1273 | 2–8 | – |
| N. Nakagawa et al. [14] | Ni–YSZ–$CeO_2$ | ≥18 | – | – | – | 973–1273 | 2–8 | 6000 |
| Achenbach et al. [7] | Ni–$ZrO_2$ | 82 | – | 1 | −1.25 | 973–1313 | 2.6–8 | – |
| A. L. Lee et al. [15] | 16 Ni–$ZrO_2$ | 17.8–23.5 | $490-4775\ mol/(g\cdot h)$ | 1 | −1.28 to −1.25 | 1073–1273 | 2–7.4 | – |
| A. Dicks et al. [17,16] | Ni–$ZrO_2$ | 118–294 | – | 1 | Negative | 973–1273 | 1–7 | – |
| A. Dicks et al. [17,16] | Ni–$ZrO_2$ | 154–253 | $21\ mol/(cm^2\cdot s\cdot bar^{-1})$ | 1 | Negative | 1073–1173 | 1–7 | – |
| Xu et al. [1] | Ni–$MgAl_2O_4$ | 240.1 | – | – | – | 673 | 3–5 | – |
| K. Ahmed et al. [8] | Ni–YSZ | 95 ± 2 | – | 0.85 ± 0.05 | −0.35 ± 0.04 | 1150–1200 | 1.4–3 | – |
| K. Ahmed et al. [8] | Modified Ni–YSZ | 208 ± 10 | – | 1.4 ± 0.01 | −0.8 ± 0.02 | 1150–1200 | 1.4–3 | – |
| Bebelis et al. [9] | Ni–$ZrO_2$($Y_2O_3$) | 19–50 | – | – | – | 1073–1173 | 0.2–16 | – |
| H. Timmermann et al. [13] | Ni–GDC | 26.3 | $4.05E+-5\ mol/(\cdot s\cdot bar^{(\alpha_{CH_4}+\alpha_{H_2O})})$ | 1.19 | 0 | 1073–1223 | 2–3 | – |
| G. Brus et al. [18] | Ni–YSZ | 117 | $41.5\ mol/(g\cdot s\cdot bar^{(\alpha_{CH_4}+\alpha_{H_2O})})$ | 0.98 | −0.09 | 873–1023 | 3–5 | – |
| G. Brus et al. [18] | Ni–SDC | 106 | $40\ mol/(g\cdot s\cdot bar^{(\alpha_{CH_4}+\alpha_{H_2O})})$ | 0.98 | −0.25 | 873–1023 | 3–5 | – |

## Experiment

A complete fuel cell with *Ni–GDC* anode was used (HC Starck) in the experiments. The electrolyte-supported planar fuel cell was $9 \times 9\ cm^2$, the anode thickness was 35 $\mu m$. The anode consisted of a functional layer containing $Ni–Gd_{0.1}Ce_{0.9}O_{2-\delta}$. The nickel content in the anode was 57 *wt%*, and the cerium content was 23 *wt%*. The cathode material was Lanthanum Strontium Manganite (*LSM*). The