Au-Mo-Fe-Ni/$CeO_2(Gd_2O_3)$ As Potential Fuel Electrodes For Internal CO_2 Reforming of CH_4 in Single SOFCs

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1. Introduction

Recycling biogas to produce syngas (H_2 + CO) through Dry Reforming of Methane (DRM) has currently attracted resurgent interest. Biogas consists mainly of CH_4 (50-70%) and CO_2 (25-50%) and is widely produced by anaerobic fermentation of biomass [1]. 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, IDRM), which simplifies the SOFC system and reduces the cost [2,3]. When biogas is directly fed to the SOFC fuel electrode at temperatures 750-900 ºC, various catalytic and electrocatalytic reactions may take place simultaneously on the electrode (Eq. 1-7) [4,5].

$$CH_4 + CO_2 \leftrightarrow 2CO + 2H_2 \qquad \Delta H^o_{298} = 247 \text{ kJ mol}^{-1} \qquad (1)$$

$$CO_2 + H_2 \leftrightarrow CO + H_2O \qquad \Delta H^o_{298} = 41 \text{ kJ mol}^{-1} \qquad (2)$$

$$CH_4 \leftrightarrow C + 2H_2 \qquad \Delta H^o_{298} = 75 \text{ kJ mol}^{-1} \qquad (3)$$

The CO_2 reforming of methane (DRM) (Eq. 1) is a strongly endothermic process and therefore high temperatures (typically >750 ºC) are required to achieve high H_2 and CO yields [6]. Moreover, the catalytic Reverse Water Gas Shift (RWGS) reaction (Eq. 2) may run in parallel, resulting in the consumption of valuable H_2 and a decrease in H_2/CO ratio to values lower than unity [7]. In addition, carbon deposition on the electrocatalyst surface due to CH_4 decomposition (Eq. 3) may also occur resulting in progressive electrocatalyst deactivation [8,9]. The CH_4 decomposition (Eq. 3) is favoured at high temperatures (> 600 ºC), whereas at temperatures below 650 ºC carbon deposits are mainly produced by Boudouard reaction ($2CO \rightarrow C + CO_2$) [7-9]. The H_2, CO and C produced, as well as the CH_4 supplied can be electrochemically oxidized by oxygen ions according to Eq. 4-7.

$$H_2 + O^{2-} \leftrightarrow H_2O + 2e^- \qquad \Delta H^o_{298} = -242 \text{ kJ mol}^{-1} \qquad (4)$$

$$CO + O^{2-} \leftrightarrow CO_2 + 2e^- \qquad \Delta H^o_{298} = -283 \text{ kJ mol}^{-1} \qquad (5)$$

$$CH_4 + O^{2-} \leftrightarrow CO + 2H_2 + 2e^- \qquad \Delta H^o_{298} = -37 \text{ kJ mol}^{-1} \qquad (6)$$

$$C(s) + O^{2-} \leftrightarrow CO + 2e^- \qquad \Delta H^o_{298} = -111 \text{ kJ mol}^{-1} \qquad (7)$$

Ni-based ceramic-metal composites with Yttria Stabilized Zirconia (YSZ) and Gadolinia Doped Ceria (GDC or $CeO_2(Gd_2O_3)$) 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_4 reforming, resistance to carbon deposition, and tolerance levels for H_2S compared to Ni/YSZ electrodes [10,11]. Authors attributed this behaviour to the capacity of CeO_2 to store and release oxygen, which favours the CH_4 oxidation and mitigates the carbon deposition [1,12]. 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 [3,13].

In this study the catalytic and electro-catalytic performance, as well as the coking resistance of un-modified and modified Ni/$CeO_2(Gd_2O_3)$ with 3 wt.% Au−0.4 wt.% Mo and 3 wt.% Au−0.5 wt.% Fe electrocatalysts were studied as half and full electrolyte supported cells under internal CO_2 reforming

of CH_4 in single SOFCs, at 750-900 °C. The aim was to elucidate their activity towards the consumption of CH_4, CO_2, the production of H_2, H_2O, CO and the production of carbon, as a function of temperature and the applied current density under a biogas fuel mixture of CH_4/CO_2=1. Additionally, the cells comprising the electrocatalysts as fuel electrodes, 8 mol% Y_2O_3 stabilized ZrO_2 (8YSZ) as electrolyte and $La_{0.6}Sr_{0.4}Co_{0.8}Fe_{0.2}O_{3-\delta}$ (LSCoF) as oxygen electrode were characterized using I-V measurements and Electrochemical Impedance Spectra (EIS) analysis in order to investigate the evolution of the ohmic and polarization resistance values as a reflection of current.

2. Results

The catalytic-kinetic measurements were performed with gas flows in the range of 150-300 cm^3/min, where the reactor was operating under differential conditions with reactants' conversions between 5-20%. In the above gas flow range the reaction rates were found to remain practically constant, which corresponds to the absence of mass transfer limitations. Figure 1 presents the Arrhenius plots for the consumption rates of CH_4 and CO_2, under differential conditions, and the derived apparent activation energies ($E_{a,app}$) for each electrocatalyst. It is observed that the modified electrodes were less active for CH_4 and CO_2 consumption with relatively high $E_{a,app}$ values, compared to unmodified Ni/GDC. According to the literature [14], non-carbon forming CH_4 activation is the rate-determining step at high temperatures for both DRM and decomposition reactions. Furthermore, it is known that CH_4 is activated on metal surface sites (e.g. Ni), whereas CO_2 is mainly activated on support sites (e.g. GDC) in the vicinity of dispersed metal particles or/and on the metallic sites [7]. In the presented study the calculated $E_{a,app}$ for Ni/GDC is 63 kJ/mol for CH_4 activation, which coincides with the $E_{a,app}$ for CH_4 dissociation on Ni (1 1 0) and Ni (1 1 1) [15].

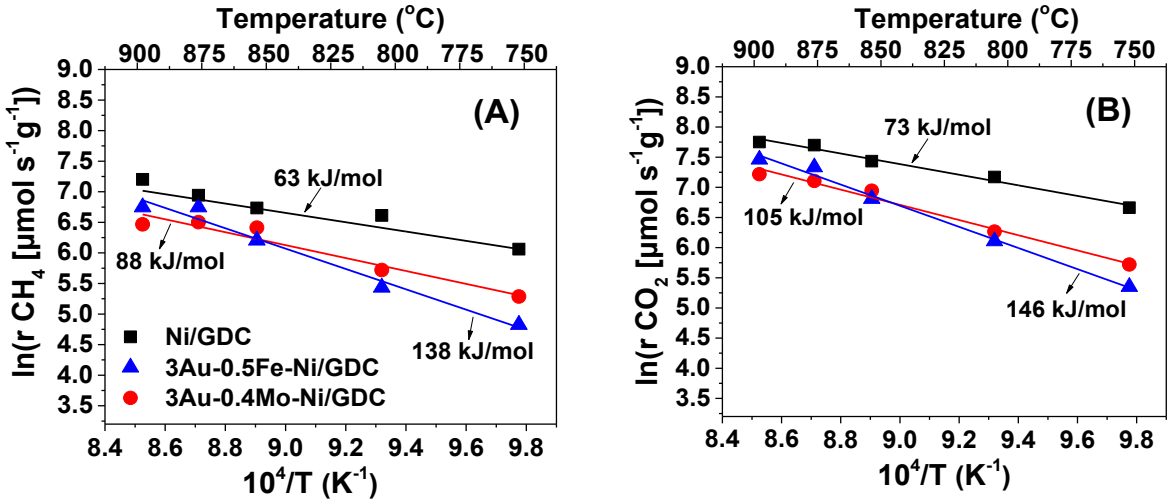

Figure 1. Arrhenius plots of the inherent consumption of (**A**) CH_4 and (**B**) CO_2 rates as a function of temperature (750-900 °C). The corresponding apparent activation energies ($E_{a,app}$, kJ/mol) are embedded. Open circuit potential and differential conditions under the mixture of 50 vol.% CH_4−50 vol.% CO_2. F_{total} is varied, 150-300 cm^3/min. Electrode mass ~6 mg/cm^2.

Furthermore, according to the catalytic measurements, the modified 3Au-0.5Fe-Ni/GDC and 3Au-0.4Mo-Ni/GDC electrodes were less active for H_2 and CO production, but at the same time were less prone to carbon formation, compared to Ni/GDC.

Figure 2 shows the characteristic i-V curves of the SOFCs comprising Ni/GDC, 3Au-0.5Fe-Ni/GDC and 3Au-0.4Mo-Ni/GDC as anodes, under a mixture of CH_4/CO_2=1, without dilution in a carrier gas, at 900 and 850 °C. Specifically, the cell with 3Au-0.5Fe-Ni/GDC exhibited the best performance, at both temperatures, since it provided in a wider range of current density at the same applied potential, compared to the other cells. In addition, the cell with 3Au-0.4Mo-Ni/GDC performed better than that with Ni/GDC, but worse than that with 3Au-0.5Fe-Ni/GDC. Another interesting observation is the effect of temperature on the performance, confirming that the highest temperature promoted faster kinetics, which is reflected on the higher performance of the cells and the lower slopes in the i-V curves.

It should be remarked that the cell with Ni/GDC exhibited the worst electrocatalytic performance for the IDRM process, compared to the cells with the modified electrodes, despite its higher DRM catalytic activity. This may be related to the different structural properties of Au-Mo and Au-Fe modified Ni/GDC electrodes. For this purpose, detailed physicochemical measurements are currently in progress, focusing on the changes of bulk and surface properties of the electrodes.

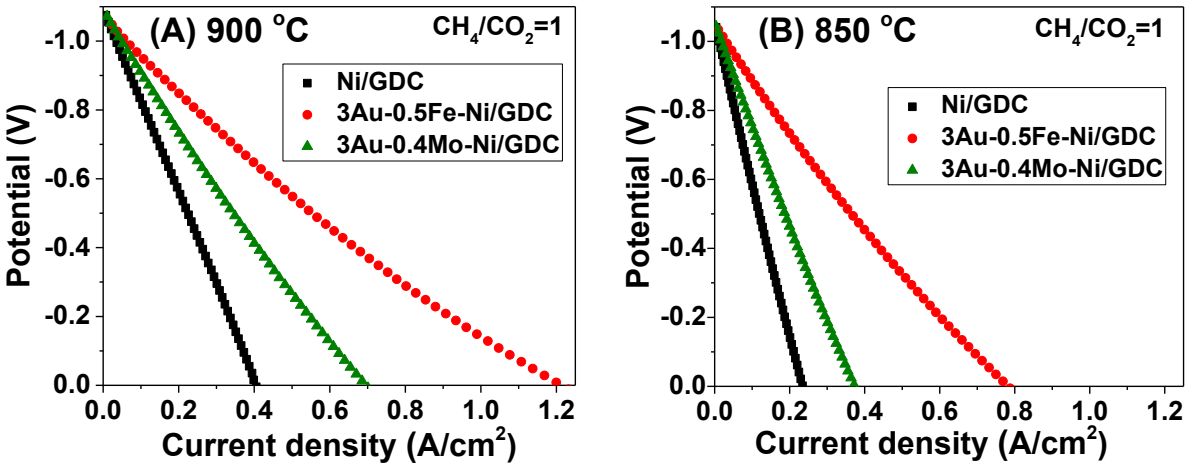

Figure 2. Polarization (i-V) curves at (**A**) 900 ºC and (**B**) 850 ºC for ESCs comprising Ni/GDC, 3Au-0.5Fe-Ni/GDC and 3Au-0.4Mo-Ni/GDC as fuel electrodes. IDRM conditions under a mixture of 50 vol.% CH_4−50 vol.% CO_2. $F_{total,\ in}$ = 50 cm^3/min.

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