

Synergistic interaction of Au-Mo modification on Ni/GDC for H₂O Electrolysis in SOECs

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INTRODUCTION

Water electrolysis at temperatures above 500 °C, with steam, using Solid Oxide Electrolysis Cells (SOECs) is a promising and fast growing technology. SOECs have identical configuration with Solid Oxide Fuel Cells (SOFCs) but reverse operation. The latter relation is quite advantageous compared to low temperature technologies, because SOECs can be built based on the significant SOFCs development, which has seen a significant research. Specifically, novel modified Ni-based fuel electrodes are continuously being processed for fuel cell (H₂/C_s: Natural Gas, Biogas) and electrolysis (H₂O, CO₂ and H₂O+CO₂) applications with improved performance and stability of the state-of-the-art Ni-based electrodes.

The present study examines the effect of Au-Mo modification on the electrochemical and physicochemical characteristics of Ni/GDC for H₂O electrolysis conditions in a single SOEC. Comparative electrocatalytic measurements with I-V curves and Electrochemical Impedance Spectra (EIS) analysis are presented in the range of 800-900 °C between electrolyte supported cells that comprise a Ni/GDC, a 3wt.% Au-Ni/GDC and a 3wt.% Au-3wt.% Mo-Ni/GDC steam/hydrogen electrode, by applying different pH₂O/pH₂ ratios.

Different structural and activity properties were observed for each cermet, where the cell comprising the Au-Mo-doped electrode exhibited the best electrochemical performance. This improvement can be ascribed to the formation of a surface Ni-Au-Mo solid solution, which causes weaker interaction of H₂O and of the resulting adsorbed O_{ads} species with the modified cermet. The outcome is an electrode with a lower degree of surface oxidation and increased “three phase boundaries” length, where the charge transfer and electrode processes are enhanced for the H₂O electrolysis reaction.

EXPERIMENTAL

The modified 3wt.% Au-NiO/GDC and 3wt.% Au-3wt.% Mo-NiO/GDC cathode powders were prepared via the Deposition - Precipitation (D.P.) or Deposition - Co Precipitation (D.CP.) methods. The commercial NiO/GDC cermet (65wt.%NiO-35wt.%GDC, Marion Technologies) was used as the support and the precursors were the H₂AuCl₄ or/and (NH₄)₆Mo₇O₂₄ (Sigma-Aldrich) solutions. Full details about synthesis can be found elsewhere^[1,2]. After filtering, the precipitate was dried at 110 °C for 24 h. All dried powders were calcined at 600 °C for 90 min and a part of them at 1100 °C for 75 min. The former batch was used for the preparation of pastes, which is described below. The batch at 1100 °C was used for the characterization of the samples. In this way, the prepared catalysts were studied at similar thermal stress as the calcined electrode-electrolyte assemblies.

The single electrolyte-supported cells comprised circular shaped planar electrolyte (8YSZ)-supported membranes manufactured by Kerafol with a diameter of 25 mm and thickness of 150 μm. The anode and cathode electrodes were deposited by means of the screen printing technique. The loading of the examined Au-Mo-modified NiO/GDC cathodes was ~10 mg/cm² with 1.8 cm²

geometric surface area and a thickness of $\sim 20 \mu\text{m}$. The anode (O_2) side was a porous $\text{La}_{0.6}\text{Sr}_{0.4}\text{Co}_{0.8}\text{Fe}_{0.2}\text{O}_{3-\delta}$ (LSCoF) (provided by SOLIDpower) and the final loading was also $\sim 10 \text{ mg/cm}^2$. Furthermore, an adhesion layer of GDC, with 5 mg/cm^2 loading, was used between the LSCoF electrode and YSZ electrolyte in order to overcome the thermal and chemical mismatch of the above materials. After the screen printing of the electrode functional layers, the cells were calcined at $1150 \text{ }^\circ\text{C}$ with a heating and cooling ramp rate of $2 \text{ }^\circ\text{C/min}$. Finally, the electrolyte-supported cells were attached on a YSZ tube and sealed airtight with glass sealing material.

The electrocatalytic experiments were carried out in galvanostatic mode in the temperature range of $800\text{--}900 \text{ }^\circ\text{C}$ under H_2O electrolysis conditions by applying different $p\text{H}_2\text{O}/p\text{H}_2$ ratios. Particularly, H_2O was introduced in the system in the form of steam. Prior its evaporation, liquid H_2O was circulated by means of a pressurized liquid H_2O vessel, which is connected to a mass flow controller. All lines and valves were heated at $160 \text{ }^\circ\text{C}$ to avoid H_2O condensation. Ni and Pt meshes were used as current collectors on the cathode and anode side, respectively. The evaluation of the electrochemical performance of Ni/GDC, 3Au-Ni/GDC and 3Au-3Mo-Ni/GDC cathodes, in single SOECs, was based on the recording of Current - Potential curves and simultaneous Electrochemical Impedance Spectra (EIS) characterization, which were carried out by using an AUTOLAB potentiostat/galvanostat, model PGSTAT302N with serial number: 84693. Specifically, the EIS were recorded in galvanostatic mode at various current densities and $p\text{H}_2\text{O}/p\text{H}_2$ ratios with an amplitude of 20 mA , in the frequency range between 100 kHz to 20 mHz . Other details regarding the experimental parameters are mentioned in the corresponding sections and/or figures.

RESULTS

The electrocatalytic measurements for the H_2O electrolysis reaction were performed by using YSZ electrolyte supported cells (ESCs), with a two electrode configuration. In all cases the cathode feed was diluted in $30 \text{ vol.}\%$ He and the anode feed was pure ($100 \text{ vol.}\%$) O_2 . Simultaneous EIS measurements were performed in an attempt to record and investigate the electrochemical effect of the H_2O electrolysis reaction conditions and of the occurring processes on the ohmic (R_{ohm}) and polarization resistance (R_{pol}) of the modified cathode electrodes. R_{ohm} is the sum of ohmic losses, including the contribution from the: (i) ionic resistance due to the O^{2-} transport through the YSZ electrolyte, (ii) electron resistance of the electrodes and specifically the part that can be electrochemically inactive and (iii) contact resistances of the connecting wires. R_{pol} is mainly related to the occurring electrode processes^[3,4] and combines both activation and concentration polarizations. Specifically, the latter type is attributed to diffusion processes (i.e. diffusion of steam through the pores of the electrode to the triple phase boundary (t.p.b.) and diffusion of H_2 out of the t.p.b.) and to the conversion of steam at the fuel electrode^[1].

Figure 1 depicts the comparison of performance between cells comprising Ni/GDC (**1A**), 3Au-Ni/GDC (**1B**) and 3Au-3Mo-Ni/GDC (**1C**) as cathodes for the H_2O electrolysis process, under the reaction mixture of $7\text{vol.}\%$ H_2 – $63\text{vol.}\%$ H_2O – $30\text{vol.}\%$ He. It is observed that the Au-Mo-modified electrode exhibited significantly better electrochemical performance compared to Au-Ni/GDC and Ni/GDC electrodes, mainly at temperatures above $850 \text{ }^\circ\text{C}$. Specifically, at $900 \text{ }^\circ\text{C}$ the cell with the 3Au-3Mo-Ni/GDC cathode showed lower overpotential losses with approximately double rates for the H_2O electrolysis reaction, at the same potential, in comparison to 3Au-Ni/GDC and 3-times higher rates compared to the cell with Ni/GDC.

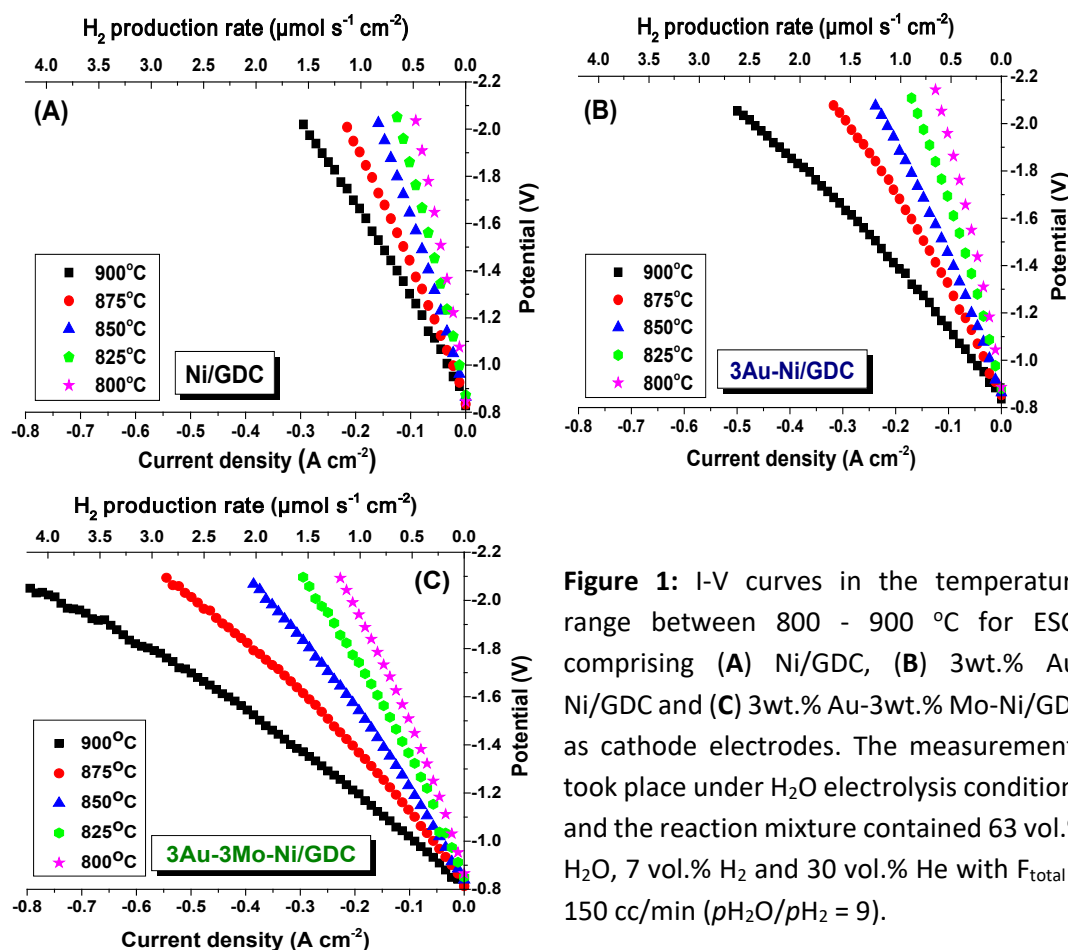


Figure 1: I-V curves in the temperature range between 800 - 900 °C for ESCs comprising (A) Ni/GDC, (B) 3wt.% Au-Ni/GDC and (C) 3wt.% Au-3wt.% Mo-Ni/GDC as cathode electrodes. The measurements took place under H₂O electrolysis conditions and the reaction mixture contained 63 vol.% H₂O, 7 vol.% H₂ and 30 vol.% He with $F_{\text{total}} = 150 \text{ cc/min}$ ($p_{\text{H}_2\text{O}}/p_{\text{H}_2} = 9$).

The effect of the applied $p_{\text{H}_2\text{O}}/p_{\text{H}_2}$ ratios (at $T = 900 \text{ }^\circ\text{C}$) on the R_{ohm} and R_{pol} values of the examined cells is presented in **Figure 2**. The comparison takes into account two requirements. The first is that the impedance spectra on each sample were recorded under similar values of applied current. The second is that the comparison is focused on EIS that lie within the same I-V region. It is observed that in all cases the R_{ohm} and R_{pol} values are relatively high. Specifically, for the ohmic resistance there is a great variety of values being reported in literature, where for similar type of YSZ-supported cells at $900 \text{ }^\circ\text{C}$ they are close to $0.9 \text{ Ohm}\cdot\text{cm}^{[2-3,5]}$ and lower for State of the Art (SoA) systems^[6]. The increased values in our case are mainly ascribed to the fact that the examined cells and the experimental setup are not SoA^[3].

In particular, the combination of various factors such as: (i) the relatively thick ($150 \text{ }\mu\text{m}$) YSZ electrolyte, (ii) the fact that the cathode electrode comprised only the studied functional layer, without other layers (e.g. adhesion and/or current collection layer), (iii) the low calcination temperature of the cathode electrode ($1150 \text{ }^\circ\text{C}$)^[6] and (iv) the additional contact resistances from the experimental setup, resulted in increased R_{ohm} and R_{pol} . Thus, considering that the examined cells had a two-electrode configuration, there was an effort to minimize the effects from the O₂ electrode. The latter was achieved by (i) trying to optimize the performance of the anode, using close to 10 mg/cm^2 of LSCoF as an optimum loading and (ii) by keeping constant reaction conditions on the O₂ side^[3].

Another interesting remark is that the Au-Mo-modified cell exhibited quite lower R_{ohm} and R_{pol} values, compared to the binary electrode and the unmodified Ni/GDC. Specifically, the lower ohmic resistance values may be connected to the suggested synergistic interaction between Au-Mo-Ni, which is realized via the formation of a ternary solid solution^[2,7,8,9] in the reduced form of the sample. The latter effect may induce better structural properties to the ternary electrode, resulting in higher electronic conductivity and this remark is currently under further investigation.

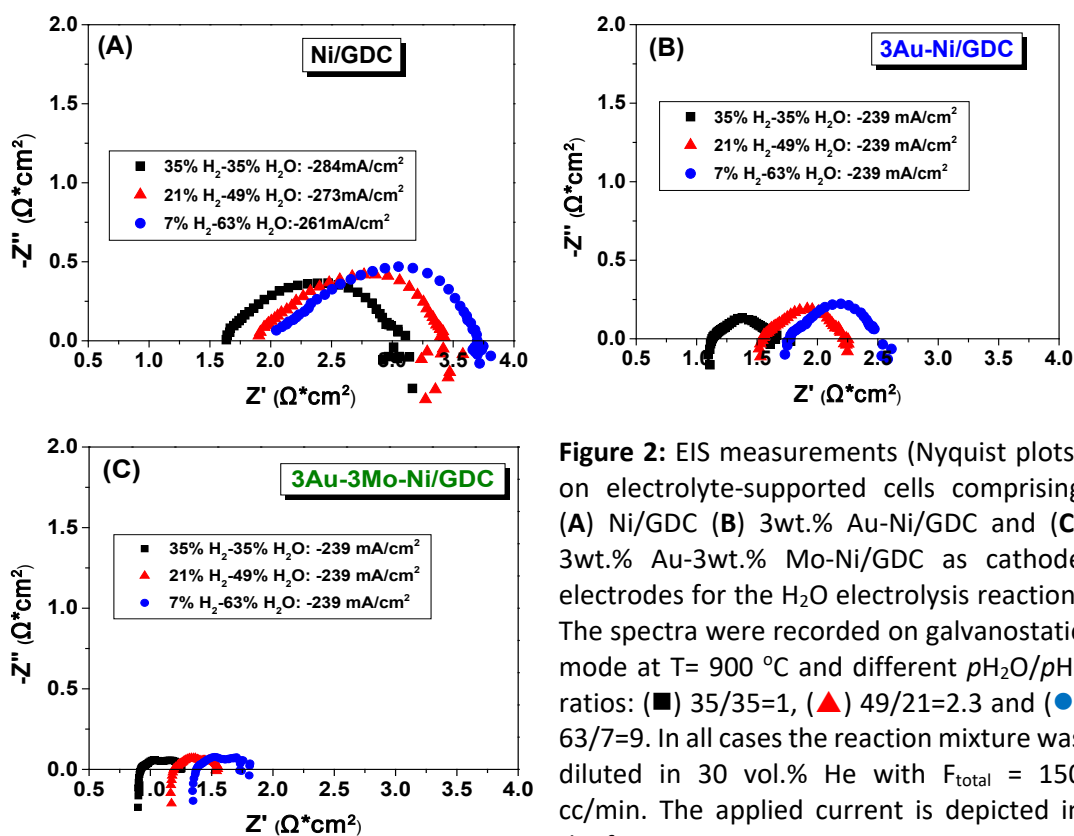


Figure 2: EIS measurements (Nyquist plots) on electrolyte-supported cells comprising (A) Ni/GDC (B) 3wt.% Au-Ni/GDC and (C) 3wt.% Au-3wt.% Mo-Ni/GDC as cathode electrodes for the H₂O electrolysis reaction. The spectra were recorded on galvanostatic mode at T= 900 °C and different p_{H_2O}/p_{H_2} ratios: (■) 35/35=1, (▲) 49/21=2.3 and (●) 63/7=9. In all cases the reaction mixture was diluted in 30 vol.% He with $F_{total} = 150$ cc/min. The applied current is depicted in the figure.

In regards to the R_{pol} , **Figure 2** shows that by increasing the applied p_{H_2O}/p_{H_2} ratio, there was increase in the polarization resistance of the cells comprising Ni/GDC and 3Au-Ni/GDC. Specifically, in the case of the cell with 3Au-Ni/GDC, the R_{pol} increment is less and overall the absolute R_{pol} values (**Figure 2B**) are lower, compared to Ni/GDC (**Figure 2A**). However, the most interesting observation is related to the cell with the 3Au-3Mo-Ni/GDC cathode, where the polarization resistance (**Figure 2C**) is almost not affected and overall the absolute R_{pol} values are quite lower, compared to the cells comprising Ni/GDC and 3Au-Ni/GDC.

The above differences can primarily explain the quite better electrochemical performance of the cell with the ternary cathode. For the time being, this improvement can be ascribed to the synergistic effect of Au-Mo-Ni solid solution which may result in (i) improved structural properties (i.e. enhanced electron conductivity) and (ii) higher re-oxidation resistance, which is connected to the inhibited activity of this sample for the catalytic H₂O dissociation reaction.

CONCLUSIONS

The presented study deals with SOEC experiments for the H₂O electrolysis reaction on ESCs, comprising Ni/GDC and Au-Mo-modified Ni/GDC as cathodes. It is presented that the ternary Au-Mo-modified electrode showed significantly better performance, especially at T = 850 °C and above. In particular, it exhibited the lowest overpotential losses having approximately double rates for the H₂O electrolysis reaction, at the same potential, in comparison to 3Au-Ni/GDC and 3-times higher rates than the cell with Ni/GDC. One of the most interesting observations is related to the effect of the increased p_{H_2O}/p_{H_2} ratio to the polarization resistance values. Simultaneous EIS analysis showed significantly lower R_{pol} values for the 3Au-3Mo-Ni/GDC electrode, which were also the least affected by increasing the partial pressure of H₂O.

The improved electrochemical performance of the cell with the ternary cathode can be attributed to the synergistic interaction between Au-Mo-Ni, which is realized via the formation of a ternary solid solution, in the reduced form of the electrode. This synergy is reflected on the polarization

resistance (R_{pol}) values of the sample, whereas it seems to induce (not presented in this manuscript) weaker interaction of H_2O_{ads} and of the O_{ads} species. These effects result in a surface and an interface with lower degree of oxidation and increased (t.p.b.) length. Overall, in the case of the binary Au-Ni/GDC, but most characteristically for the ternary 3Au-3Mo-Ni/GDC cathode and at temperatures higher than 850 °C, the charge transfer and electrode processes are significantly enhanced towards a more efficient H_2O electrolysis reaction.

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