INVESTIGATION OF THE R.W.G.S. REACTION IN SOECs FOR THE H2O/CO2 CO-ELECTROLYSIS

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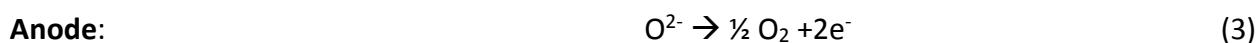*(*niakolas@iceht.forth.gr)*

ABSTRACT

Ni/GDC is known as an effective electrode in suppressing coke formation under humidified hydrocarbon fuels. Its performance can be further improved by dispersing trace amounts of various elements (noble and/or non-noble) metals. Following this approach, in the presented investigation X-Ni/GDC electrodes (where X = Au, Mo and Fe) are studied, in the form of half-electrolyte supported cells, for their performance in the RWGS through catalytic-kinetic measurements. The samples were tested at open circuit potential conditions in order to elucidate their catalytic activity towards the production of CO (r_{co}), which is one of the products of the H_2O/CO_2 co-electrolysis reaction. Physicochemical characterization is also presented, in which the samples were examined both in the form of powders and as half cells with BET, H_2-TPR, Air-TPO and TGA re-oxidation measurements in the presence of H_2O.

In brief, it was found that the rate of the produced CO (r_{co}) increases by increasing the operating temperature and the partial pressure of H_2 in the reaction mixture. In addition, the first results revealed that Fe and Mo modification enhances the catalytic production of CO, since the 2wt.% Fe-Ni/GDC and 3wt.% Mo-Ni/GDC electrodes were proved to perform better compared to the other samples, in the whole studied temperature range (800-900 °C), reaching the thermodynamic equilibrium. Furthermore, carbon formation was not detected. The electrocatalytic investigation on full electrolyte-supported cells is currently in progress.

INTRODUCTION

Co-electrolysis of H_2O and CO_2 in a SOEC yields synthesis gas (CO + H_2) which in turn can be used towards the formation of various types of synthetic fuels[1]. Using SOECs for CO_2 capture/recycling would therefore be an attractive method to provide CO_2 neutral synthetic hydrocarbon fuels. According to thermodynamics, SOECs offer thermodynamic benefits of operating endothermic reactions, such as H_2O and/or CO_2 electrolysis, at temperatures >700 °C because a larger part of electrical energy can be substituted by thermal energy[2]. In addition, high temperatures can lead to a significant decrease in the internal resistance of the cell and acceleration of the electrode reaction processes due to fast reaction kinetics[3].

Co-electrolysis is a much more complex process compared with pure steam or CO_2 electrolysis, because three reactions take place simultaneously; namely H_2O electrolysis, CO_2 electrolysis and the catalytic Reverse Water Gas Shift reaction (RWGS). More specifically, in the cathode of SOECs two electrochemical reactions occur simultaneously at the triple phase boundaries, i.e. H_2O and CO_2 electrochemical reductions. The oxygen ions, produced by these reactions, are transferred through an oxygen ion-conducting electrolyte (YSZ) to the anode, where oxygen gas is formed[4]:

Cathode: $\qquad\qquad\qquad H_2O + 2e^- \rightarrow H_2 + O^{2-}$ (1)

$\qquad\qquad\qquad\qquad\qquad CO_2 + 2e^- \rightarrow CO + O^{2-}$ (2)

Anode: $\qquad\qquad\qquad O^{2-} \rightarrow \frac{1}{2} O_2 + 2e^-$ (3)

Besides the electrolysis reactions mentioned above, the reversible water gas shift (RWGS) catalytic reaction also occurs at the cathode with the co-existence of CO_2 and H_2O.

Cathode: $\qquad\qquad\qquad H_2 + CO_2 \rightarrow H_2O + CO$ (4)

It thus appears that CO can be produced either electrochemically by the dissociation of CO_2 or catalytically via the RWGS reaction. Controversial observations have been presented in the literature about the role of the RWGS reaction in CO production. Most of the studies report that CO is mainly produced electrochemically and RWGS has a small contribution[5,6], while a few studies report that CO is totally produced catalytically via the RWGS reaction[7]. Until now no agreement has been reached and as a result it is crucial to quantify the degree of CO formation for each reaction.

Ni-containing ceramic cathodes with Yttria-Stabilized Zirkonia (YSZ) and Gadolinia-Doped Ceria (GDC) are known as effective electrodes in high temperature H_2O/CO_2 co-electrolysis, similarly to the case of H_2O electrolysis[5-7]. Their performance can be further improved by dispersing trace amounts of various elements (noble and/or non-noble metals)[8]. Following this approach, in the presented investigation modified Au-Mo-Fe-Ni/GDC electrodes (half cells) are studied for their performance in the RWGS reaction through catalytic-kinetic measurements. The samples were tested at open circuit potential conditions in order to elucidate their catalytic activity towards the production of CO (r_{co}), which is one of the products from the H_2O/CO_2 co-electrolysis reaction. The latter approach is considered as an attempt to create a reference profile for the catalytic performance of the candidate electrodes, by applying the same reaction conditions as those under the co-electrolysis operational mode.

EXPERIMENTAL

The modified cathode powders were prepared via the Deposition - Precipitation (D.P.) or Deposition - Co Precipitation (D.CP.) methods by using the commercial NiO/GDC cermet (65wt.% NiO-35wt.% GDC, Marion Technologies) as the support. The precursors for the 3wt.% Au-NiO/GDC, 3wt.% Mo-NiO/GDC 3wt.% Au-3wt.% Mo-NiO/GDC and 2wt.% Fe-NiO/GDC samples were the $HAuCl_4$ (Sigma-Aldrich), $(NH_4)_6Mo_7O_{24}$ (Sigma-Aldrich) and $Fe(NO_3)_3 x 9H_2O$ (Sigma-Aldrich) solutions, respectively.

The fuel electrode was deposited by using the screen printing technique. In particular, a paste was prepared by using an appropriate amount of the electrocatalyst (modified NiO/GDC powder), terpineol (Sigma-Aldrich) as the dispersant and PVB (polyvinylbutyral, Sigma-Aldrich) as binder. The loading of the examined electrodes varied in the region between 10-12 mg/cm^2 with 1.8 cm^2 geometric surface area and 20 μm thickness.

The prepared half cells were catalytically investigated at Open Circuit Potential (OCP) conditions for the RWGS reaction, in the presence of Ni mesh. The catalytic experiments were carried out in the temperature range of 800-900 °C under various $H_2O/CO_2/H_2$ mixtures, by keeping in all cases the pH_2O/pCO_2 ratio constant. In regards to the experimental part of these measurements, H_2O was introduced and handled in the reactor in the form of steam, as in the SOEC measurements. Reactants and products were analyzed by on-line gas chromatography, using a Varian CP-3800 gas chromatograph with a thermal conductivity detector.

RESULTS

All the prepared samples, in the form of half-electrolyte supported cells, were tested at Open Circuit Potential (OCP) conditions in order to elucidate their catalytic activity towards the production of CO, which is one of the products from the H_2O/CO_2 co-electrolysis reaction[9]. Furthermore, there is an investigation of the effect of the modification (type of dopant: Au, Mo, Fe) on the catalytic activity for the production of CO, through the RWGS reaction. The latter approach is considered as an attempt to create a reference profile for the catalytic performance of the candidate electrodes, under the same experimental conditions as in co-electrolysis (including the presence of current collector). This is an important step, because it will provide detailed experimental feedback on the possible contribution of the RWGS reaction to the production of CO and the extent of this contribution to the electrochemical reduction of CO_2, during the co-electrolysis mode.

In regards to the "homogenous" catalytic production of CO, the rate has been found to be negligible, in the range of $r_{CO, homogenous} = 0.05$ μmol/s, for a fuel feed comprising 30 vol.% He - 24.5 vol.% H_2O - 24.5 vol.% CO_2 - 21 vol.% H_2. Concerning the current collector, Ni-mesh shows some catalytic activity for the production of CO (r_{CO}), which increases by increasing the operating temperature and the partial pressure of H_2. However, comparative r_{CO} measurements (not shown here) of a Ni/GDC electrode with and without the presence of Ni mesh as current collector, as well as of the bare Ni mesh, suggest that there is no direct catalytic correlation/contribution of the Ni mesh to the activity of the electrocatalysts.

Figure 1A presents the comparison of the produced r_{CO} for Ni/GDC and for modified-Ni/GDC electrodes, under a specific $H_2O/CO_2/H_2$ mixture, whereas the corresponding CO_2 conversions for the same mixture are depicted in **Figure 1B.** The values are low enough to be considered in the differential region, apart from the case of 2Fe-Ni/GDC in reaction mixture (A), which is relatively high. The % conversion of CO_2 was calculated by the following formula:

$$CO_2 \text{ conversion (\%)} = \frac{F_{CO}^{out}}{F_{CO_2}^{in}} \cdot 100 \tag{5}$$

where: F_{CO}^{out} and $F_{CO_2}^{in}$ correspond to the rate (μmol/s) of the produced CO and of the introduced CO_2 in the reactants feed, respectively.

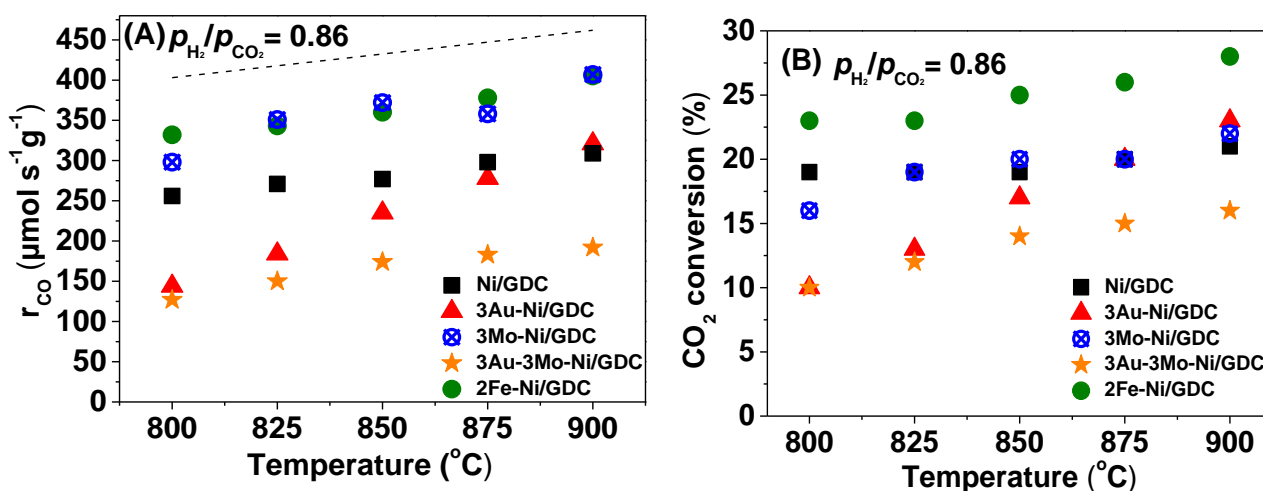***Figure 1. (A)*** *CO production rates (μmol s⁻¹ g⁻¹) and the corresponding **(B)** %CO₂ conversion resulting from the R.W.G.S. reaction on ESCs (half cells) comprising: Ni/GDC, 3Au-Ni/GDC, 3Mo-Ni/GDC, 3Au-3Mo-Ni/GDC and 2Fe-Ni/GDC as fuel electrodes, in the range of 800-900 °C under a mixture of 24.5% H₂O - 24.5% CO₂ -21% H₂ (**p_H2/p_CO2 = 0.86**). Dilution of He: 30 vol.% and F_total = 140 cm³/min (at STP conditions of 0 °C and 1 atm) in all cases. The dash line (− −) corresponds to the r_CO values in thermodynamic equilibrium. All studied electrodes have similar loading in the range of 10-12 mg/cm².*

It is shown (**Figures 1A, 1B**) that 2Fe-Ni/GDC and 3Mo-Ni/GDC have the highest catalytic activity, of the examined electrodes, for the RWGS reaction. In fact, 2Fe-Ni/GDC is the most active in terms of the produced CO. The above performance is observed for all applied fuel feeds (p_{H2}/p_{CO2} = 0.86, 0.50 and 0.22), whereas it is enhanced by increasing (i) the operating temperature and (ii) the partial pressure of H_2 in the fuel feed. The enhanced catalytic performance of the Fe-modified sample, can be primarily ascribed to the possible stronger adsorption and consequent catalytic dissociation of CO_2 on the active sites of the catalyst. This first conclusion is going to be further examined with specific CO_2 Temperature Programmed Desorption (TPD) measurements.

Another noteworthy remark is that the produced CO rates were compared to the thermodynamic equilibrium rates (dash line in **Figure 1A**), for the specific $H_2O/CO_2/H_2$ reaction mixture. The

equilibrium rates were calculated, by using the equilibrium constant (K_{eq}) formula that is reported in the reference[10]. It was found (**Figure 1A**) that Ni/GDC, the binary Au- and the ternary Au-Mo-modified samples exhibit CO production rates, which are lower than the thermodynamic equilibrium for all of the examined reaction conditions. The performances of 2Fe-Ni/GDC and 3Mo-Ni/GDC are closer to the equilibrium, but cannot be considered as thermodynamically limited.

The results from the measurements in **Figure 1A** can also be interpreted into Arrhenius plots, depicted in **Figure 2**, where the derived apparent activation energies ($E_{a, app}$), for the production of CO and consequently for the RWGS reaction, are listed in **Table 1**.
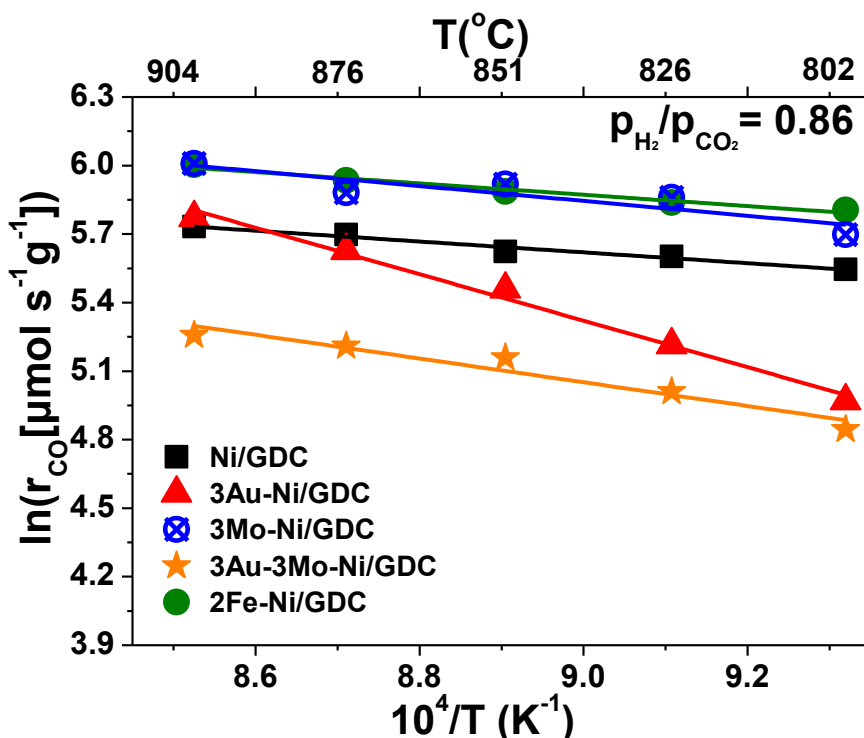

Figure 2. *Arrhenius plots of the CO production rates (µmol s^{-1} g^{-1}) resulting from the RWGS reaction on ESCs (half cells) comprising: Ni/GDC, 3Au-Ni/GDC, 3Mo-Ni/GDC, 3Au-3Mo-Ni/GDC and 2Fe-Ni/GDC, as fuel electrodes, in the range of 800-900 ^{o}C, under the mixture 24.5% H_2O - 24.5% CO_2 -21% H_2 (**p_{H2}/p_{CO2} = 0.86**). Dilution of He: 30 vol.% and F_{total} = 140 cm^3/min (at STP conditions of 0 ^{o}C and 1 atm) in all cases.*

Table 1. *Apparent Activation Energies ($E_{a,app}$, kJ/mol) for the RWGS reaction on ESCs for three different mixtures: (A) 24.5% H_2O - 24.5% CO_2 -21% H_2 (**p_{H2}/p_{CO2} = 0.86**), (B) 28% H_2O − 28% CO_2 − 14 % H_2 (**p_{H2}/p_{CO2} = 0.50**) and (C) 31.5% H_2O - 31.5% CO_2 -7% H_2 (**p_{H2}/p_{CO2} = 0.22**)*

Sample	$E_{a, apparent}$ (kJ mol^{-1}) and A* (µmol s^{-1} g^{-1}), per reaction mixture					
	p_{H2}/p_{CO2}=0.86		p_{H2}/p_{CO2}=0.50		p_{H2}/p_{CO2}=0.22	
Ni/GDC	20	2.3×10^3	22	3.6×10^3	20	1.0×10^3
3Au-Ni/GDC	85	1.9×10^6	74	5.0×10^5	46	1.5×10^4
3Mo-Ni/GDC	27	6.5×10^3	14	1.1×10^3	21	1.4×10^3
3Au – 3Mo-Ni/GDC	43	1.7×10^4	45	1.5×10^4	50	1.6×10^4
2Fe-Ni/GDC	21	3.3×10^3	19	1.6×10^3	21	1.3×10^3

*A: *The pre-exponential factor* in the Arrhenius equation r=A·exp($-\frac{E_{a,app}}{R \cdot T}$)

The Arrhenius plots (**Figure 2**) and the the calculated $E_{a, app}$ (**Table 1**) show that 2Fe-Ni/GDC, 3Mo-Ni/GDC and Ni/GDC have practically the same $E_{a, app}$. However, the Fe- and Mo- modified samples exhibit higher pre-exponential factors that explains the higher production rates of CO. 3Au-Ni/GDC

shows the highest $E_{a, app}$, which is an additional indication for its worst catalytic activity. Finally, the ternary 3Au-3Mo-Ni/GDC sample shows an apparent activation energy, which lies in between of that for 2Fe-Ni/GDC and 3Au-Ni/GDC. However, the activity of the ternary sample is the lowest, due to the low pre-exponential factor.

The effect of H_2 partial pressure on the catalytic rate of CO formation is further verified in **Figure 3** for all samples at 900 °C and 800 °C. 2Fe-Ni/GDC and 3Mo-Ni/GDC are the most active and 3Au-3Mo-Ni/GDC is the least one. The 3Au-Ni/GDC catalyst at 900 °C shows similar performance with that of Ni/GDC. In addition, by decreasing the temperature at 800 °C, the catalytic activity of 3Au-Ni/GDC exhibits the highest reduction, which is further explained by the calculated $E_{a,app}$ (**Table 1**). Most importantly, the kinetic behavior of all samples suggests that the formation rate of CO exhibits a positive order dependence on the partial pressure of H_2.
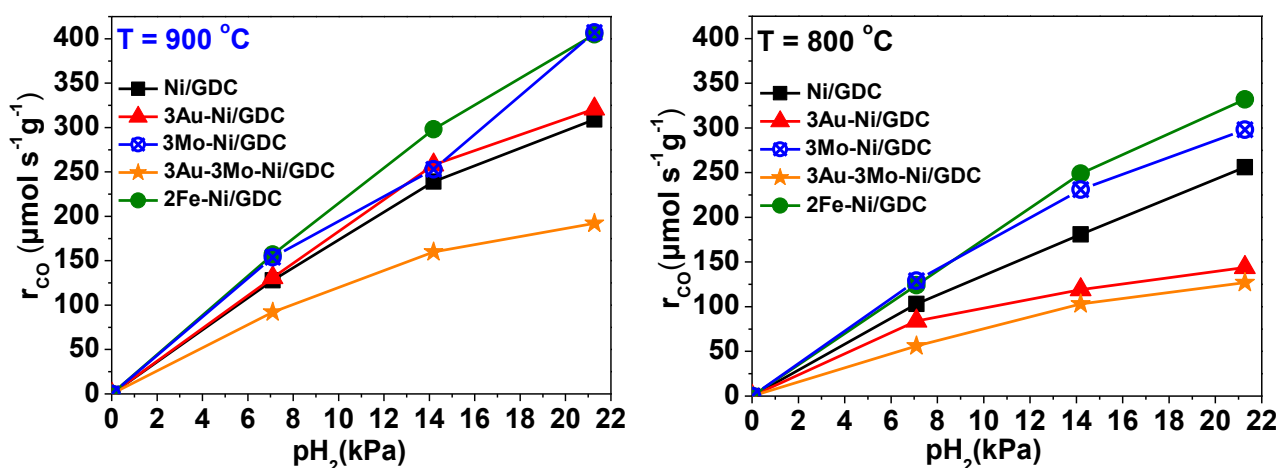

Figure 3. *Steady state effect of the H_2 partial pressure (pH2, kPa) on the CO production rates (μmol s^{-1} g^{-1}) on ESCs comprising: Ni/GDC, 3Au-Ni/GDC, 3Mo-Ni/GDC, 3Au-3Mo-Ni/GDC and 2Fe-Ni/GDC, for 900 and 800 °C. The pH2O/pCO2 ratios are fixed.*

CONCLUSIONS

The presented study deals with the kinetic investigation of Ni-based (modified or not) electrodes towards their performance for the RWGS reaction. The samples were examined in the form of electrolyte-supported (half) cells and the measured kinetic parameter was the production rate of CO. The main objective was to clarify the effect of the modification on the catalytic activity for the RWGS, which is considered as a key reaction for the CO production under H_2O/CO_2 co-electrolysis operation. The reaction conditions were similar to those that are going to be applied under co-electrolysis mode.

The kinetic study of the candidate electrocatalysts showed that Au modification inhibits the catalytic production of CO, through the RWGS reaction, while modification with Fe or Mo induces an enhancement of r_{CO}. In fact, the 2wt.% Fe-Ni/GDC sample is the most active both in terms of %CO_2 conversion and of the produced CO. In addition, a negative synergy was observed for the ternary Au-Mo-Ni modified sample. Specifically, the 2wt.% Fe-Ni/GDC and 3wt.% Mo-Ni/GDC samples showed similar apparent activation energy for the RWGS reaction as that of Ni/GDC, while the 3wt.% Au-Ni/GDC and 3wt.% Au–3wt.% Mo-Ni/GDC samples showed lower $E_{a,app}$. The above performance is observed for all applied fuel feeds (P_{H2}/P_{CO2} = 0.86, 0.50 and 0.22), whereas it is enhanced by increasing (i) the operating temperature and (ii) the partial pressure of H_2.

Finally, SOEC experiments for the H_2O/CO_2 co-electrolysis reaction on ESCs, comprising the presented modified-Ni/GDC cathodes are currently in full progress.

REFERENCES

[1] S.D. Ebbesen, M. Mogensen, Electrolysis of carbon dioxide in Solid Oxide Electrolysis Cells. J. Power Sources 193 (2009) 349-358.

[2] L. Kleiminger, T. Li, K. Li, G.H. Kelsall, Syngas (CO-H_2) production using high temperature micro-tubular solid oxide electrolysers. Electrochimica Acta 179 (2015) 565-577.

[3] X. Zhang, Y. Song, G. Wang, X. Bao, Co-electrolysis of CO_2 and H_2O in high temperature solid oxide electrolysis cells: Recent advance in cathodes. J. Energy Chemistry 26 (2017) 839-853.

[4] X. Sun, M. Chen, S.H. Jensen, S.D. Ebbesen, C. Graves, M. Mogensen, Thermodynamic analysis of synthetic hydrocarbon fuel production in pressurized solid oxide electrolysis cells. Int. J. Hydrogen Energy 37 (2012) 17101-17110.

[5] X. Sun, M. Chen, Y.L. Liu, P. Hjalmarsson, S.D. Ebbesen, S.H. Jensen, et al, Durability of solid oxide electrolysis cells for syngas production fuel cells, electrolyzers and energy conversion. J. Electrochem. Soc. 160 (2013) F1074-80.

[6] C. Graves, S.D. Ebbesen, M. Mogensen, Co-electrolysis of CO_2 and H_2O in solid oxide cells: performance and durability. Solid State Ionics, 192 (2011) 398-403.

[7] P. Kim-Lohsoontorn, J. Bae, Electrochemical performance of solid oxide electrolysis cell electrodes under high-temperature coelectrolysis of steam and carbon dioxide. J. Power Sources 196 (2011) 7161-7168.

[8] E. Ioannidou, Ch. Neofytidis, L. Syggelou, D.K. Niakolas, Au-doped Ni/GDC as an improved cathode electrocatalyst for H_2O electrolysis in SOECs. Appl. Cat. B: Environ. 236 (2018) 253-264.

[9] E. Ioannidou, S. Neophytides, D.K. Niakolas, Experimental Clarification of the RWGS Reaction Effect in H_2O/CO_2 SOEC Co-Electrolysis Conditions. Catalysts, 9 (2019) 1-19, https://doi.org/10.3390/catal9020151.

[10] C. Caitlin, Kinetics and catalysis of the water-gas-shift reaction: A Microkinetic and Graph Theoretic Approach, Worcester Polytechnic Institute (2006).