

Exploring the Stability of Direct Ethanol Solid Oxide Fuel Cells at Intermediate Temperature

F. C. Fonseca^a, F. Tabuti^a, T. Moraes^a, R. Abe^b, R. M. Guimarães^b, Y. Miura^c, and Y. Fukuyama^c

^a Nuclear and Energy Research Institute, IPEN-CNEN/SP, University of São Paulo, São Paulo, Brazil

^b Nissan do Brasil Automóveis Ltda, R&D Department, Rio de Janeiro, Brazil

^c Nissan Motors Company, Ltd, Nissan Research Center, EV System Laboratory, Yokosuka-shi, Kanagawa, Japan

Anode supported fuel cells were tested in direct (no water added) bioethanol at intermediate temperature (600 °C and 700 °C). The standard fuel cell has reasonable short-term stability under dry ethanol if current is continuously drawn at a minimum fuel utilization factor at 700 °C. However, the YSZ/Ni anode develops carbon deposits as inferred from post fuel cell test analyses and fixed bed steam reforming catalytic tests at 600 °C. Thus, an active catalytic layer with tailored properties for ethanol internal reforming was studied. Initial tests investigated the Ir/gadolinium-doped ceria catalysts previously proven stable at 850 °C. The main results have shown that the catalytic layer has no significant effect on the performance of the fuel cell running under hydrogen. The use of a ceria-based catalytic layer has enhanced the stability of the fuel cell under dry ethanol at 700 °C, but stable operation at 600 °C requires the development of more active catalyst.

Introduction

Direct ethanol SOFC have gained increasing attention in the last decade due to a series of attractive properties of such renewable fuel. Sugar-cane derived ethanol is possibly the most successful example of biofuel with well-developed industries in different continents. An increasing number of countries, such as Brazil and USA, have a wide distribution infrastructure that makes ethanol a readily available fuel. Ethanol SOFC has a great potential for several applications, including as a range extender for electric vehicles as recently demonstrated by Nissan. Nevertheless, to reduce the complexity and cost of fuel cell systems, several studies have aimed at internal reforming taking advantage of the SOFC operating temperature. Nonetheless, critical issues such as the stability of the anodes and thermal stress arising from the endothermic reforming reactions still impose great challenge for the internal reforming in SOFC. As the YSZ/Ni remains the best anode under hydrogen, preserving this component and adding a catalytic layer tailored for the desired fuel is a promising strategy (1-4).

A series of previous studies have demonstrated direct ethanol SOFCs operating with excellent stability for more than 600 hours at 850 °C (5-8). On the other hand, relatively few studies have investigated direct ethanol SOFCs at $T < 800$ °C. Intermediate operating

temperatures facilitate material selection, inhibit thermally activated degradation processes, and allow a fast start of the system. However, critical issues such as the stability of the anode require careful development for stable operation at intermediate temperature (600 - 700 °C). Usually, ethanol steam reforming (SR) in this temperature range demands specific catalysts to avoid the formation of carbon deposits. Therefore, it is necessary to develop stable catalysts that are resistant to carbon formation at intermediate temperature to facilitate the commercialization of the direct ethanol SOFC technology.

The aim of this study is to evaluate the stability of direct ethanol fuel cell and the effect of the catalytic layer in SOFC operating at intermediate temperature (600 - 700 °C).

Experimental

For the direct ethanol SOFC testing we have used anode supported button cells samples (Fuel Cell Materials) with 20 mm diameter. Such samples have standard Ni/yttria-stabilized zirconia anodes, yttria-stabilized zirconia electrolytes and strontium-doped lanthanum cobaltate cathode.

A ceria-based catalyst was synthesized. Gadolinia-doped ceria ($\text{Ce}_{0.9}\text{Gd}_{0.1}\text{O}_{2-x}$, CGO) containing 0.1 wt.% of Ir catalyst was prepared by incipient wetness impregnation technique, using CGO (Praxair, $43 \text{ m}^2\text{g}^{-1}$) and iridium acetylacetonate (Aldrich) in toluene (8, 9).

The SOFC electrochemical tests were performed using an open flange test system (Fiacell) with an Inconel sample holder and a Zahner IM6 electrochemical station. The current collector on the cathode side was a platinum mesh and the anode side used a gold mesh. Gases and ethanol were delivered to the fuel cell by a home-made system controlled by a personal computer. Such a delivery system contains mass flow controllers for gases (H_2 , synthetic air, and N_2) and a sealed stainless-steel bottle for ethanol. The ethanol container is heated with a temperature controller and monitored by a K-type thermocouple for ethanol deliver using N_2 as a carrier gas. The anode side is fed with a heated line kept above ethanol condensation temperature.

For SOFC tests, samples were heated to the anode reduction temperature (T_{red}) defined 100 °C above the target measuring temperature (i.e., $T_{\text{red}} = 800 \text{ °C}$ if maximum measuring $T = 700 \text{ °C}$) with heating rate of 5 °C min^{-1} under N_2 flow on the anode side. When the T_{red} was stable, the N_2 was replaced by H_2 (200 ml min^{-1}) for 1 h. The temperature was decreased to the desired measuring T (600 or 700 °C) and synthetic air was flown on the cathode side (200 ml min^{-1}). The OCV was monitored and both polarization (I-V) curves and impedance spectroscopy (EIS) at OCV measurements were taken under hydrogen. Then, the system was polarized at 0.6 V (or 0.5 V, depending on the measuring temperature and the estimated fuel utilization factor, U_F) and allowed to run under H_2 for ~20 hours during which both I-V curves and EIS data were collected (under polarization). The fuel was changed during a time interval of ~30 min by gradually decreasing the hydrogen flow while ethanol was increased until the fuel cell was running on dry ethanol. The total fuel rate (200 ml min^{-1}) was maintained and ethanol flow rate was set to keep the theoretical number of electrons constant as compared to hydrogen by using the H_2 /ethanol flow ratio = 1/6. Ethanol flow rate was defined by the temperature of the stainless-steel bottle and the

N₂ carrier flow rate. The stability tests under dry ethanol were carried out under constant polarization for up to 200 hours of continuous operation. During the stability test both I-V and EIS data collected. The I-V curves were measured from the polarization potential down to 0.2 V to avoid steam starvation at OCV for the ethanol internal reforming. The EIS data were measured under polarization with ac amplitude of 100 mV from 100 kHz to 0.1 Hz.

Along with the electrochemical testing the studied catalysts were tested for ethanol SR reaction. Ethanol SR was conducted in a fixed bed reactor at 600 °C and 700 °C in a catalytic test bench at atmospheric pressure. Before the reaction, the samples (50 mg) were reduced with pure H₂ (30 mL/min) at 600 °C for 1 h and then purged under N₂ for 30 min. The reactant mixture (2.5% ethanol; 7.5% water, 90.0% nitrogen) was obtained by flowing two N₂ streams (30 mL/min) through each saturator containing ethanol and water separately, which were maintained at the temperature required to obtain the desired H₂O/ethanol molar ratio of 3.0. The reactants and the reaction products were analyzed by gas chromatograph (Agilent 7890A), equipped with a thermal conductivity detector (TCD) and a flame ionization detector (FID) connected in series.

Results and Discussion

The initial tests were important to define the limits of the stability of the standard SOFC button cell under ethanol. Firstly, the stability of the standard YSZ/Ni anode of the as-received samples both at 600 °C and 700 °C was checked (Figure 1).

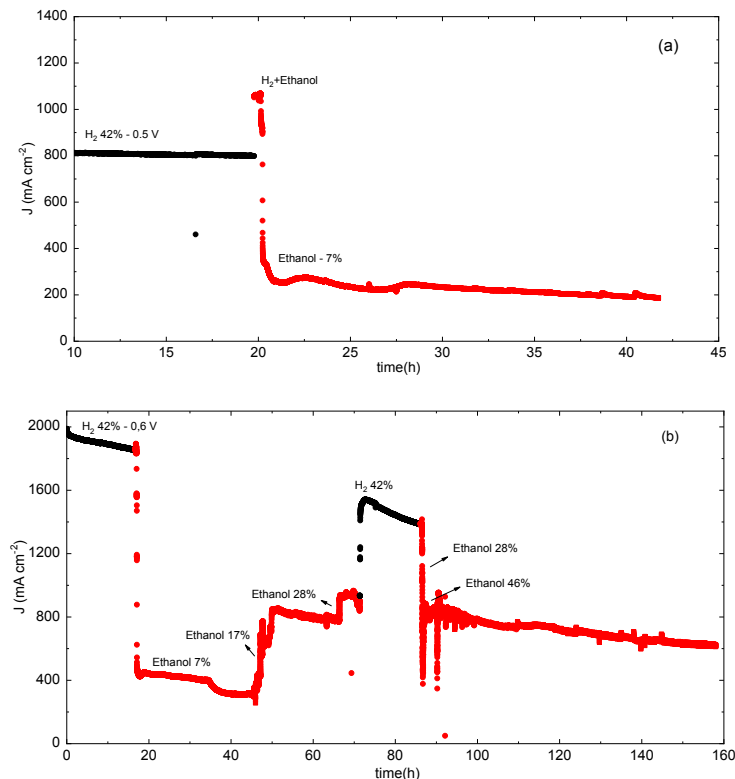


Figure 1. Potentiostatic stability test of as-received anode support solid oxide fuel cells under hydrogen (black) and ethanol (red) without water. a) at 0.5 V and 600 °C and b) at 0.6 V and 700 °C.

During the initial ~20 hours of operation both cells presented different degradation rates under hydrogen. The degradation rate at 700 °C is much more pronounced, a feature likely associated with a fabrication issue of the sample. The potentiostatic curves showed a significant decrease of the current output upon changing the fuel from hydrogen to ethanol. Under ethanol, fuel cells ran for ~25 hours and ~140 hours at 600 °C and 700 °C, respectively. Both samples have shown a progressive decrease of the current output with increasing measuring time following a similar degradation rate of that in hydrogen. At 700 °C we have checked the dependence of the current output on both the N₂ carrier flow rate and the ethanol temperature, as shown in Figure 2.

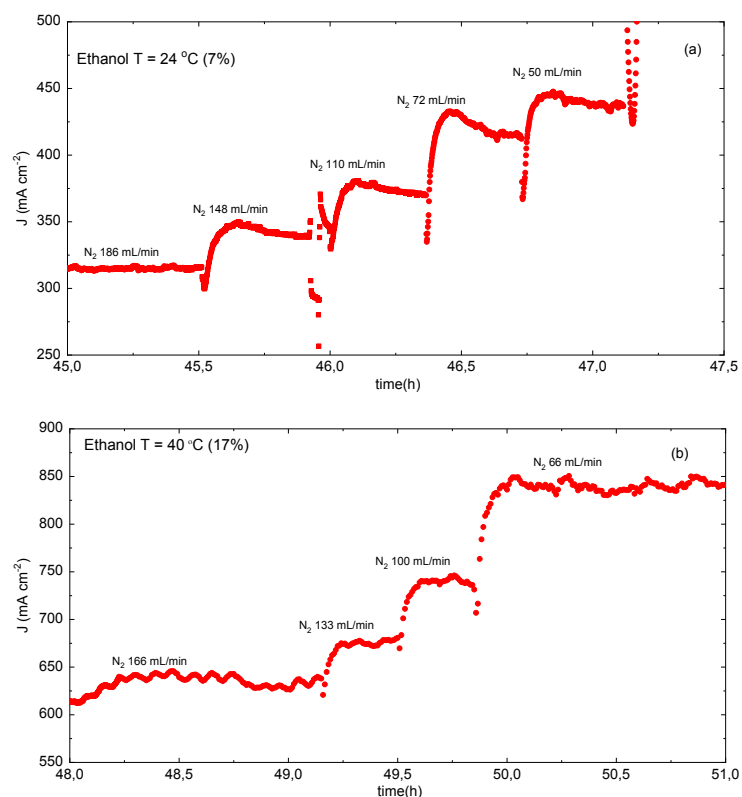


Figure 2. Current output (at 0.6 V and 700 °C) dependence on the ethanol concentration and N₂ carrier flow rate for (a) 7% ethanol (T = 24 °C) and (b) 17% ethanol (T = 40 °C) for the as-received fuel cell.

The stability tests at 700 °C (Figure 1b) included experiments of the dependence of the current output on both the ethanol concentration and flow rate, as shown in Figure 2. It was observed that the current output responds accordingly to variations of both flow rate and concentration of ethanol. The current output can be significantly increased by increasing the ethanol concentration and decreasing the N₂ flow rate, i.e., increasing the residence time/fuel utilization. By increasing the ethanol temperature from 24 °C to 40 °C, corresponding to an increase of 7% to 17% ethanol concentration, resulted in a proportional current density output from ~315 mA cm⁻² to 635 mA cm⁻². However, despite the relatively slow degradation rate, characterization of the anode after the stability tests showed carbon deposit formation, a feature much more pronounced at 600 °C than at 700 °C.

To further understand the YSZ/Ni behavior under ethanol we have carried out fixed bed ethanol SR reactions using YSZ/Ni extracted from the anode of the button cells. A

small piece of the anode support was ground in agate mortar and used as the catalyst in the fixed bed reactor for ethanol SR. Figure 3 shows ethanol conversion and product distributions as a function of time on stream (TOS) for SR of ethanol at 600 and 700 °C.

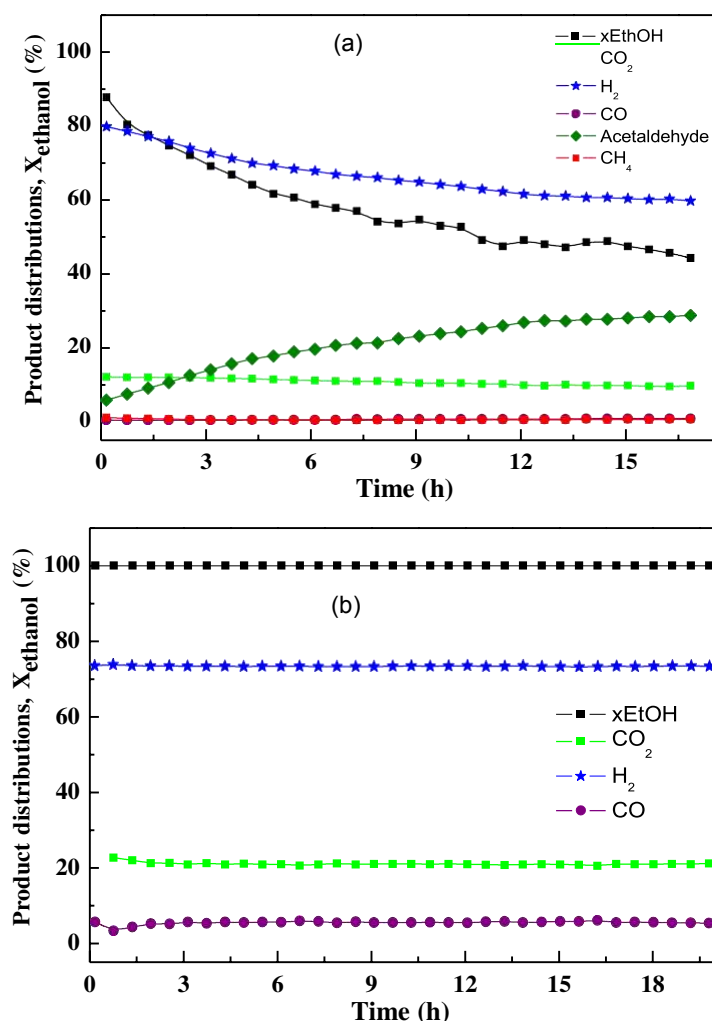
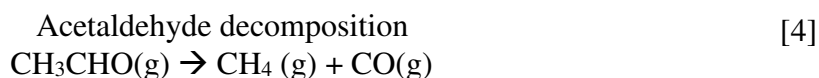
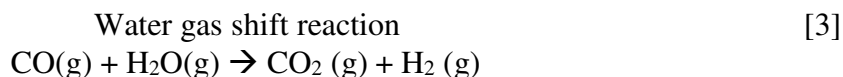
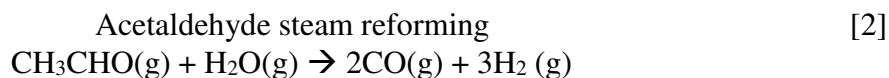
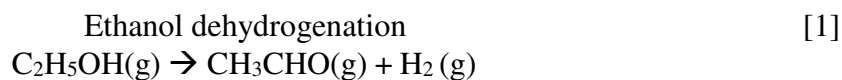


Figure 3. Ethanol conversion and product distributions versus TOS for SR of ethanol under H₂O/ethanol molar ratio = 3.0 over the YSZ/Ni anode at 600 °C (a) and 700 °C (b).

According to the previously proposed mechanism over Ni supported catalysts (10), the main reaction pathway of ethanol SR includes three reactions: dehydrogenation of ethanol (Eq. 1), steam reforming of acetaldehyde (Eq. 2), and water gas shift reaction (Eq. 3). Ethanol is firstly dehydrogenated to acetaldehyde and H₂. Acetaldehyde can react with water generating CO and H₂ and can be decomposed in CH₄ and CO (Eq. 4). In this study, the products formed at 600 °C indicate the occurrence of both dehydrogenation of ethanol and steam reforming of acetaldehyde reactions followed by the shift reaction. As the catalyst deactivates a large amount of acetaldehyde is produced, indicating that the dehydrogenation of ethanol was the main reaction taking place. However, increasing the reaction temperature to 700 °C greatly improved the stability of the catalyst and H₂, CO₂ and CO, were the main products formed, indicating that ethanol SR was the main reaction at 700 °C.



The formation of carbon was investigated by performing TG analysis of the spent catalysts after 20 h of TOS (Figure 4). YSZ/Ni anode at 600 °C exhibited an oxidation peak at 660 °C indicating that the deactivation of the catalysts is due to carbon deposition. The TG analysis of YSZ/Ni anode at 700 °C did not detect any oxidation peak of carbonaceous materials, which explains the stability of this catalyst.

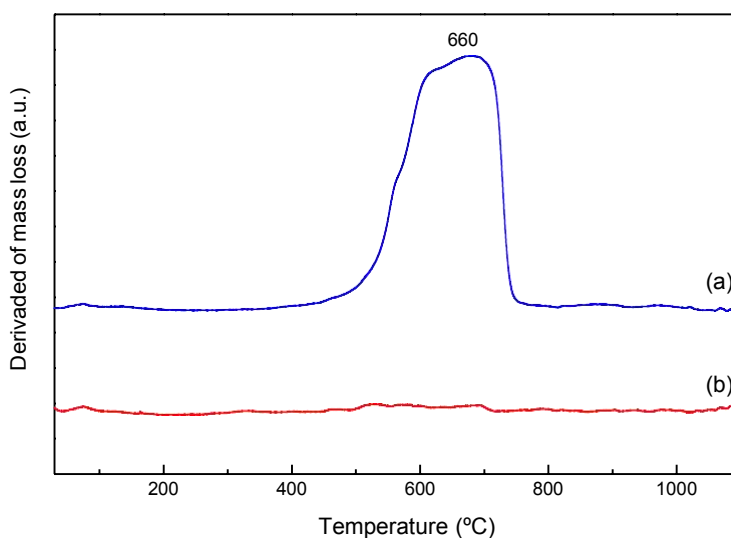


Figure 4. TPO profiles of the spent YSZ/Ni anode after SR of ethanol at 600 °C (a) and 700 °C (b).

The combined experimental results indicate that the anode deactivation due to carbon deposit seems slower in fuel cell tests as compared to the catalytic test. Such feature can be related to the higher amount of available active Ni sites in the fuel cell anode, but it also can be related to a possibly higher ethanol/water ratio in the fuel cell test than in the fixed bed reactor. At the investigated polarization voltage, a water/ethanol ratio >3 can be available for the internal reforming depending on the U_f . Previous reports have demonstrated that provided that a minimum U_f is attained the standard YSZ/Ni anode can sustain the operation under carbon containing fuels with a reasonable stability (11). Such a feature is possible because the stoichiometry of the electrochemical oxidation of hydrogen in the anode provides water in excess for the ethanol SR (7, 8). Nevertheless, the

results evidenced the need of more active catalyst than the YSZ/Ni for stable direct ethanol fuel cells running at intermediate temperatures.

Therefore, we have investigated the Ir/CGO catalyst, previously demonstrated stable for the ethanol SR at 850 °C. The first series of SOFC measurements compared the electrochemical performance of both the as-received sample and the sample with a deposited Ir/CGO catalytic layer. The I-V data of the as-received SOFC button cells reproduced the specification provided by the supplier (current density $\sim 0.42 \text{ Acm}^{-2}$ at 0.95 V at 700 °C). More importantly, both the as-received and the cell with catalytic layer exhibited comparable electrochemical properties as show in Figure 5. The I-V curves of both samples have similar OCV (1.1 V) and I-V profile with dominant ohmic polarization in the investigated current range. Interestingly, the sample with deposited Ir/CGO layer displays higher current output than the as-received sample. Such result indicates that the catalytic layer has no evident negative impact on the properties of the single cell as long microstructural properties of the anode, such as the required porosity, are preserved.

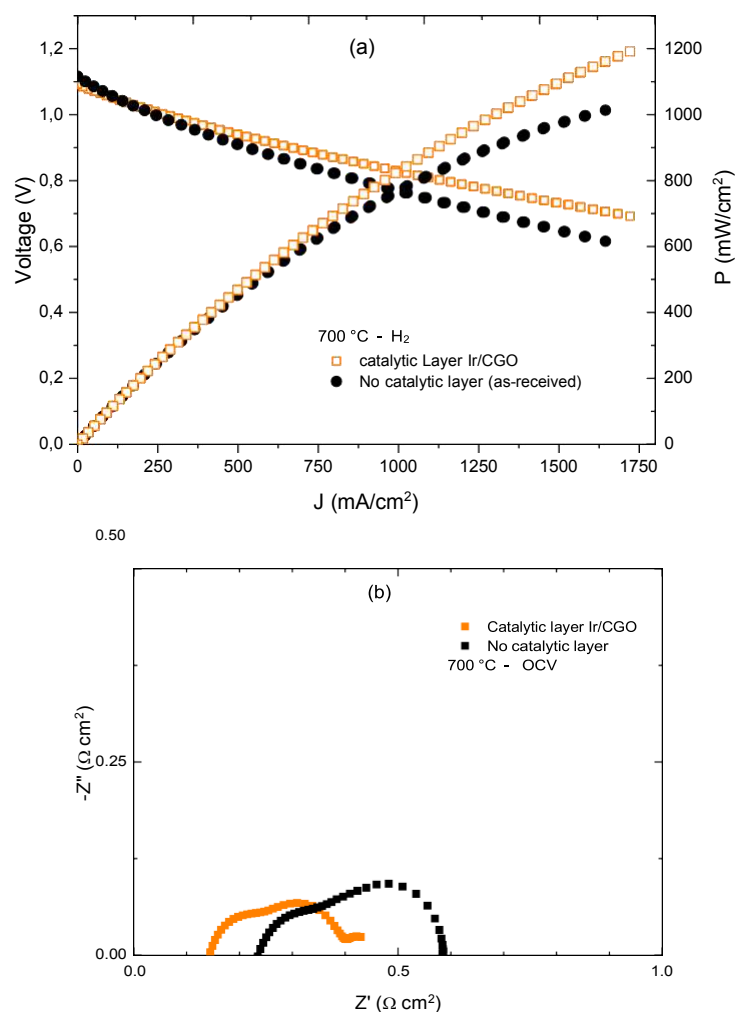


Figure 5. a) I-V curves of fuel cell as-received and with Ir/CGO catalytic layer running on hydrogen at 700 °C and b) corresponding EIS diagrams taken at OCV.

Moreover, no apparent reaction between the anode and the catalyst resulting in isolating phases occurred and an efficient current collection is attained in both samples. The impedance data showed in Figure 5b revealed a lower ohmic resistance for the samples with the catalytic layer that can be ascribed, for example, to small differences of the active

contact area for current collection. A slightly lower polarization resistance along with an additional small contribution at the low-frequency end were observed in the catalytic layer sample. Such features deserve more detailed studies to infer whether such differences are related to the catalytic layer.

To evaluate the behavior of Ir/CGO catalyst prior to fuel cell testing, ethanol SR reactions were carried out in the fixed bed reactor. At 600 °C Ir/CGO was shown to deactivate very quickly (Figure 6a). The ethanol conversion was decreased to ~40% in the initial 5 hours of testing, with acetic acid being the main product of the reaction. At 700 °C, the catalyst showed no deactivation in the tested conditions, with ethanol conversion of 100% and H₂ selectivity ~70% during the 24 hours of testing. Post-reaction analyses showed a mass loss corresponding to carbon oxidation that took place at relatively low temperature (~300-500 °C range) for the catalyst tested at 600 °C, indicating amorphous carbon formation. The catalyst tested at 700 °C showed no significant mass low in the thermogravimetric profile.

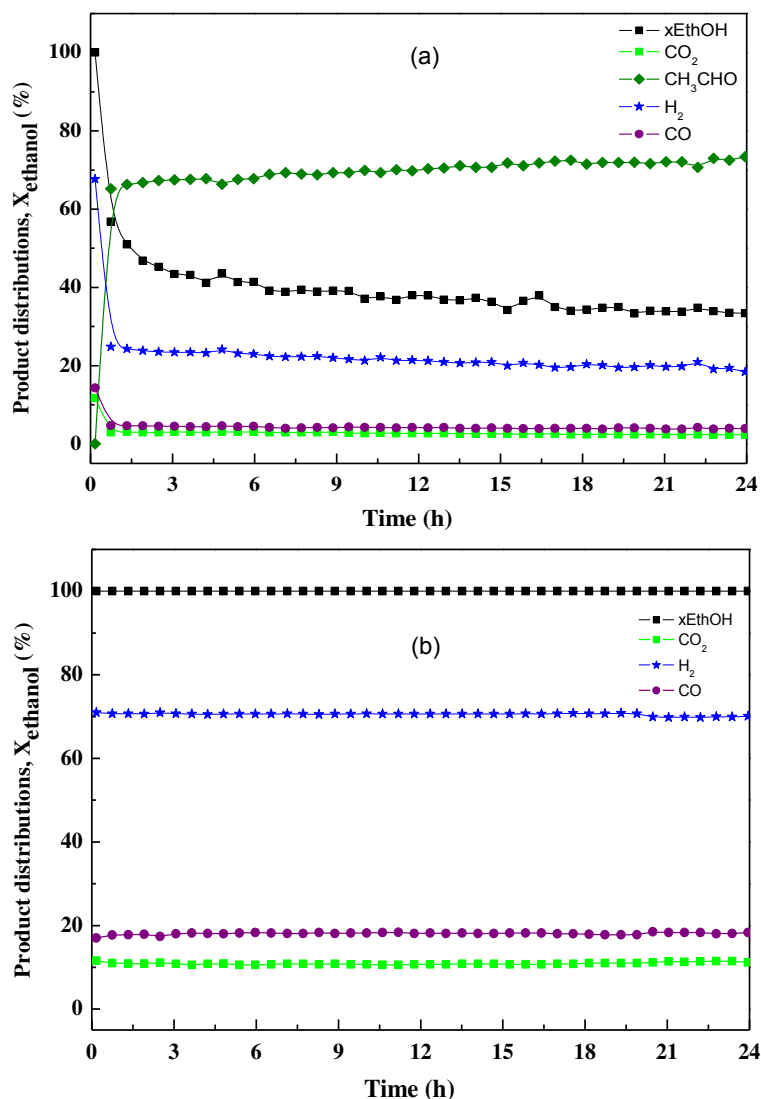


Figure 6. Ethanol conversion and product distributions versus TOS for SR of ethanol under H₂O/ethanol molar ratio = 3.0 over the Ir/CGO at 600 °C (a) and 700 °C (b).

Raman analyses of the Ir/CGO catalysts were carried out to investigate possible causes for catalyst deactivation during ethanol SR as shown in Figure 7. Raman spectroscopy data confirmed formation of carbon deposits for the Ir/CGO catalyst reacted at 600 °C.

The Raman spectra of the spent Ir/CGO catalysts after reaction at 600 °C shows two bands centered at 1330 cm^{-1} and 1600 cm^{-1} , which are known as the D-band and G-band, respectively. The D-band is attributed to the vibrations of carbon atoms with dangling bonds in disordered graphite planes, while the G-band is attributed to the stretching mode of carbon sp^2 bonds of ordered graphite (12). These results suggest that carbon deposition is likely the main cause of Ir/CGO catalyst deactivation at 600 °C. Increasing the reaction temperature to 700 °C decreased substantially the intensity of the D- and G-bands.

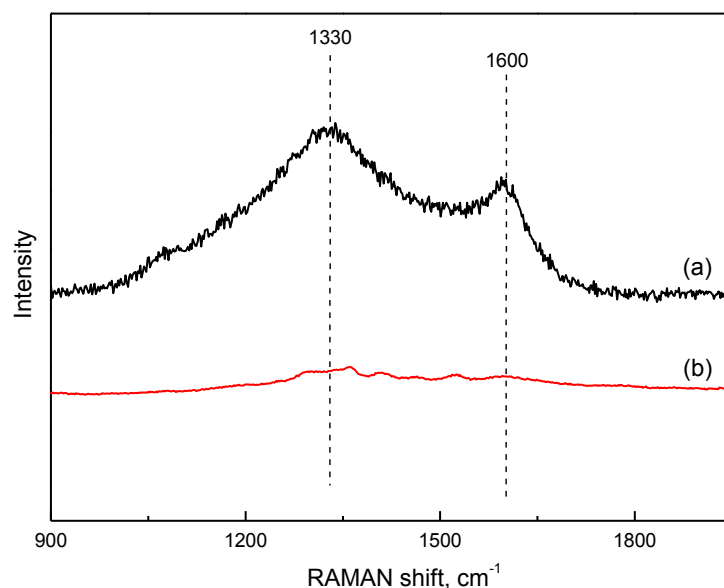


Figure 7. Raman spectra of Ir/CGO after ethanol SR at 600 °C (a) and 700 °C (b).

Considering the ethanol SR results in Figures. 6 and 7 we have carried out direct ethanol solid oxide fuel cell stability test using Ir/CGO catalytic layer at 700 °C (Figure 8). The data in Figure 8 shows a stable performance during ~40 hours under direct ethanol.

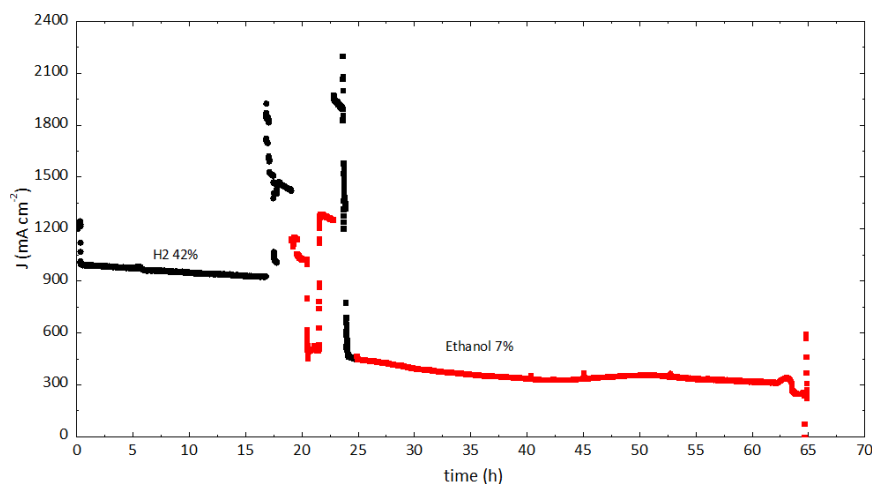


Figure 8. Stability test at 0.7 V under dry ethanol of SOFC with Ir/CGO catalytic layer at 700 °C.

After cooling the system down to room temperature under nitrogen flow, a small carbon deposit in our fuel cell test fixture was observed. However, such carbon was ascribed to amorphous carbon that is possibly reoxidized during fuel cell operation. Further analyses are underway to study the stability of the fuel cell at 700 °C.

Conclusion

The combined experimental results of fuel cell testing and fixed bed reactor confirmed that standard anode YSZ/Ni is unstable in direct ethanol at intermediate temperatures. At 600 °C, both the YSZ/Ni and the Ir/CGO deactivate very rapidly due to carbon deposit formation. On the other hand, increasing the temperature to 700 °C resulted in a much more stable reaction of both YSZ/Ni and Ir/CGO. The comparison of the samples with and without catalytic layer showed no apparent negative impact of the additional layer to the fuel cell performance. The stability tests using Ir/CGO showed improved stability as compared to the YSZ/Ni anode. The main results evidenced the need of a more stable and active catalyst for fuel cells running at 600 °C.

Acknowledgments

Authors are thankful for the support of IPEN-CNEN/SP and Nissan. FCF is a CNPq fellow. FAPESP 2019/115110-2, 2017/11937-4 and 2014/09087-4 partial support is acknowledged.

References

1. M. Kleitz, F. Petitbon, *Solid State Ionics*, **92**, 65 (1996).
2. Y. Lin, Z. Zhan, S. A. Barnett, *J. Power Sources*, **158**, 1313 (2006).
3. J. M. Klein, M. Hénault, P. Gélín, Y. Bultel, S. Georges, *Electrochem. Solid-State Lett.*, **11**, B144 (2008).
4. R. Muccillo, E. N. S. Muccillo, F. C. Fonseca, D. Z. de Florio, *J. Electrochem. Soc.*, **155**, B232 (2008).
5. M. A. Elharati, M. Dewa, Q. Bkour, A. M. Hussain, Y. Miura, S. Dong, Y. Fukuyama, N. Dale, O. G. Marin-Flores, S. Ha, *Energy Technol.*, **8**, 2000350 (2020).
6. S. D. Nobrega, M. V. Galesco, K. Girona, D. Z. de Florio, M. C. Steil, S. Georges, F. C. Fonseca, *J. Power Sources*, **213**, 156 (2012).
7. S. D. Nobrega, P. Gelin, S. Georges, M. C. Steil, B. L. Augusto, F. B. Noronha, F. C. Fonseca, *J. Electrochem. Soc.*, **161**, F354 (2014).
8. M. C. Steil, S. D. Nobrega, S. Georges, P. Gelin, S. Uhlenbruck, F. C. Fonseca, *Appl. Energy*, **199**, 180 (2017).
9. M. Wisniewski, A. Boréave, P. Gélín, *Catal. Commun.*, **6**, 596 (2005).
10. S. Ogo, Y. Sekine, *Fuel Process. Technol.*, **199**, 106238 (2020).
11. J. Liu, S. A. Barnett, *Solid State Ionics*, **158**, 11 (2003).
12. A. E. Galetti, M. F. Gomez, L. A. Arrúa, M. C. Abello, *Appl. Catal. A*, **348**, 94 (2008).