

ENHANCED RSOC OPERATION OF Ni/GDC BY MEANS OF Fe-Au-DOPING: ELECTROCHEMICAL INVESTIGATION FOR THE OPTIMUM Fe-Au-CONTENT

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ABSTRACT

Nowadays, electricity is mainly produced by fossil fuels. However, when fossil fuels are combusted to produce power, they release large amounts of carbon dioxide and other greenhouse gases into the atmosphere, contributing in this way to global warming. To address the latter problem, there is a growing emphasis on transitioning to cleaner and more sustainable energy fuels such as green hydrogen (H₂). In this context, a reversible solid oxide cell (rSOC) is an electrochemical device that can produce green H₂ or use it as a fuel to produce electricity. rSOCs are highly versatile and suitable for energy storage applications due to their ability to operate under both fuel cell and electrolysis modes with high energy efficiencies. The most common electrocatalysts for these systems (i.e. Ni/YSZ and Ni/GDC), despite their high activity, are prone to oxidation, which results in Ni coarsening, agglomeration, depletion/migration, and ultimately de-activation. In this regard, the addition of small amounts of transition metals can significantly improve the performance and stability of the Ni-based fuel electrode ^[1].

The present study deals with the modification of commercial Ni/GDC by dispersing Fe and Au. The aim was to find the optimum value of Fe/Au ratio, to achieve high electrocatalytic activity and stability under rSOC operation and low production cost. With this in mind, several electrocatalysts were synthesized, where Au varied between 0.5 and 3 wt.% and Fe was kept at 0.5 wt.% and evaluated under reversible operation (i.e. rSOC cycles) at 900-800 °C. The electrochemical characterization was conducted by means of i-V curves and Electrochemical Impedance Spectroscopy (EIS) analysis. The experimental data showed that the modification of NiO/GDC with Fe and Au decreased the polarization and ohmic resistance and increased the performance, especially under electrolysis conditions. The enhancing effect of the Fe-Au-modification was also observed on stability measurements cells under rSOC operation.

KEYWORDS: Fuel cell, water electrolysis, hydrogen, rSOCs, high temperature

INTRODUCTION

Hydrogen is believed to be the connecting link between renewable energy technologies and green energy economy as a great energy carrier. Hydrogen “stores” electricity during times of abundant power supply and then reacts with oxygen to release the stored renewable energy and stabilize the grid. Nowadays, the majority of hydrogen production (>90%) is based in steam reforming of methane. This reaction produces greenhouse gas emission (CO₂), thereby posing environmental issues ^[2]. The electrolysis of H₂O combined with renewable electricity for hydrogen production is a

promising path to a decarbonized energy network.

Solid Oxide Cells (SOCs) present numerous advantages that stem from their functioning conditions and building materials. Firstly, operating at high temperatures (up to 600 °C) favors thermodynamics, which results in higher efficiencies, compared to the low temperature technologies, and improves the reaction kinetics [3]. SOC offer versatile and efficient energy conversion solutions across various fuel types such as, syngas, biogas, natural gas and hydrogen for power generation in stationary applications, such as residential and commercial electricity generation, as well as in remote or off-grid locations or even transportation. Additionally, these systems can operate bi-directionally. In the Solid Oxide Electrolysis (SOE) mode, hydrogen is produced via Power-to-Gas process (P2G) and the same module can operate in the reverse mode as a Solid Oxide Fuel Cell (SOFC) and produce power, via Gas-to-Power process (G2P) [4]. It has been demonstrated that a SOFC system can achieve low electrode overvoltages even for high current densities. Furthermore, under the SOE operation an electrical-to-hydrogen conversion efficiency above 100% is feasible [3]. In the fuel electrode of a SOEC steam combines with electrons from the external circuit to form hydrogen gas and negatively charged oxygen ions (O^{2-}) (Eq. 2). The oxygen ions pass through the solid oxide electrolyte and react at the oxygen electrode to form oxygen molecules and release electrons (Eq. 3). The produced hydrogen then, can be the feed supply in the fuel electrode for the SOFC mode. The temperature operation range is identical with the SOE mode. Gaseous oxygen is inserted in the oxygen electrode and is reduced to oxygen ions consuming two electrons. The ions migrate through the electrolyte to the fuel electrode where they react with hydrogen to generate electrons. The electrons involved in the reactions are transferred from the electrodes through an outer circuit connected to the cell, thus giving electrical power [5].



State-of-the-art electrocatalysts for the fuel electrode are Ni-based materials such as Nickel-Yttria-Stabilized Zirconia (Ni/YSZ), Nickel-Gadolinia-Doped Ceria (Ni/GDC) and Ni-Scandia-Stabilized Zirconia (Ni/ScSZ), due to their low cost and high activity under the oxidizing conditions during electrolysis and the reducing environment at fuel cell mode. Nevertheless, Ni-based electrodes have many drawbacks as Ni is oxidized easily in the presence of water resulting to Ni migration, agglomeration and/or volatilization [6]. The deactivation of the fuel electrode can also be promoted at high temperatures and increased current density values (aside the operation). Previous studies of our group have proven that the modification of these electrodes particularly of the Ni/GDC electrocatalyst with non-noble and noble compounds enhance the performance and the stability of the electrode [6]-[7]. Especially, modified 0.5 wt.% Fe-Au-Ni/GDC electrodes have shown enhanced and more stable performance in comparison to commercial NiO/GDC catalyst under rSOC operation. With this in mind, the aim of this research is the investigation of the optimum Au content for the fuel electrode.

METHODOLOGY

Preparation of powders and cells: X wt.% Au-NiO/GDC and 0.5 wt.% Fe-X wt.% Au-NiO/GDC (where X = 0.5, 1, 3 wt.%) were prepared via Deposition (Co-)precipitation method by using the commercial NiO/GDC (65 wt.% NiO-35 wt.% GDC, Marion Technologies) powder as the support and the metal precursors HAuCl₄ and Fe(NO₃)₃·9H₂O (Sigma-Aldrich). The electrolyte-supported single fuel cells

consisted of a circular shaped disk ZrO_2 (8%mol Y_2O_3) or 8YSZ electrolyte (Kerafol) with 25 mm diameter and 150 μm thickness. The fuel and oxygen electrodes were deposited on 8YSZ disks via screen-printing. The slurry was composed of a proper amount of powder, terpineol (Sigma-Aldrich) as solvent and polyvinyl butyral (PVB, Sigma-Aldrich) as binder. The electrodes were calcined at 1150 $^\circ\text{C}/2$ h with a heating/cooling ramp rate of 2 $^\circ\text{C}/\text{min}$. The resulting loading of the fuel electrode layer was fixed at 10-12 mg cm^{-2} . The oxygen electrode was $\text{La}_{0.6}\text{Sr}_{0.4}\text{Co}_{0.8}\text{Fe}_{0.2}\text{O}_{3-\delta}$ (LSCoF, SolydEra) with a loading of 10-12 mg cm^{-2} . In the oxygen side, an adhesion layer of GDC10 (10-12 mg cm^{-2}) was applied and pre-calcined at 1300 $^\circ\text{C}/2$ h (2 $^\circ\text{C}/\text{min}$), to overcome the thermal and chemical mismatch between LSCoF-8YSZ.

Electrocatalytic measurements: Each electrocatalyst constituted the only functional layer of the fuel electrode. Ni and Pt meshes (Alfa-Aesar) were used as current collectors on the fuel and oxygen side, respectively. Temperature was set at 900 $^\circ\text{C}$ and the cell was subjected to reversible cycling, where it was switched from SOFC mode (i.e., 100 vol% H_2 , with $F_{\text{total}} = 150 \text{ cm}^3 \text{ min}^{-1}$) to SOE (reaction mixture 63 vol% $\text{H}_2\text{O}/7$ vol% H_2 , $p_{\text{H}_2\text{O}}/p_{\text{H}_2} = 9$ with $F_{\text{total}} = 150 \text{ cm}^3 \text{ min}^{-1}$) and vice versa. This procedure was applied for 3 consecutive cycles operating for 3 h in each mode in the form of short "screening" rSOC tests for 900-800 $^\circ\text{C}$ with 50 $^\circ\text{C}$ step. Polarization i-V curves were recorded, by using a potentiostat/galvanostat, (Autolab PGSTAT30), between the open circuit potential and 0 V, at a scan rate of 5 mV s^{-1} and a step potential of 10 mV. Subsequent Electrochemical Impedance spectra (EIS) were measured in galvanostatic mode at various current densities, with an amplitude that was each time 10% of the applied current, in the frequency range from 100 kHz to 20 mHz.

RESULTS AND DISCUSSION

The effect of reversible operation after three rSOC cycles is presented in **Figure 1**. The I-V curves correspond to the comparison between the 1st and the 3rd rSOC cycle. It is observed that all the cells with the modification with Fe-Au exhibited enhanced performance in comparison to Ni/GDC as they are provided in a wider range of current density values at the same applied potential range. Specifically, in the case of the samples with low Au content (0.5 wt.% and 1 wt.%) the performance is rather similar, and they seem more stable during the 3rd cycle in comparison to the electrode with the high Au content (3 wt.%).

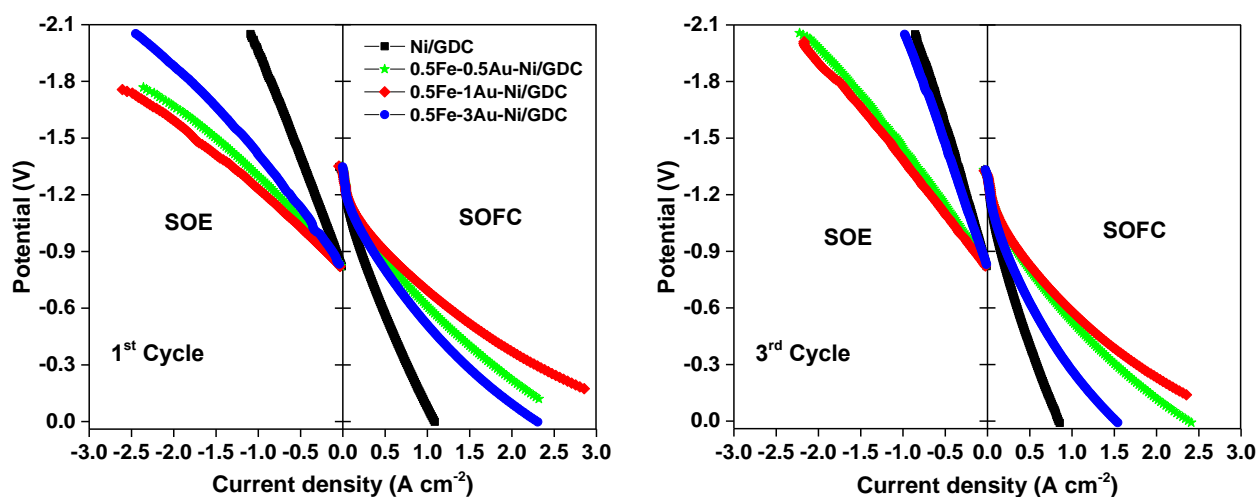
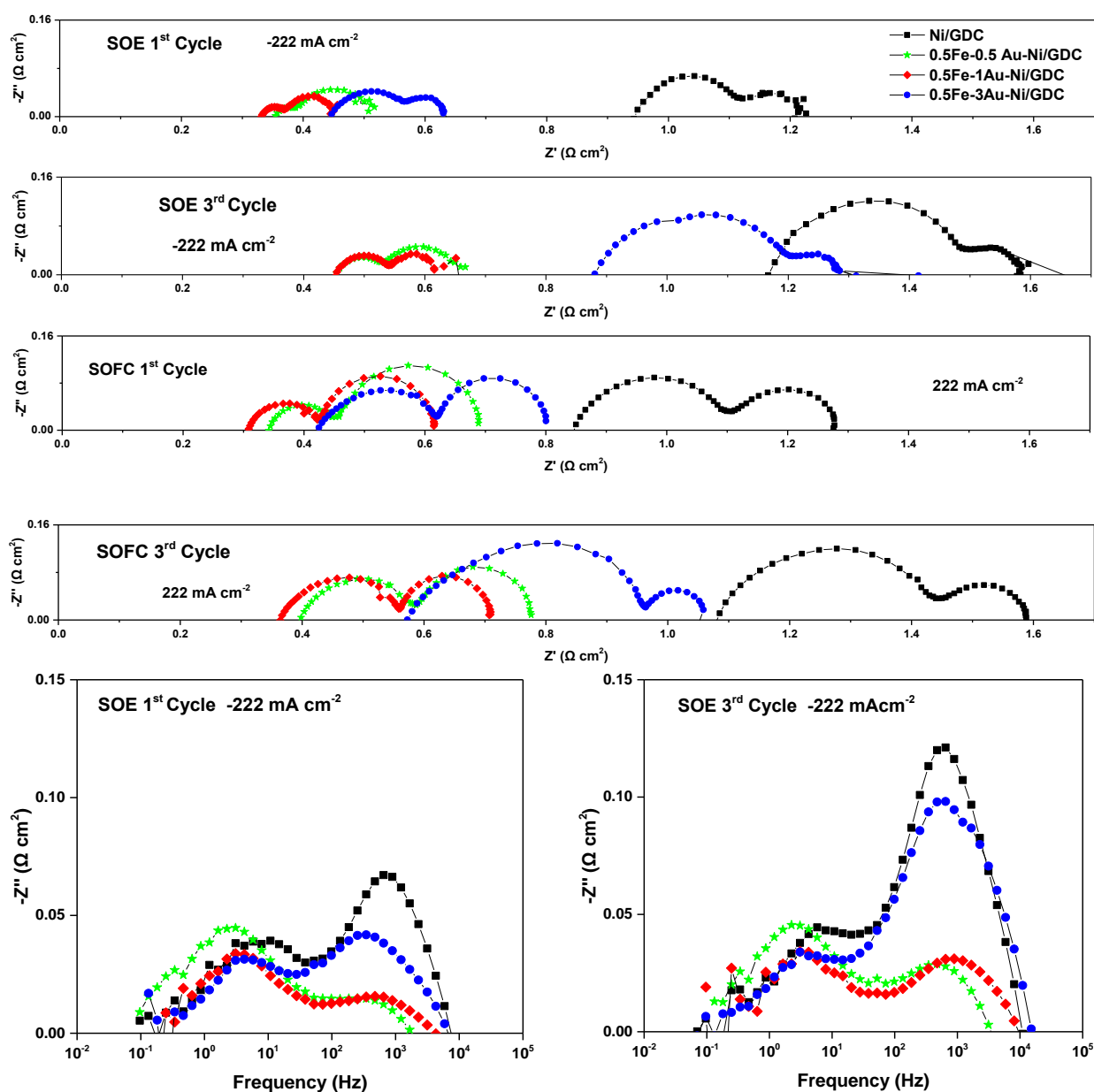


Figure 1. Polarization I-V curves at $T = 900 \text{ }^\circ\text{C}$ for ESCs comprising: (-■-) Ni/GDC, (-★-) 0.5Fe-0.5Au-Ni/GDC, (-◆-) 0.5Fe-1Au-Ni/GDC and (-●-) 0.5Fe-3Au-Ni/GDC, as fuel electrodes. The presented measurements took place during the 1st and 3rd rSOC cycle.

In order to further elucidate the synergy of Fe-Au-Ni transition metals on the electrochemical processes of the cells, EIS analysis was performed. More specifically, the effect of modification on

the ohmic and polarization characteristics of the cells is presented on the Nyquist ($-Z_{im}$ vs. Z_{re}) and Bode plots (**Fig. 2**). In the Nyquist plots, the ohmic resistance, R_{ohm} , as well as the polarization resistance, R_{pol} , are determined by the intersections of the Z_{re} axis with each Nyquist plot at high and low frequencies respectively. It is obvious that under SOE operation the cells with 0.5Fe-1Au-Ni/GDC and 0.5Fe-0.5Au-Ni/GDC exhibit the lowest R_p and R_{ohm} resistances at the beginning of the experiment. This behavior remains the same till the end of the cycles, while the corresponding values for the cell with Ni/GDC are negatively affected. Based on previous publications of our research group [1], [8], the electrodes that exhibit low resistances, they also have high electrocatalytic activity. Furthermore, after the 3rd cycle under fuel cell mode the modified electrodes seem to be more stable in comparison to the commercial Ni/GDC electrode which exhibited high R_{pol} and R_{ohm} resistances. Moreover, their superior electrocatalytic performance is confirmed from the semi-logarithmic plots of the imaginary EIS part ($-Z''$) as a function of the frequency (**Fig. 2**), where under SOE operation decreased capacitance values are observed, especially in the intermediate frequencies region.



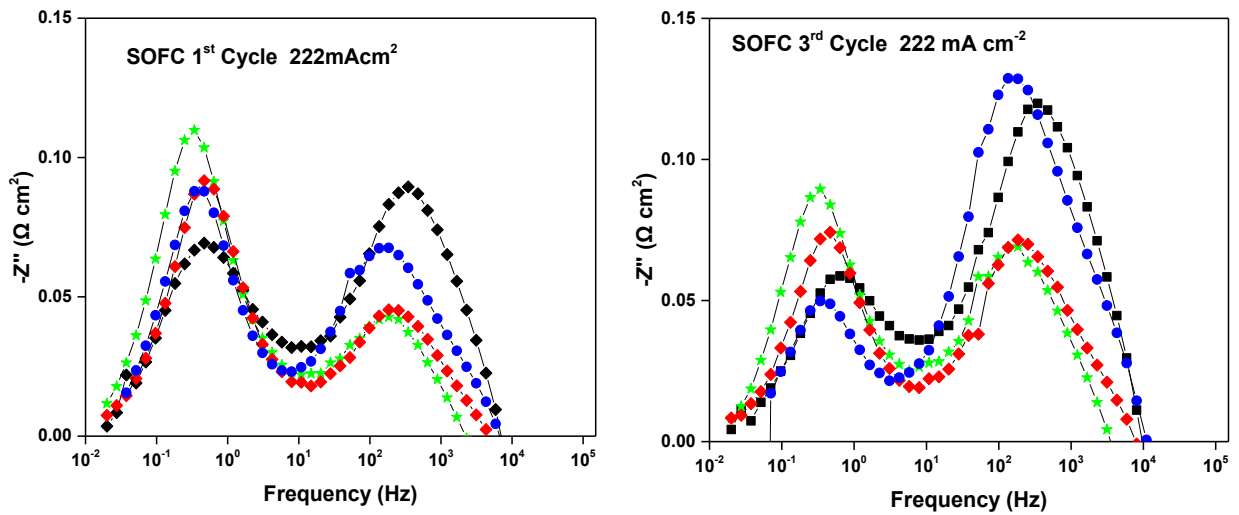
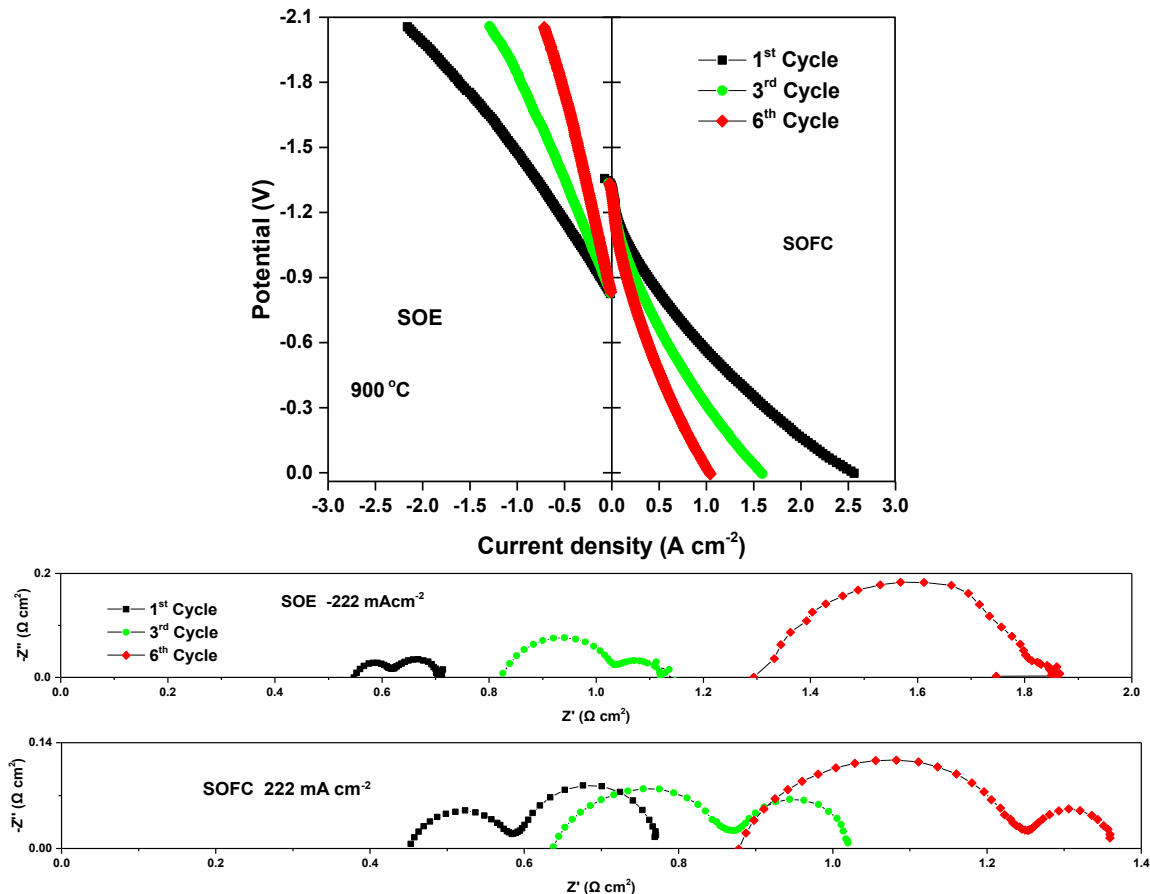


Figure 2. EIS measurements (Nyquist and Bode plots) on ESCs comprising: (-■-) Ni/GDC, (-★-) 0.5Fe-0.5Au-Ni/GDC, (-◆-) 0.5Fe-1Au-Ni/GDC and (-●-) 0.5Fe-3Au-Ni/GDC, as fuel electrodes. The presented spectra were recorded on galvanostatic mode at $T = 900\text{ }^{\circ}\text{C}$.

To further validate the above results, a new experimental procedure has been conducted. The latter focused on the investigation of the effect of more reversible cycles in the sense of Accelerated Stress Tests (AST). In this respect, a new series of electrolyte-supported cells were tested from SOFC mode to SOE and vice versa, where the cells were subjected to 6 rSOC cycles. The diagrams in **Figure 3** show that the cell with Ni/GDC fuel electrode under AST rSOC operation presented higher degradation in the SOE mode, than in the SOFC, especially after the 3rd cycle. The objective of the on-going study is to test the modified cells under these intense (AST) conditions and to further clarify the beneficial effect of the Fe-Au modification.



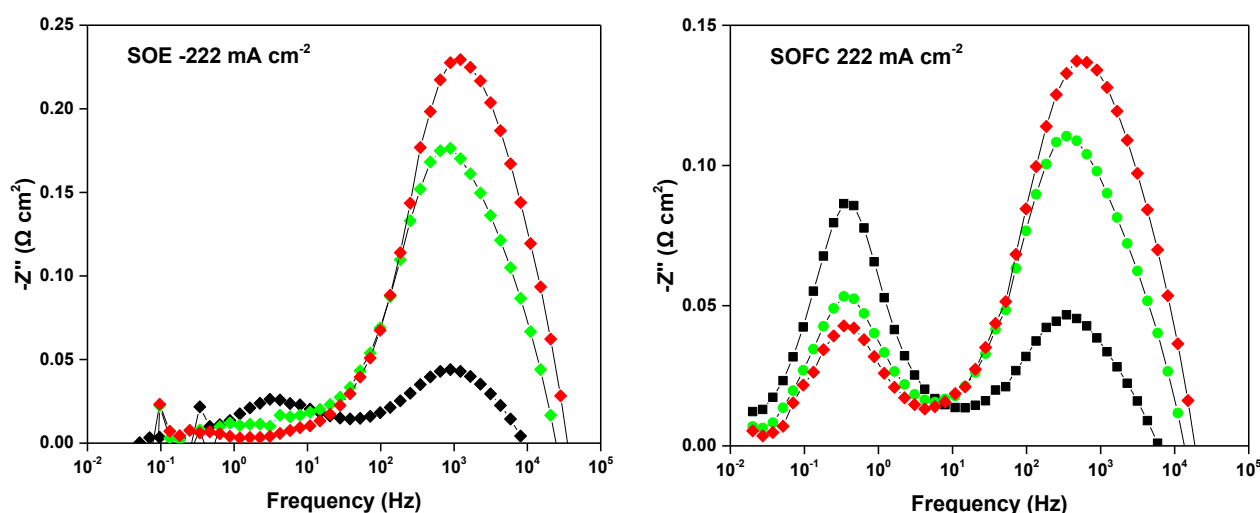


Figure 3. Polarization I-V curves and EIS measurements (Nyquist and Bode plots) at $T= 900\text{ }^{\circ}\text{C}$. The fuel electrode is the commercial Ni/GDC, the oxygen electrode LSCF and the electrolyte 8YSZ.

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