

## Modified Ni-based electro-catalysts for dry reforming of methane as potential electrodes for SOFCs

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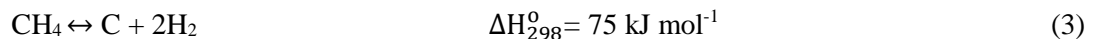
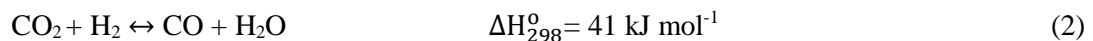
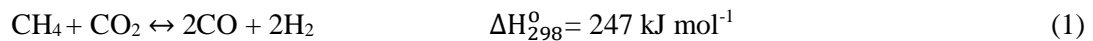
### ABSTRACT

The presented study is related to modified Au-Mo-Fe-Ni/GDC electrodes, in the form of half-electrolyte supported cells, for their performance and coking resistance under CO<sub>2</sub> reforming of CH<sub>4</sub> in single SOFCs, at 750-900 °C, through catalytic-kinetic measurements. Ni/GDC, 1 wt.% Au-Ni/GDC, 3 wt.% Au-Ni/GDC, 0.5 wt.% Fe-Ni/GDC, 2 wt.% Fe-Ni/GDC, 3 wt.% Au-0.4 wt.% Mo-Ni/GDC and 3 wt.% Au-0.5 wt.% Fe-Ni/GDC electrodes were tested at open circuit potential conditions to elucidate their catalytic activity towards the consumption of CH<sub>4</sub>, CO<sub>2</sub>, the production of H<sub>2</sub>, H<sub>2</sub>O, CO and the production of carbon, under a biogas fuel with CH<sub>4</sub>/CO<sub>2</sub>=1. 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 CH<sub>4</sub>/CO<sub>2</sub> feed conditions as those under IDRDM operational mode without applying a current. The catalytic-kinetic measurements were carried out for a cell with Ni/GDC, under differential conditions, at various CH<sub>4</sub> and CO<sub>2</sub> partial pressures. The samples were also physicochemically characterized including measurements for the catalytic dissociation of CH<sub>4</sub> and CO<sub>2</sub>.

### INTRODUCTION

Recycling biogas to produce syngas (H<sub>2</sub> + CO) through Dry Reforming of Methane (DRM) has currently attracted resurgent interest. Biogas consists mainly of CH<sub>4</sub> (50-70%) and CO<sub>2</sub> (25-50%) and is widely produced by anaerobic fermentation of biomass. DRM provides a feasible solution to eliminate greenhouse gases via production of useful chemicals and hydrocarbons.

Considering the DRM energy applications the produced syngas can be used as a fuel in high temperature solid oxide fuel cells (SOFCs) for electricity production or biogas can be directly fueled in the cell without the need of an external reformer (Internal Dry Reforming of Methane, IDRDM), which simplifies the SOFC system and reduces the cost. When biogas is directly fed to the SOFC fuel electrode at temperatures 750-900 °C, various catalytic (Equations 1-3) and electrocatalytic reactions may take place simultaneously on the electrode [1,2].



The CO<sub>2</sub> reforming of methane (DRM) (Equation 1) is a strongly endothermic process and therefore high temperatures (typically >750 °C) are required to achieve high H<sub>2</sub> and CO yields. Moreover, the catalytic Reverse Water Gas Shift (RWGS) reaction (Equation 2) may run in parallel, resulting in the consumption of valuable H<sub>2</sub> and a decrease in H<sub>2</sub>/CO ratio to values lower than unity [2]. In addition, carbon deposition on the electrocatalyst surface due to CH<sub>4</sub> decomposition (Equation 3) may also occur resulting in progressive electrocatalyst deactivation. The CH<sub>4</sub> decomposition (Equation 3) is favoured at high temperatures (> 600 °C), whereas at temperatures below 650 °C carbon deposits are mainly produced by Boudouard reaction (2CO → C + CO<sub>2</sub>). The H<sub>2</sub>, CO and C produced, as well as the CH<sub>4</sub> supplied can be electrochemically oxidized by oxygen ions [1].

Ni-based ceramic-metal composites with Ytria Stabilized Zirconia (YSZ) and Gadolinia Doped Ceria (GDC) are widely used as electrocatalysts in SOFCs because of their activity and inexpensiveness. According to the literature, Ni/GDC fuel electrodes show higher electrocatalytic activity for CH<sub>4</sub> reforming, resistance to carbon deposition, and tolerance levels for H<sub>2</sub>S compared to Ni/YSZ electrodes [3]. Authors attributed this behaviour to the capacity of CeO<sub>2</sub> to store and release oxygen, which favours the CH<sub>4</sub> oxidation and mitigates the carbon deposition. The carbon tolerance

and anti-sintering tendency of nickel can be enhanced further, by dispersing trace amounts of transition noble (Rh, Pt, Pd, Ru, Au) or non-noble (Co, Cu, Mo, Fe) metal elements [3,4].

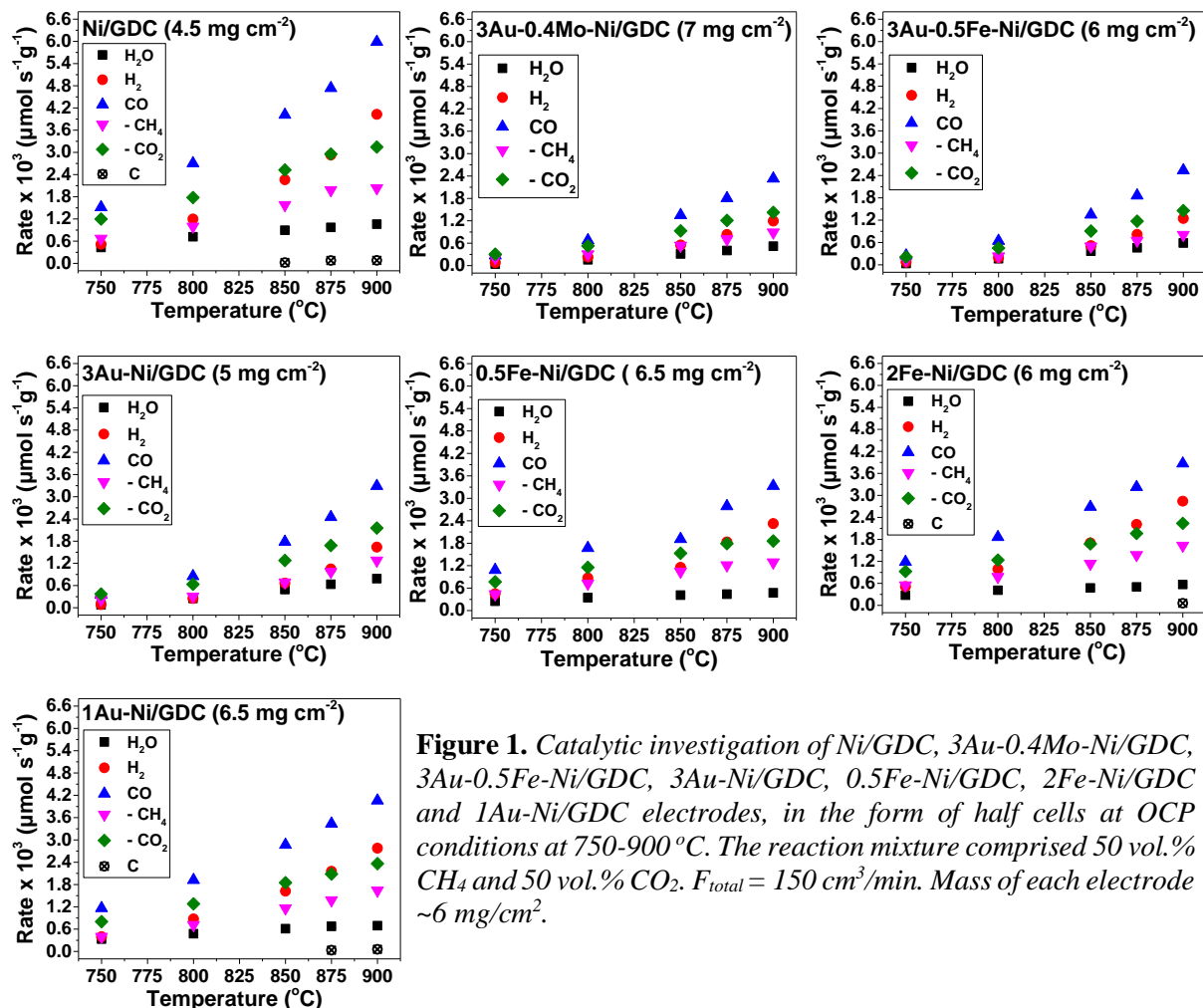
## EXPERIMENTAL PART

The modified powders were prepared via Deposition-Co Precipitation (D.CP.) by using the commercial NiO/GDC cermet (65 wt.% NiO-35 wt.% GDC, Marion Technologies) as the support and  $\text{HAuCl}_4$  (Sigma-Aldrich),  $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24}$  (Sigma-Aldrich) and  $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$  (Sigma-Aldrich) solutions as precursors [3,4]. The half cells consisted of circular shaped planar 8YSZ electrolyte (by Kerafol) with a 25 mm diameter and 300  $\mu\text{m}$  thickness. A paste was applied by screen-printing and comprised the electrocatalyst, terpineol (Sigma-Aldrich) and PVB (polyvinylbutyral, Sigma-Aldrich). After the deposition, the cell was sintered at 1150  $^\circ\text{C}$ . The loading of the examined electrodes varied in the region of 5–7  $\text{mg}/\text{cm}^2$  with a 1.8  $\text{cm}^2$  geometric surface area. The prepared half cells were adjusted on a ceramic YSZ tube.

The prepared half cells were catalytically investigated at OCP conditions for  $\text{CO}_2$  reforming of  $\text{CH}_4$ , in the presence of Ni mesh. The catalytic experiments were accomplished at temperatures between 750–900  $^\circ\text{C}$  under a fuel with  $\text{CH}_4/\text{CO}_2=1$  and for total gas flows varying from 150 to 300  $\text{cm}^3/\text{min}$ . Reactants and products were determined by using an on-line gas chromatograph (Varian CP-3800) with a thermal conductivity detector.

## RESULTS

**Figure 1** shows the catalytic performance of each electrode at 750-900  $^\circ\text{C}$ , through the consumption rates of  $\text{CH}_4$ ,  $\text{CO}_2$  and the production rates of  $\text{H}_2$ ,  $\text{CO}$ ,  $\text{H}_2\text{O}$  and of the formed carbon, for the  $\text{CO}_2$  reforming of  $\text{CH}_4$  ( $\text{CH}_4/\text{CO}_2=50/50$ ).



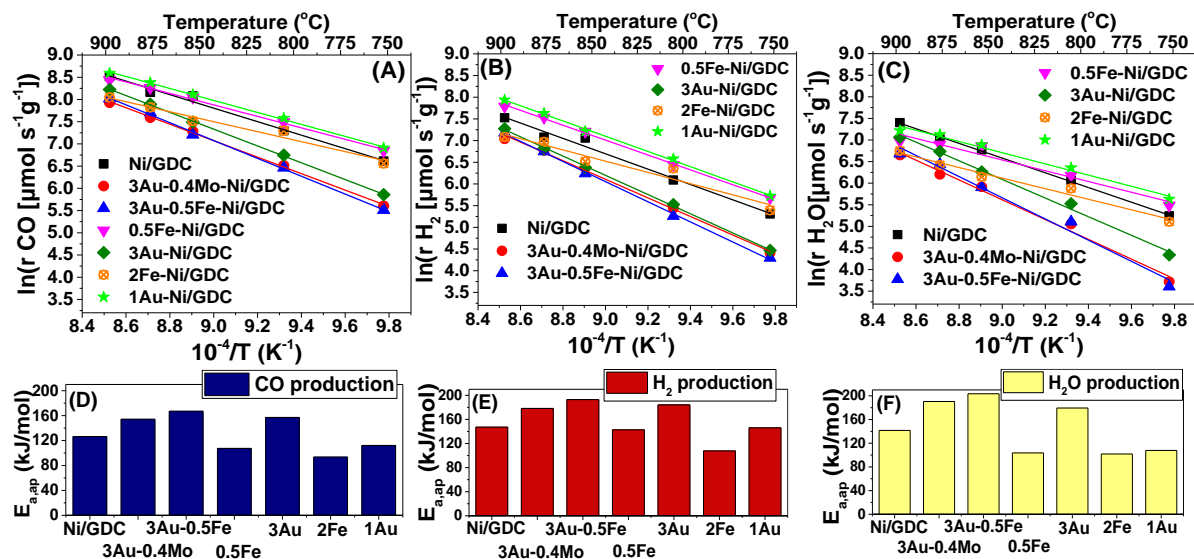
**Figure 1.** Catalytic investigation of Ni/GDC, 3Au-0.4Mo-Ni/GDC, 3Au-0.5Fe-Ni/GDC, 3Au-Ni/GDC, 0.5Fe-Ni/GDC, 2Fe-Ni/GDC and 1Au-Ni/GDC electrodes, in the form of half cells at OCP conditions at 750-900  $^\circ\text{C}$ . The reaction mixture comprised 50 vol.%  $\text{CH}_4$  and 50 vol.%  $\text{CO}_2$ .  $F_{\text{total}} = 150 \text{ cm}^3/\text{min}$ . Mass of each electrode  $\sim 6 \text{ mg}/\text{cm}^2$ .

The measurements were performed on half cells that comprised only the electrocatalyst and the current collector (Ni mesh). Comparative measurements of Ni/GDC with and without the presence of Ni mesh, suggest that there is no direct catalytic contribution of Ni mesh to the activity of the electrocatalysts. In respect to the catalytic performance, Ni/GDC was found to be the most active electrode for the CO<sub>2</sub> reforming of CH<sub>4</sub> reaction, yielding the highest production rates of H<sub>2</sub> and CO. However, it exhibited carbon formation rates, which were calculated by using the measured production rates of H<sub>2</sub>, CO and H<sub>2</sub>O in the mass balance equation of carbon (Equation 4):

$$r_C \left[ \frac{\mu\text{mol}}{\text{s}} \right] = \frac{r_{\text{H}_2} + 2r_{\text{H}_2\text{O}} - r_{\text{CO}}}{2} \quad (4)$$

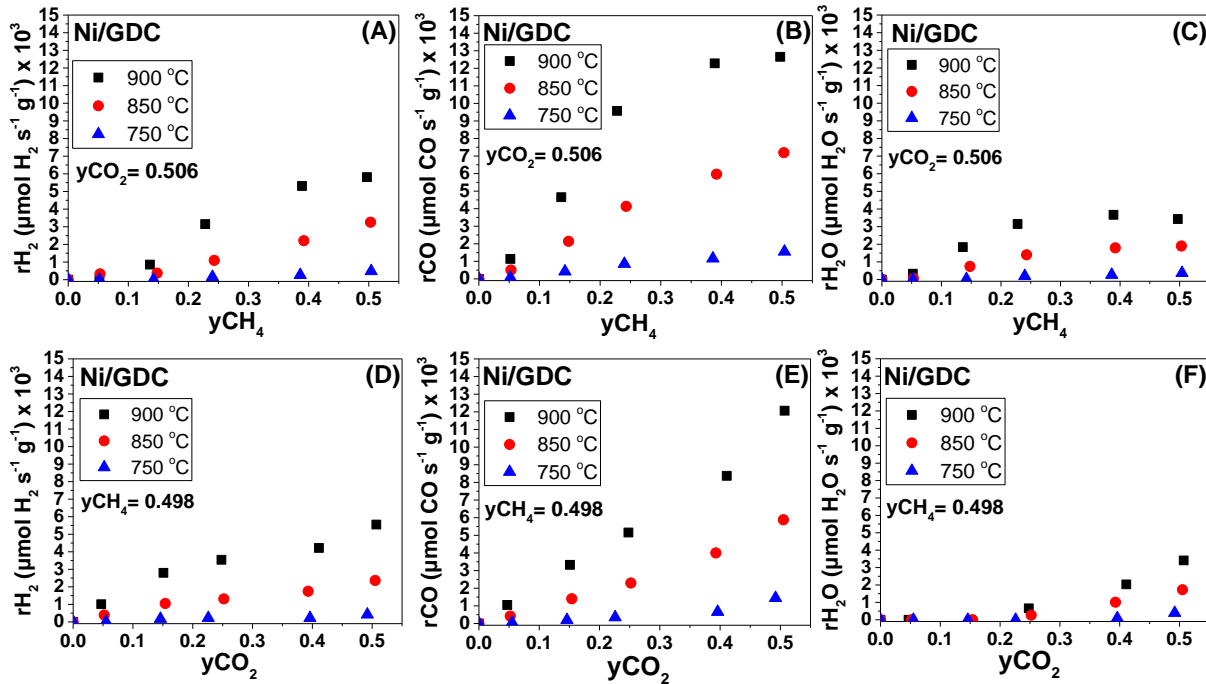
On the other hand, 3Au-0.4Mo-Ni/GDC, 3Au-0.5Fe-Ni/GDC, 3Au-Ni/GDC and 0.5Fe-Ni/GDC electrodes were less active in terms of H<sub>2</sub> and CO production and at the same time exhibited resistivity to carbon deposition.

The kinetic measurements were performed with gas flows in the range of 150-200 cm<sup>3</sup>/min, where the reactor was operating under differential conditions with reactants' conversions between 5% and 20%. In the above gas flow range the reaction rates were found to remain practically constant, which corresponds to the absence of external mass transfer limitations. **Figure 2(A-C)** presents the Arrhenius plots for the production rates of CO, H<sub>2</sub> and H<sub>2</sub>O under differential conditions and **Figure 2(D-F)** exhibit the derived apparent activation energies ( $E_{a, \text{app}}$ ) for the production of CO, H<sub>2</sub> and H<sub>2</sub>O for each electrocatalyst. The derived  $E_{a, \text{app}}$  for the production of H<sub>2</sub>O corresponds to the apparent activation energy for the RWGS reaction which consumes the valuable H<sub>2</sub> for the fuel cell. A proper electrocatalyst should exhibit (a) the lowest  $E_{a, \text{app}}$  for H<sub>2</sub> and CO production, (b) the highest  $E_{a, \text{app}}$  for H<sub>2</sub>O production and (c) negligible carbon deposition rates. The Arrhenius plots, the calculated  $E_{a, \text{app}}$  and the formation carbon rates (**Fig. 1**) show that 3Au-0.4Mo-Ni/GDC, 3Au-0.5Fe-Ni/GDC, 3Au-Ni/GDC and 0.5Fe-Ni/GDC have practically the highest  $E_{a, \text{app}}$  for the RWGS reaction and exhibit high resistance to carbon formation, whereas they are less active for H<sub>2</sub> and CO production.



**Figure 2.** Arrhenius plots of (A) CO, (B) H<sub>2</sub> and (C) H<sub>2</sub>O production rates ( $\mu\text{mol s}^{-1}\text{g}^{-1}$ ) on ESCs. The reaction mixture comprised 50 vol.% CH<sub>4</sub> and 50 vol.% CO<sub>2</sub>. The corresponding apparent activation energies ( $E_{a, \text{app}}$ , kJ/mol) for each sample for the (D) CO production, (E) H<sub>2</sub> production and (F) H<sub>2</sub>O production are presented in the bar charts. Differential conditions.

The catalytic-kinetic measurements under various CH<sub>4</sub> and CO<sub>2</sub> partial pressures were carried out under differential conditions with gas flows between 150 and 200 cm<sup>3</sup>/min. The electrode was Ni/GDC with a loading of 2.5 mg/cm<sup>2</sup>. The effect of CH<sub>4</sub> and CO<sub>2</sub> molar fractions on the catalytic rates of H<sub>2</sub>, CO and H<sub>2</sub>O formations at 750, 850 and 900 °C is shown in **Figure 3**.



**Figure 3.** Steady-state effect of (A),(B),(C):  $CH_4$  molar fraction ( $y_{CH_4}$ ) under fixed  $CO_2$  molar fraction ( $y_{CO_2}=0.506$ ) and (D),(E),(F):  $CO_2$  molar fraction ( $y_{CO_2}$ ) under fixed  $CH_4$  molar fraction ( $y_{CH_4}=0.498$ ) on the (A),(D)  $H_2$  production rate, (B),(E)  $CO$  production rate and (C),(F)  $H_2O$  production rate under OCP conditions. ESC: Ni/GDC ( $2.5 \text{ mg/cm}^2$ ). Differential conditions.

It is observed that the formation rates of  $H_2$  and  $CO$  exhibit a positive order dependence either on  $y_{CH_4}$  or on  $y_{CO_2}$  at 850 and 900 °C. On the other hand, the formation rate of  $H_2O$  exhibits an initially positive and then zero order dependence on  $y_{CH_4}$ , whereas the dependence of  $r_{H_2O}$  on  $y_{CO_2}$  is positive at the same temperatures (850 and 900 °C). At 750 °C the catalytic activity is inhibited towards the production of  $H_2$ ,  $CO$  and  $H_2O$ . In all cases, the  $CO$  formation is higher than  $H_2$  formation due to the fact that  $CO$  is produced both through DRM (Equation 1) and RWGS (Equation 2) reactions. Additionally, under low  $y_{CO_2}$  ( $<0.25$ ) the production of  $H_2O$  through the RWGS reaction is negligible and as a result the produced  $CO$  is derived solely from DRM reaction. In the last case, in this region of  $y_{CO_2} < 0.25$ , the produced  $r_{H_2}$  should be identical with the produced  $r_{CO}$ , which is confirmed (Fig. 3D and E).

## CONCLUSIONS

Overall, the half cell catalytic measurements lead the investigation to the comparison of the electrocatalytic performance of Ni/GDC, 3Au-0.4Mo-Ni/GDC, 3Au-0.5Fe-Ni/GDC, 3Au-Ni/GDC and 0.5Fe-Ni/GDC. In this new series of investigation, the most active catalyst for the  $CO_2$  reforming of  $CH_4$  (Ni/GDC) that is also prone to carbon formation/deposition will be examined versus modified electrodes, which are less active for the main reactions (DRM and RWGS) but at the same time show negligible rates of carbon formation.

## ACKNOWLEDGMENTS

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## REFERENCES

- [1] M.J. Escudero, J.L. Serrano, *Int. J. Hydrogen En.* 44, 36 (2019) 20616-20631.
- [2] I.V. Yentekakis, P. Panagiotopoulou, G. Artemakis, *Applied Cat. B.: Environ.* 296 (2021) 120210.
- [3] D.K. Niakolas, M. Athanasiou, V. Dracopoulos, *et al*, *Appl. Cat. A.: Gen.* 456 (2013) 223-232.
- [4] Ch. Neofytidis, E. Ioannidou, M. Kollia, *et al*, *Int. J. Energy Res.* 44, 13 (2020) 10982-10995.