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A Simple Approach to make the Commercial Solid Oxide Fuel Cells Flexible in the Use of Fuels

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A Simple Approach to make the Commercial Solid Oxide Fuel Cells Flexible in the Use of Fuels – CK-3L05

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Abstract

In this paper, we propose a simple approach consisting in the use of a coating layer on a commercial SOFC in order to increase its fuel flexibility. Using the same CO₂-laser-cut cell, we compared the I-V curves and impedance spectra (EIS) of four experiments. Three different ceramics (NiCu-CGO, NiFe-CGO, and NiCo-CGO) were evaluated as protective layers for cells fed with dry biogas or bioethanol, with the goal of determining which layer would be most promising. Electrochemical experiments revealed that an additional layer adds resistance to the cell, which negatively affects its performance. A slight decrease in maximum performance was observed when the coated cells were fed H₂. However, power density was not significantly different from the bare cell at potentials between 0.7 and 0.8 V, which are generally considered acceptable. Additionally, such an approach improved the effectiveness of cells in using simulated biogas and ethanol as demonstrated by I-V curves and EIS analysis. As shown in the test results, NiCo-CGO provided the highest power density of 0.56W cm⁻² at 0.6V. However, all the cells with protective layers performed significantly better than the bare cell in the dry biofuel tests.

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Keywords

Green Deal; Renewable fuel; SOFC; Cermet; Ni-alloy

1. Introduction

Increasing energy efficiency is one of the EU's main priorities in the current global situation. One only needs to recall that candles were replaced by incandescent lamps and then by LEDs to grasp this concept. Despite minor energy consumption, this improved the quality of lighting in each house. This simple example demonstrates the need to develop advanced technologies and understand their physico-chemical mechanisms in order to address Europe's current energy challenges. Solid Oxide Fuel Cells (SOFCs), which can currently boast an electrical efficiency of 50% or higher depending on the operating conditions[1-3], may provide a solution to the current energy crisis in the EU by addressing the power generation problem, particularly for residential purposes[4-7]. Developed in the 1980s, this technology relies on ceramics and requires high temperatures to work effectively[8]. Today, this technology has reached a maturity level where it is capable of operating continuously at intermediate temperatures (650 to 800 degrees Celsius)[9-14] for a long period of time (over 90000 hours)[15]. Several difficulties still exist when using organic fuels (like biogas or ethanol) derived from biomass, mainly due to nickel being used as an anode[16-18]. It is unlikely to be feasible to replace this material at least in the short- to medium-term due to the cost involved in changing the production chain[19], but a pre-catalytic layer directly attached to the anode may help to mitigate degradation mechanisms that occur during the conversion of organics to electricity[20]. In the event this approach becomes feasible, it may be a better alternative since it does not require any hardware complexity in the SOFC-based system[21-23] and may improve overall efficiency by maintaining cell production costs. Despite the need for further optimization, this research group has been able to design cells with a pre-catalytic layer that are adaptable to most SOFC and SOEC applications[24-

32]. The present work reviews the electrochemical results achieved in this field over the past few years by adopting Ni-based alloy coating layers [25, 33, 34] and discusses the possibility of applying pre-layers to commercial SOFCs for power generation using biofuels.

2. Experimental

By using a CO₂ laser, large planar commercial cells were cut into button cells for electrochemical experiments. This method provided us with a convincing method for comparing electrochemical results obtained with a variety of coating layers. Our findings here come from examining cells coated with a class of materials consisting of cermets (ceramic and metal alloy mixture) prepared by an original synthesis procedure called “oxalic method” [35] developed to enhance the alloying effect between Ni and metals with different electronic, reticular distance and/or allotropic structures.

Coating the cells is a necessary step in the preparation of tests. Spray coating and a subsequent thermal treatment of up to 1100°C are required (except for NiCu-based cermet, which is treated at a temperature of 1000°C). This treatment is a compromise between obtaining a sufficient interface connection between the coating layer and the support (i.e., the anode) while preventing excessive coarsening of the particles.

Measurements were conducted using a test bench produced by Greenlight Innovation, which consists of two alumina tubes pressing on the test cells in the middle. In order to seal the gas, two thermiculite o-rings are used, while gold grids connected to four gold wires are pressed against the electrodes to ensure contact with the cell and to measure electrochemical properties of interest (i.e. open circuit voltage (OCV), polarization curve (I-V curve), impedance spectroscopy (EIS), durability test). In commercial cells, nickel oxide anodes (anode supporting cells) are used, so reducing them to metallic nickel requires a preliminary conditioning procedure. To obtain a stable OCV before conducting electrochemical experiments, the procedure typically requires 3 hours at 800°C with 10% He in H₂.

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Following this, the cell was fed with a much larger amount of dry fuels than expected for faradic conversion. The fuels included hydrogen, biogas (CH₄:CO₂=60:40 vol%), and ethanol with Ar carriers. Generally, an experiment like this is considered acceptable for examining the resilience of cells to the use of dry organic fuels.

3. Results

The following results include those obtained with bare cells of the same stock. To begin, we compare in figure 1 the performance achieved when feeding H₂. In the bare cell, a maximum power density of 535 mW cm⁻² was achieved at 0.5 V. In general, cell voltages below 0.7 V are not considered feasible for practical purposes, while conditions between 0.8 and 0.7 V are preferred[36, 37]. By examining the polarization curve of the NiCu-CGO-coated cell, it can be seen that the cell had an improved ohmic resistance. It resulted from the limited annealing temperature (1000 °C) used for creating adhesion between the coating layer and substrate. When NiFe-CGO was deposited as a coating layer, the OCV decreased by about 70 mV and the ohmic resistance increased, which both affected the performance of the cell. An OCV of 140 mV lower was observed in the cell coated with NiCo-CGO than in the bare cell, but the ohmic constraint remained substantially the same. The differences in OCV could be attributed to a different sealing grade of the cells, since o-rings were used to ensure sealing. Our results indicate that in the range of cell potential between 0.8-0.7 V , the cells in this study displayed limited performance differences ranging between 0.26 and 0.32 W cm⁻². Therefore, a coating layer designed to minimize the risks associated with organic fuels will not adversely affect the performance of a commercial cell operating at 0.7-0.8V on hydrogen.

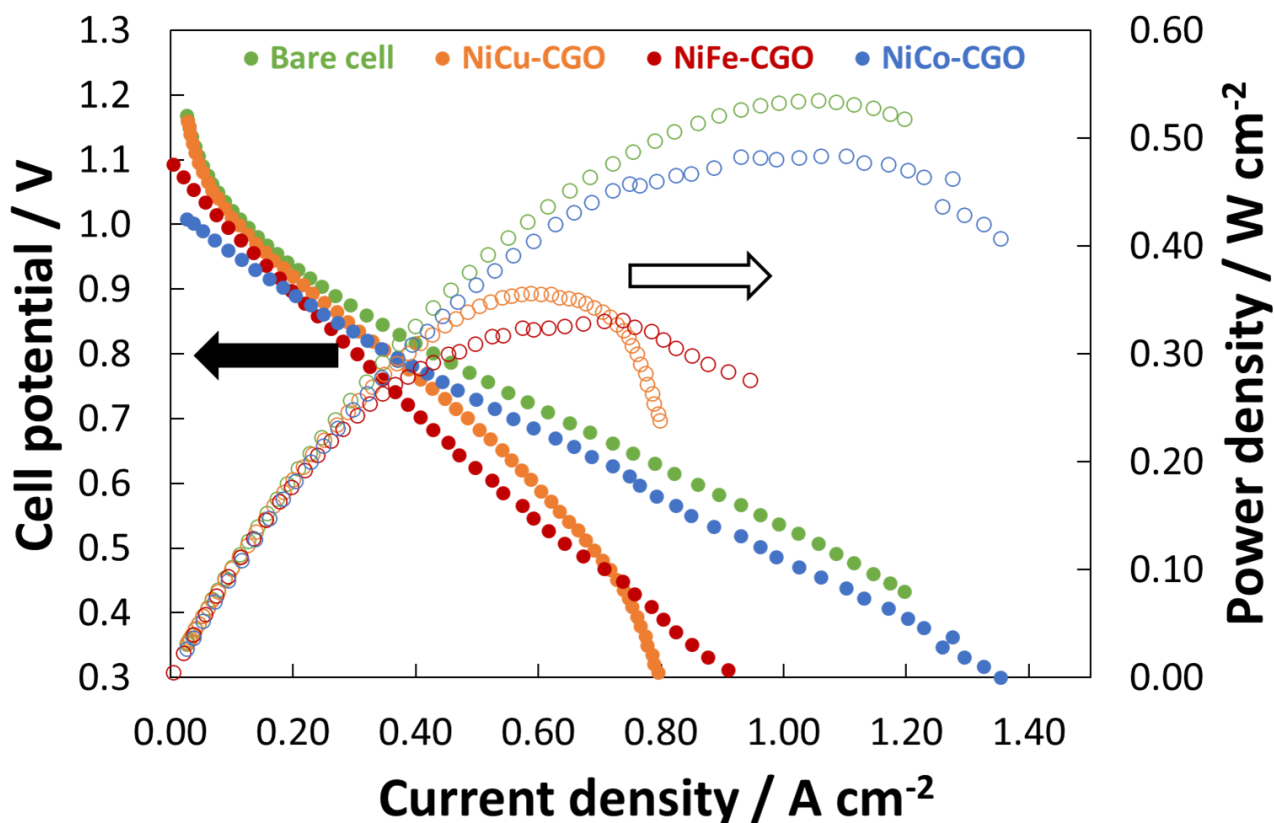
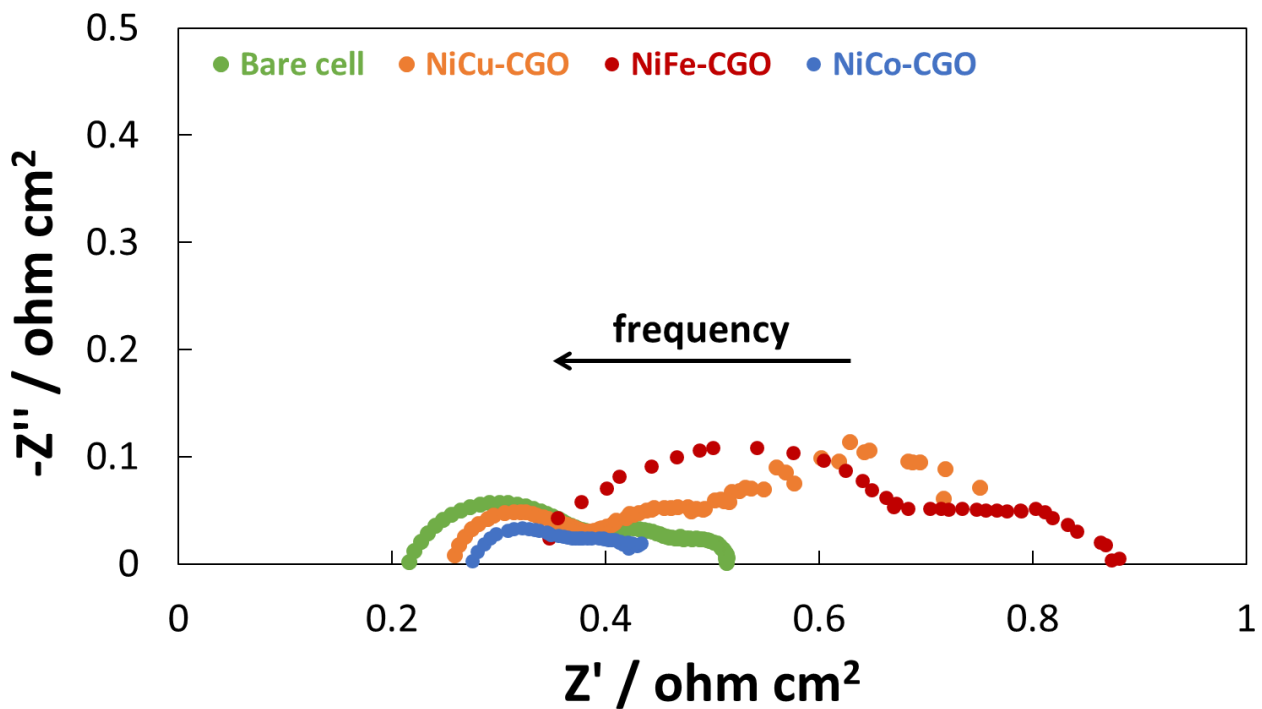


Figure 1. Comparison of polarization curves of four cells fed with dry H₂ and measured at 800 °C.

Next, the impedance spectra collected immediately after the polarization curves reported in figure 1 were compared. A cell potential of 0.8V was used for all measurements. According to figure 2, adding a coating layer improved the series resistance (R_s), which represents the intercept of spectra with the x-axis at high frequency. In an ideal cell, the R_s is due to the electrolyte's resistance. In practice, all layers might have unoptimized electronic conductivity constraints, which affects the R_s values in each cell's spectrum. Accordingly, an increase in R_s was observed when additional layers were added. This can be explained in part by the different redox properties of each metal, in part by the unoptimized interface between the coating layer, and in part by the unoptimized electronic percolation into the added layer. A total of three apparent semicircles were observed, attributed to mechanisms

1 occurring at the anode and cathode, while adding a coating layer did not significantly improve the
2 complexity of the spectra. It is also worth noting that the total resistance R_t (intercept of the spectrum
3 with the x-axis at low frequency) was strongly affected by the coating layer. In particular, NiCu- and
4 NiFe-based cermets increased the R_t , reflecting a greater difficulty of electrochemical mechanisms,
5 while the use of NiCo-CGO improved the electroconversion efficiency into the cell.
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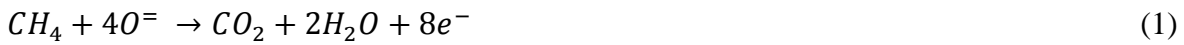


43 **Figure 2.** A comparison of the impedance spectra of four cells fed with dry H_2 and measured at 800 °C and
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52 Upon feeding the anode with biogas, a significant change in the characteristic I-V curves was
53 observed. As Figure 3 illustrates, the behavior of the unprotected cell becomes quite unstable, and the
54 OCV drops to 0.93 V as a result of a reduced tendency towards the mechanisms involving the oxidation
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of CH₄ from biogas, which can occur by means of an improbable direct electrooxidation reaction

(eq.1):



Meanwhile, the large probable mechanism involves the catalytic dry reforming of CH₄ to produce CO and H₂ (eq. 2):



Afterwards, CO or H₂ can be electrooxidized (eqs 3-4):



There are, however, other parallel mechanisms that can occur in the anodic chamber as well. Methane reforming is one of them (eq. 5):



however the large flux used in this experiment compared to the fuel used makes this highly unlikely (evaluated using the faradaic formula).

A further reaction that may impact the cell is methane cracking (eq. 6):



which Ni has a high tendency to exhibit [38]. Accordingly, an alloy formed by combining another metal with Ni and the addition of doped ceria may be effective in suppressing this reaction[39].

Combined with the oxygen spillover properties of doped ceria[40], these materials work because of their different electronic properties. In spite of this, the extent of alloying between Ni and the other metal affects coking suppression (eq. 6). In fact, as reported in the literature, interatomic distance plays an important role in determining methane's coking[41].

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3 In the same way, a loss of cell potential of 0.9 mV was observed in the NiCo-CGO coated cells. The
4 cell still exhibited a fairly stable curve with no activation constraints. In addition, ohmic constraints
5 impacted the slope of the curve until about 330 mA cm⁻². Nevertheless, at higher current densities,
6
7 diffusion control determined a rapid decline in electrochemical efficiency. A positive feature was that
8 it achieved 240 mW cm⁻² at 0.7 V, which is not too far from practical voltages for such devices.
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15 In contrast to the above described experiments, the NiCu- and NiFe-based cermets coated cells
16 showed higher OCVs. In both cases the OCV was over 1.02 V, there was relatively limited activation
17 control, and the slopes were the same at least up to 400 mA cm⁻². After this current density, the curve
18 of cell coated with NiCu-CGO was controlled by diffusion, whereas this effect was not observed in
19 the NiFe-CGO-coated cell. Consequently, the highest power density for biogas (i.e. 252 mW cm⁻²)
20 was achieved with NiFe-CGO-protected cells at 0.45 V and this is not a positive feature for this cell.
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30 As said above, voltages below 0.7 V are not considered practical. Furthermore, low potential
31 generally leads to extensive reoxidation of Ni, which could be detrimental to the cell[42].
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35 Consequently, this comparison showed that all of the cells had poor or absent activation control
36 towards reactions occurring in the anode chamber. Despite their different I-V curves, their power
37 densities (i.e. 0.17-0.20 mW cm⁻²) in the range 0.8-0.7 V were similar. Additionally, bare cells had a
38 very unstable I-V curve that was highly susceptible to decay. As a result, after measuring the
39 impedance spectra described in the next figure, this cell was immediately fed with dry ethanol to
40 ensure a subsequent test with another fuel (i.e. ethanol).
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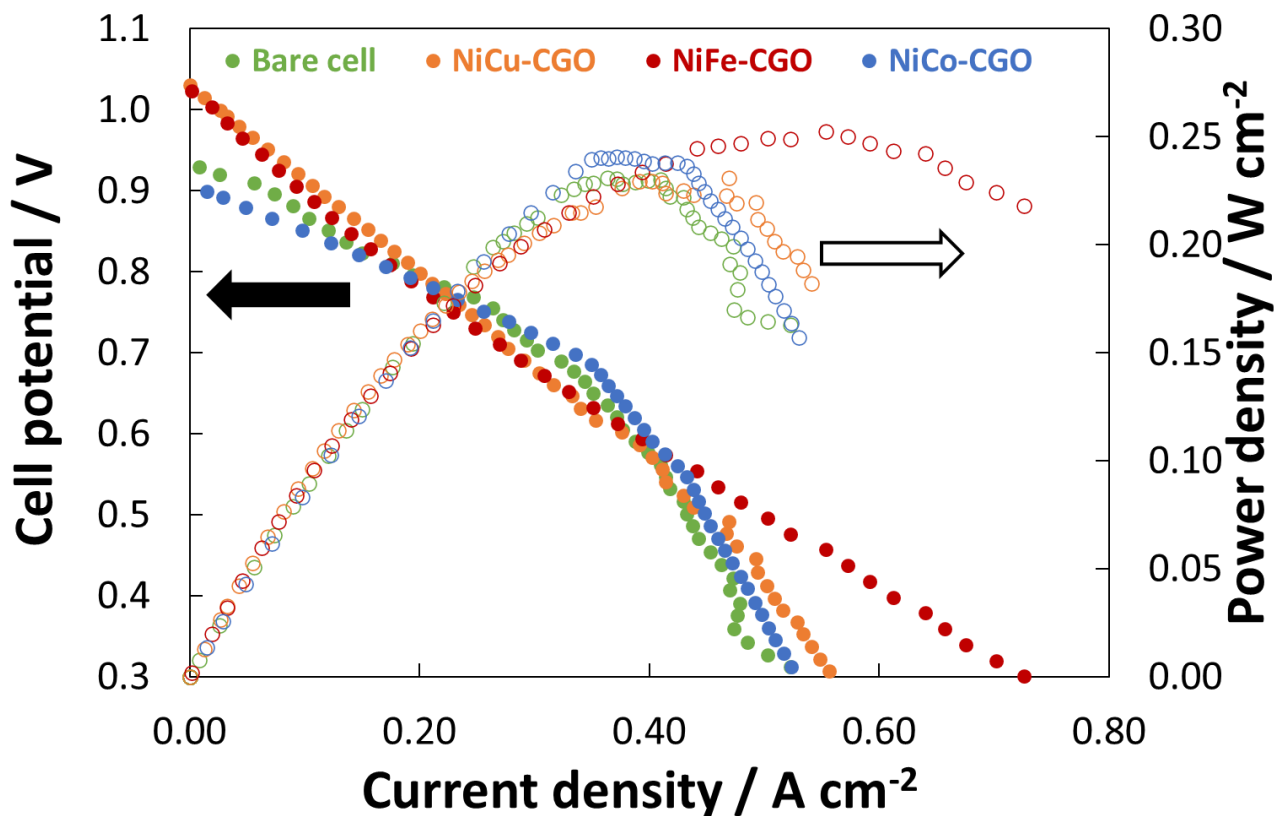


Figure 3. Comparison of polarization curves of four cells fed with dry biogas and measured at 800 °C.

EIS spectra in biogas (figure 4) showed an opposite trend to those in H₂ (figure 2). The NiCo-CGO-coated cell showed lower R_s and R_t than the bare cell, while the NiCu- and NiFe-coated cells exhibited higher R_s, as we observed in H₂-fed cells. Further, the R_t of the bare cell was comparable to that of NiCu- and NiFe-coated cells. The scattering observed in the EIS spectrum of bare cells further demonstrates the vulnerability of Ni-based anodes to dry biofuel use and the potential risk of soot formation.

Additionally, biofuel tests produced EIS consisting of at least three semicircles. Comparing these spectra with those measured in H₂, the semicircle at high frequency reflects the cathodic reaction (i.e. reduction of oxygen), whereas the two other semicircles (at intermediate and low frequencies) are attributed to anodic reactions that have become larger due to the complex mechanisms involved in methane conversion.

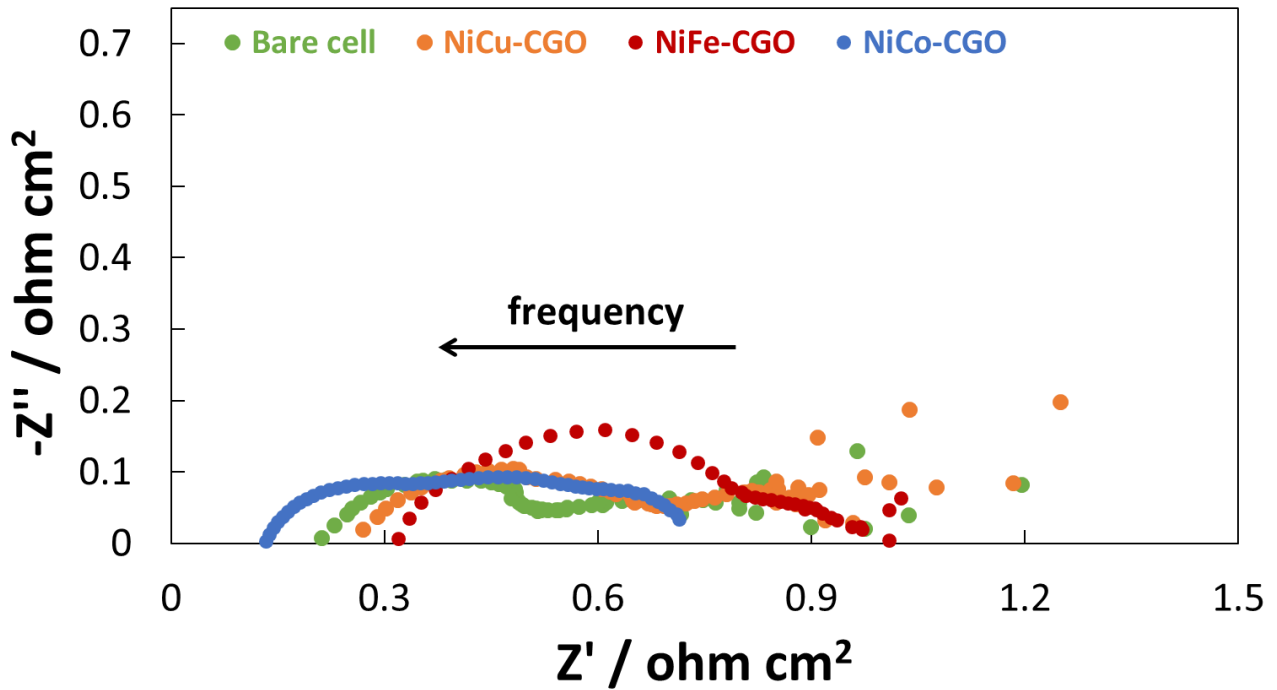


Figure 4. A comparison of the impedance spectra of four cells fed with dry biogas and measured at 800 °C and 0.8 V.

In the final testing, dry ethanol-fed cells were electrochemically analyzed to determine their characteristic performance curve. Although the noisy I-V curve for the bare cell is evident in figure 5, it was much better than the biogas curve (figure 3) in terms of OCV (1.04 V for ethanol vs. 0.93 V for biogas), current collected at 0.3 V (0.8 A cm⁻² for ethanol vs. 0.50 A cm⁻² for biogas) and diffusive constraints (ethanol had a slope change at 0.41 V whereas biogas had a slope change at 0.66 V).

Considering the I-V curve features, we can conclude that ethanol is more reactive than methane, since it contains an O-atom, which facilitates its oxidation, and produces a higher current density after complete oxidation. It can be achieved by direct and complete electrooxidation:



There is also a high probability of partial electrooxidation reactions:





Pyrolysis and catalysis can also degrade ethanol into a variety of secondary products



CO and H₂ can then rapidly react into the functional layer of anode through electrochemical reactions

3 and 4.

In comparison to biogas, the cells coated with NiCu- and NiFe-based cermets showed a significant reduction of OCV (i.e. around 0.94 and 0.96 V in ethanol and 1.02 V in biogas). However, their characteristic I-V curves did not show a significant activation control, whereas these were mainly influenced by ohmic constraints. Starting at 700 mA cm⁻², only a slight diffusive mechanism affected the curve of the NiCu-CGO coated cell.

In spite of this, NiCo-CGO coated cells showed the highest performance. It was mainly because of the higher OCV value (i.e. 1.13 V) and the milder sloped curve compared to other cells in the figure.

Even so, we observed that at current densities exceeding 1 A cm⁻², the I-V curve was strongly affected by diffusive constraints. Most likely, this is due to the difficulty of approximating reactants to the triple phase boundaries (TPB) of the functional layer, or to the difficulty of removing products from the same reactive solid sites. With its characteristic I-V curve, this NiCo-CGO coated cell achieved a power density of 0.56W cm⁻² at 0.6V, indicating high potentialities. Furthermore, when using

ethanol as fuel, the behaviour of four cells in the range of practical potentials differs significantly, indicating the NiCo-CGO coating is more effective.

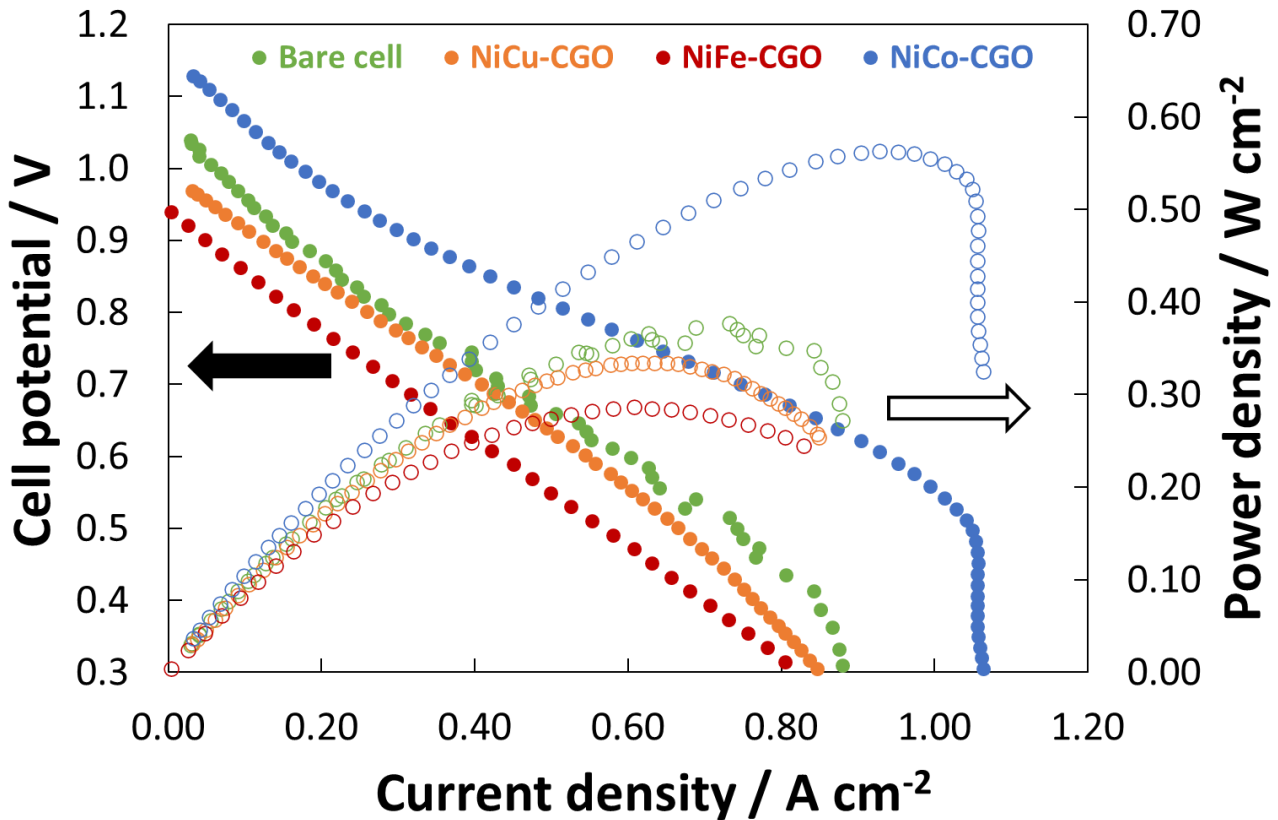


Figure 5. Comparison of polarization curves of four cells fed with dry ethanol and measured at 800 °C.

All the cells fed with ethanol reduced their R_s , except the bare cell, whose EIS remained scattered throughout the entire frequency range. According to figure 6, this behavior could be due to an increased conductivity of electrolyte during experiments at 0.8 V, although soot formation could also increase conductivity. As well, some differences in the gas sealing of the cell and the gold contacts with electrodes cannot be excluded and are within the expected error range, which could lead to differences in spectra. Nevertheless, these differences were largely a result of the coatings used in the anode. The bare cell spectrum remained quite scattered due to the poor electrocatalytic properties of

1 Ni towards dry organic fuel conversion. This was confirmed by the high carbon deposits observed in
2 the cell and in the tube after the experiment had been closed[24, 43]. In the case of the cell coated
3 with NiCu-CGO, the EIS spectrum was quite scattered only at low frequencies domain, possibly due
4 to the complexity and oxidation kinetics of the heaviest intermediates. Generally, when the frequency
5 is low, the reactions involve more complex intermediates (e.g. aldehydes, acids, alkenes) than
6 electrooxidation reactions involving CO and H₂[44].
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15 Regarding the other experiments, the cell coated with NiFe-CGO showed an EIS spectrum dominated
16 by the semicircle at intermediate frequencies, indicating an anodic process and reflecting the poor
17 redox property of Fe.
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23 Nevertheless, the NiCo-CGO-coated cell showed the highest resistance contraction. A reduction of
24 R_s at 0.09 ohm cm² was observed in this case, and a particularly depressed second semicircle to
25 indicate highly efficient electrooxidation of H₂ e CO, while the semicircle at a low frequency
26 indicated that the electrooxidation kinetics of semiproducts are not as huge as those reported in figure
27 6 for the other cells.
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36 As observed after shutdown, no carbon deposits were visible on the surface of the coated cells or in
37 the reactor's alumina tube [25, 33, 45]. Consequently, a protective layer can be considered an effective
38 method for feeding dry biofuels directly to commercial cells.
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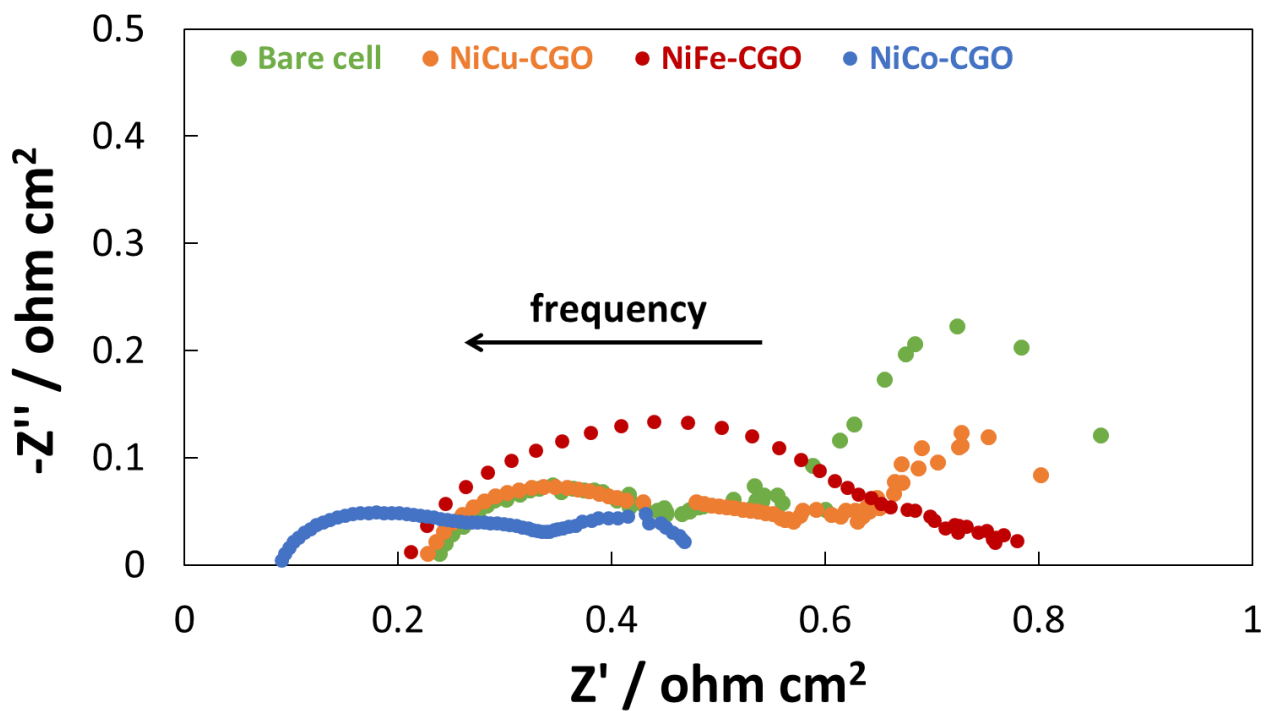


Figure 6. A comparison of the impedance spectra of four cells fed with dry ethanol and measured at 800 °C and 0.8 V.

A summary of the electrochemical test data is presented in Table 1. The data pertains to the R_s and R_t of impedance spectra measured at 0.8 V with H_2 , biogas, and ethanol as well as the power density of each characteristic curve at 0.8 V. These values are depicted in figure 7 as a graphical representation. Apart from the bare cell, whose series resistance increased slightly with the complexity of fuel and reactions involved, all other cells showed a reduction in this value, in particular the cell coated with NiCo-CGO, which reached the value of 0.09 ohm cm^2 . A peculiar pattern was observed for the R_t , which reached a maximum with biogas, probably due to the difficulty oxidizing methane in comparison to hydrogen. All cells examined followed this pattern.

With regard to power density, the trend follows R_t , and the only cell performing better than H_2 was the NiCo-CGO coated cell, which showed a power density of 0.41W cm^{-2} .

Table 1. An overview of the most relevant electrochemical data.

	H ₂			BIOGAS			ETHANOL		
	Power density @ 0.8V W cm ⁻²	Rs ohm cm ²	Rt ohm cm ²	Power density @ 0.8V W cm ⁻²	Rs ohm cm ²	Rt ohm cm ²	Power density @ 0.8V W cm ⁻²	Rs ohm cm ²	Rt ohm cm ²
Bare cell	0.34	0.21	0.51	0.15	0.21	1.19	0.23	0.24	0.86
NiCu-CGO	0.28	0.26	0.75	0.16	0.27	1.18	0.21	0.23	0.8
NiFe-CGO	0.24	0.35	0.88	0.14	0.32	1	0.13	0.21	0.78
NiCo-CGO	0.28	0.27	0.43	0.14	0.13	0.71	0.41	0.09	0.47

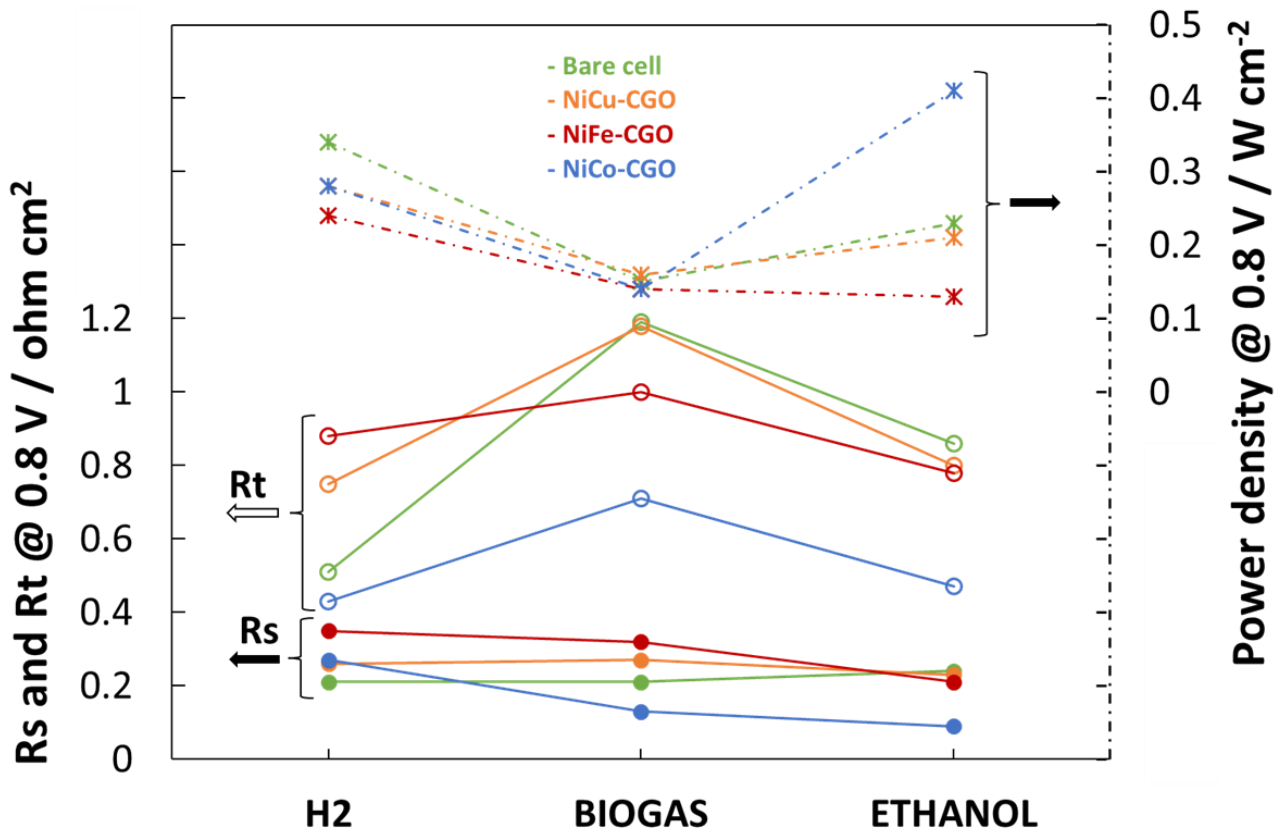


Figure 7. A graphic representation of the most pertinent electrochemical data.

Conclusions

The experiments reported in this paper were designed to demonstrate a feasible approach for increasing the fuel flexibility of SOFCs. Currently, one of the factors preventing the widespread adoption of such devices for residential uses is their need for hydrogen. A fuel processor may provide a technological solution to the use

1
2 of biofuel in SOFCs, but it requires a dedicated temperature and inlet gas control system and generally adds
3 complexity. Therefore, a coating layer protecting the anode of cells from soot formation could simplify the
4 system and improve energy output. Based on the results of the experiments reported in this paper, NiCo-
5 CGO may be deemed a more affordable biofuel coating. In spite of this, the use of protective layers has been
6 shown to be an effective method of increasing acceptance of cells by ensuring that the production chain
7 remains intact.
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30 Provider in a Distributed Grid" granted by MAECI.
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Declaration of interests

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

The authors declare the following financial interests/personal relationships which may be considered as potential competing interests:

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On behalf of the authors


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