Nickel based anodes for single chamber solid oxide fuel cells: a catalytic study
Geoffroy Gadacza, Sorina Udriou, Jean-Paul Viricelle, Christophe Pijolat, Michèle Pijolat

To cite this version:

HAL Id: hal-00508540
https://hal.archives-ouvertes.fr/hal-00508540
Submitted on 4 Aug 2010

HAL is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L’archive ouverte pluridisciplinaire HAL, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d’enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.
Nickel based anodes for single chamber solid oxide fuel cells: a catalytic study

GEOFFROY GAĐACZ(1,2), SORINA UDRIOU(1), JEAN-PAUL VIRICELLE(1)*, CHRISTOPHE PIJOLAT(1), MICHELLÈ PIJOLAT(2)

(1) Ecole Nationale Supérieure des Mines de Saint Etienne, Centre SPIN ; Département MICC ; LPMG -UMR CNRS 5148, 158 Cours Fauriel - 42023 Saint-Étienne Cedex 2, France
(2) Ecole Nationale Supérieure des Mines de Saint Etienne, Centre SPIN ; Département ProcESS ; LPMG -UMR CNRS 5148, 158 Cours Fauriel - 42023 Saint-Étienne Cedex 2, France

Abstract

Single chamber solid oxide fuel cells (SCFC) are an alternative concept to traditional SOFC’s. Conventional anodes, which consist of a cermet of metallic Ni and ionic conductor, have to work under a mixture of hydrocarbon and oxygen. This paper presents a catalytic study of C₃H₈ oxidation by Ce₀.₉Gd₀.₁O₁.₉₅ and nickel. The influence of temperature and oxygen to propane ratio on the nickel oxidation state are clarified thanks to catalytic tests and electrical conductivity measurements. The results show that the temperature must be higher than a critical value in order to maintain the nickel particles in the metallic state. Furthermore, at high temperature, the conversion of the initial mixture leads to the water-gas-shift equilibrium.

Keywords: anode; Nickel; single chamber; SOFC; solid oxide fuel cells; catalytic study; C₃H₈ oxidation; Ce₀.₉Gd₀.₁O₁.₉₅; oxygen; propane; electrical conductivity measurements

I. Introduction

Fifteen years ago, Hibino [1] has shown the feasibility of a fuel cell consisting of only one chamber, with a mixture of reducing and oxidizing gases (generally hydrocarbon and oxygen). This concept allows avoiding the sealing procedure of traditional fuel cell, and a better control of gases. Single Chamber Fuel Cells (SCFC’s) have quickly shown good results, close to traditional SOFC’s power densities [2-7]. Some research groups nevertheless reported some drawbacks such as voltage oscillation and nickel-based anode instability [8]. They attributed these oscillations to oxidation/reduction cycles of the metal. However, to our knowledge, very few studies have been devoted to the anode properties in the working conditions of SCFC’s. Traditional anodes consist of a cermet, based on a solid ionic conductor (for example GDC: Ce₀.₉Gd₀.₁O₁.₉₅) mixed with an electronic conductor, such as metallic nickel. They are generally used in hydrogen, which is easily dissociated in presence of metallic nickel. Because of the problems involved by the direct use of H₂, an alternative way is to use the catalytic partial oxidation of hydrocarbons, leading to a mixture of CO and H₂. An example is given by the partial oxidation of propane [1] (ΔH° (850K) = -206 kJ.mol⁻¹):

\[ C_3H_8 + \frac{3}{2}O_2 \rightarrow 3CO + 4H_2 \]  

* Auteur à qui la correspondance devait être adressée : viricelle@emse.fr
Nickel is known to have a good catalytic activity for this reaction [9]; the exothermicity of the reaction helps to maintain the temperature of the cell, and the oxygen partial pressure limits the carbon deposition. But, using propane with oxygen may induce an undesirable reaction (2) \((\Delta H^\circ (850K) = -2043 \text{kJ.mol}^{-1})\) which consists of the direct total oxidation:

\[
\text{C}_3\text{H}_8 + 5 \text{O}_2 \rightarrow 3\text{CO}_2 + 4\text{H}_2\text{O}
\] (2)

The conditions of stability of metallic nickel versus its oxidation into NiO, and competition effects between reactions (1) and (2) have to be clarified for achieving a good SCFC efficiency. In this paper, we present first the catalytic activity and stability of GDC and Ni powders in presence of propane and oxygen mixtures. Then, the variation of the electrical conductivity of Ni-GDC anodes is reported as a function of temperature in presence of a mixture of propane and oxygen. The results are interpreted on the basis of the oxidation state of nickel together with its catalytic properties.

### II. Experimental

#### II.1. Samples

GDC \((\text{Ce}_{0.9}\text{Gd}_{0.1}\text{O}_{1.95})\) was supplied by Fuel Cell Materials™ (Nextech™ division). Its specific surface area, measured using BET method with nitrogen (Micromeritics ASAP 2000) was 8m².g⁻¹. The average particle size corresponding to this area surface is 0.1µm, assuming spherical particles of a same size. The powder was then characterized by laser granulometry (Malvern Mastersizer 2000), as presented in Figure 1. The particle size distribution of GDC powder as supplied showed three maxima at 1, 5 and 110 µm. A sieving procedure at 100µm was able to eliminate the largest agglomerates.

NiO was supplied by Sigma-Aldrich™. Its BET specific surface area was equal to 5 m².g⁻¹, corresponding to a particle size of 0.13µm, which is very close to that of GDC. Laser Granulometry analyses see Figure 1 revealed a very broad particule size distribution with various maxima, the most important being at 4 and 500 µm. To lower the NiO average particule size, a grinding procedure has been applied using a planetary ball mill (stainless steel balls) at 180 rpm for 30 min. XPS analyses after treatment did not show any pollution of the surface due to grinding. Laser granulometry analyses show that all the agglomerates have been broken into aggregates smaller than 100 µm. Sieved GDC or ground and sieved NiO will be refered as “treated” powders in the following.

![Figure 1: Laser granulometry study of the initial and treated GDC and NiO powders](image-url)
II.2. Catalytic activity

The treated powders were mixed with alpha-alumina powder from Alpha-Aesar™ to obtain samples of 10 (or 20%wt) of NiO or GDC. Alpha-alumina was used in order to minimize over temperature effects due to the exothermicity of reactions (1) and (2). This powder was also inert with respect to the gaseous mixtures.

The catalytic activity was measured in a catalytic reactor equipped with a tubular 10 mm diameter quartz tube. Quartz wool was placed in the middle of the tube to support the sample, allowing a fixed bed reactor. A thermocouple protected by an alumina tube to avoid catalytic artefacts was fixed near the powder. The tube was introduced inside a vertical furnace whose temperature was regulated by a thermocouple placed near to the sample bed. A condenser at the outlet of the tube allowed to trap water before gas analyses. The composition of the gaseous mixture was then determined with a micro-gas chromatograph coupled with a mass spectrometer (SRA instruments™). The different partial pressures of the system were calculated using calibrated gases. It allows to determine partials pressures of around 10⁻² atm with a precision of ± 10⁻⁴ atm.

Prior to the catalytic activity measurements, the GDC / α-alumina mixtures were heated at 580°C and maintained during 1h at this temperature in order to eliminate adsorbed species from the surface. In case of NiO / α-alumina mixtures, a reduction step treatment in hydrogen (2% H₂ in Ar at 10 l.h⁻¹) was first done at 580°C during 3 hours in order to transform NiO particles into metallic nickel. Then, once the desired temperature was established under flowing argon. O₂ / C₃H₈ / Ar was introduced in the reactor (for example 0.6 / 0.4 / 9 l.h⁻¹ respectively) and the catalytic activity was measured after a stabilization period of one hour, during which the reactor reaches a constant value after an initial increase due to the exothermicity of the reactions. Temperature tests were done by decreasing temperature after the stabilization time at a fixed ratio, with a constant ramping rate of 1°C.min⁻¹. Gas analyses were done every ten minutes, corresponding to a measure every ten degrees.

In all the experiments, the amount of propane and oxygen never exceeded 10% of the gaseous phase for two reasons. First, it ensured that whatever the ratio O₂ / C₃H₈ could be, the reactor gaseous atmosphere was far from exploding conditions ; second at low partial pressures, the volume expansion of the gas due to the reactions is low and thereby the errors of outlet quantitative analysis. The various O₂: C₃H₈ volumic ratios were comprised between 1:9 and 9:1 in argon and the total flow rate was fixed to 10 l.h⁻¹, for all experiments. In the following the notation x / 10-x will be used for the oxygen to propane ratio, which means x % of oxygen and (10-x) % of propane in the gaseous mixture.

II.3. Electrical conductivity

Four points measurements of the electrical conductivity of Ni – GDC cermet supported on GDC pellets were done in order to follow the oxidation state of nickel as a function of temperature in the O₂ / C₃H₈ / Ar mixture.

First, a GDC support was prepared from the treated powder by sintering at 1200°C for 6 hours, then at 1350°C for 4 hours a pellet previously pressed at 100MPa. The initial and final diameter of the pellet was 22mm and 19mm respectively; the thickness of the sintered pellet was 1.5mm. The Ni-GDC cermet was deposited onto the GDC sintered pellet using screen-printing technology. First, treated powders were mixed using 60%wt of NiO and 40%wt of GDC, then a commercial binder and a solvent (supplied by ESL Europe) were added. The final ink was shaken using an UltraTurrax™ for 20 min.

After deposition due to an Aurel™ device, we obtained a homogeneous layer whose thickness was 25µm. Four platinum contacts located on the edges of the cermet, allowed to monitor the electrical conductivity according to the Van der Pauw method, with a current source of I= ±50mA (Keithley Sourcemeter 2600C). The sample was placed in a tubular furnace equipped with a quartz tube of 3 cm diameter.

The NiO-GDC as prepared cermet anode was treated with the same conditions as for the catalytic powder reactor in order to achieve the reduction of NiO into metallic Ni. Then the
electrical conductivity of the sample was measured for various temperatures under a flowing 6 / 4 ratio at 20 l.h⁻¹.

X-ray diffraction (Siemens D5000) has been used to characterize the samples after the catalytic activity and electrical measurements. The X-ray emission has been done with a copper anticathode. The detector is a scintillator with a graphite monochromator.

### III. Results and discussions

#### III.1. Catalytic activity

**III.1.1. GDC results**

The results concerning GDC catalytic activity at 590°C (sample mass: 15 mg of GDC mixed with 85mg of α-Al₂O₃) are presented in Figure 2 as a function of the O₂ / C₃H₈ ratio. It can be seen that the maximum catalytic activity is reached at 6-7% of O₂ (and respectively 4 and 3% of C₃H₈), leading to a high production of carbon dioxide. This maximum suggests that the major reaction taking place in this case is the total oxidation of propane, producing CO₂ and H₂O according to reaction (2). Effectively, the stoechiometric proportions of this reaction would correspond to an O₂ / C₃H₈ ratio equal to 8.33 / 1.67 which is near to the experimental observed ratio. In addition to this reaction, it can be observed a small quantity of CO and H₂ corresponding to the propane partial oxidation, according to reaction (1). The maximum amount for these gases is observed around 6 / 4 oxygen to propane ratio, which is in agreement with the stoechiometric proportions of reaction (1). Finally, some C₂H₄ and CH₄ could be observed, especially at low O₂ / C₃H₈ ratios. Both products were also identified during a blank test (without any powder in the reactor) showing that propane cracking takes place in the gas phase, according to reaction (3).

$$C_3H_8 \rightarrow CH_4 + C_2H_4$$  \hspace{1cm} (3)

CH₄ was not detected for most of the ratios, probably because it is readily oxidized.

![Figure 2: Catalytic activity of GDC (15 mg; 10%wt in alumina) at 590°C, as a function of the O₂/C₃H₈ ratio.](image)

Figure 3 presents the catalytic activity of GDC as a function of temperature obtained for a 6 / 4 oxygen to propane ratio. It can be seen that the catalytic activity increases with the temperature increase. The maximal conversion for propane and oxygen was 9 and 22 % respectively, the major reaction product being CO₂ for all temperatures. Arrhenius plot deduced from the CO₂ catalytic production leads to a value of the apparent activation energy
equal to 75 kJ.mol$^{-1}$. Other temperature tests have shown good reproducibility, by starting measurements at low temperature, and applying a increasing ramping rate of 1°C.min$^{-1}$.

![Figure 3: Catalytic activity of GDC (15 mg; 10%wt in alumina) as a function of temperature, with an O$_2$/C$_3$H$_8$ ratio equal to 6/4.](image)

### III.1.2. Ni/ NiO results

As for GDC, the reduced nickel samples have been exposed to various O$_2$/C$_3$H$_8$ ratios at 580°C. Figure 4 shows the results of catalytic activity measurements obtained as a function of O$_2$/C$_3$H$_8$ ratio. The produced gases correspond to the reactions (1) and (2). For mixtures rich in propane, namely from 1/9 to 4/6 ratios, carbon dioxide is the major product. The amount of carbon monoxide and hydrogen increase when the O$_2$/C$_3$H$_8$ ratio increases. The maximum observed in CO and H$_2$ filled in the range 6/4 − 7/3. The O$_2$ conversion was close to 100%. For this last ratio, for such high conversions, over-temperatures of 15°C could be observed, consequently to the strong exothermic reactions taking place. For ratios of 8/2 and 9/1, the catalytic activity decreased drastically, leading to practically carbon dioxide production.

![Figure 4: Catalytic activity of Ni (8 mg; 10%wt in alumina) at 580°C, as a function of the O$_2$/C$_3$H$_8$ ratio.](image)
The catalytic activity of O$_2$ and C$_3$H$_8$ is much higher with Ni than with GDC, especially at high temperature. Due to this comparative study, it appears that the contribution of GDC to the catalytic activity of Ni-GDC cerments for the conversion of O$_2$ and C$_3$H$_8$ mixtures into CO$_2$ is practically negligible.

After measurement of the catalytic activity at 580°C for 2 hours, (with 6/4, 7/3, 8/2 and 9/1 oxygen to propane ratio), the samples were analysed by X-Ray diffraction. Figure 5 shows the various diffraction patterns in which NiO peak at 63° can be easily noticed for the highest O$_2$/C$_3$H$_8$ ratio (9/1), and suspected for the ratio equal to 8/2. This means that in oxygen rich mixtures, metallic nickel is not stable and is oxidized into NiO. This corresponds to the drop of the catalytic activity, especially in CO and H$_2$ (see Figure 4).

\[ \text{CO} + \text{H}_2\text{O} \rightleftharpoons \text{CO}_2 + \text{H}_2 \]  \hspace{1cm} (3)

If this equilibrium occurs and reach an equilibrium state at high temperature, the values of $K_{\text{exp}}$ defined as:

\[ K_{\text{exp}} = \frac{p(\text{CO}_2)p(\text{H}_2)}{p(\text{CO})p(\text{H}_2\text{O})} \]  \hspace{1cm} (4)

should be equal to those deduced from thermodynamic data ($K_{\text{ref}}$).
In our experiments, the amount of water was unknown, but from the mass balance equation upon oxygen, it could be estimated and the values of $K_{\text{exp}}$ could be calculated at each temperature. Figure 7 displays the results obtained for $K_{\text{exp}}$ compared to the thermodynamic prediction. It can be seen that above 570°C, the values deduced from gas analyses and mass balance are very close to those of the equilibrium constant, and follow a similar variation versus temperature, whereas it is not the case at lower temperatures. Consequently, taking into account the imprecision on the estimation of the water amount, it appears that the water gas shift equilibrium controls the gas composition above 570°C.

**Figure 6:** Catalytic activity of Ni (16 mg; 20%wt in alumina) as a function of temperature, with an $O_2 / C_3H_8$ ratio equal to 6/4.

**Figure 7:** Comparison between thermodynamic constant $K$ obtained by calculation(—), and the apparent constant obtained by experimentation(*), considering water gas-shift reaction.

At lower temperatures than 570°C, the gas composition was found to change significantly with temperature. Figure 8 which represents the Arrhenius plot for carbon dioxide
production, indicates the existence of two distinct values of the apparent activation energy (70 and 140 kJ.mol$^{-1}$) on both sides of a limiting temperature of 520°C which is approximately the temperature at which began the production of CO and H$_2$ according to reaction (2) (partial oxidation).

Since CO$_2$ can only be produced by reaction (1) (total oxidation), a change in the catalyst surface must be suspected. The oxidation of nickel has already been mentioned for a temperature equal to 580°C and oxygen rich O$_2$/C$_3$H$_8$ ratios. Here the O$_2$/C$_3$H$_8$ ratio was fixed equal to 6/4, so the oxidation of nickel may be expected at a different temperature. Since XRD is not able to detect very small amounts of phases, or superficial oxidation in case of very thin layers, electrical measurements were performed on a Ni-GDC cermet.

### III.2. Electrical measurements

A 25µm thickness Ni-GDC anode, supported on GDC has been placed under a O$_2$/C$_3$H$_8$ ratio of 6/4, in order to follow the electrical conductivity change with temperature. Figure 9 shows the total cermet conductivity and temperature, as a function of time. At the beginning of the experiment, the temperature was equal to 580°C, and metallic nickel was present due to the H$_2$ reduction treatment: value of the conductivity was as high as 800 S.cm$^{-1}$. The O$_2$/C$_3$H$_8$ mixture was introduced, the conductivity decrease during a short period, probably due to the time necessary to reach a homogeneous mixture, and then returned to a high value of 900 S.cm$^{-1}$. Temperature was set up to 590°C and then decreased stepwise down to 520°C. The conductivity remained at a high value except when the temperature was changed from 530 to 520°C where a sharp decrease was monitored. When the temperature decreases, the conductivity is quiet stable except some small oscillations. They are probably due to a carbon deposition to the anode (black appearance of the cermet after measurements), which is a good electronic conductor.
Such a behaviour can be explained by the oxidation of nickel into NiO. The limiting temperature corresponds to that of CO and H$_2$ production and to the different slopes in the Arrhenius plot for CO$_2$ production. As a consequence, as far as Ni is maintained in the metallic state, CO and H$_2$ are produced according to reaction (2). Below a limiting temperature, which depends of the O$_2$ / C$_3$H$_8$ ratio (cf Figure 5), Ni-GDC cermet is not suitable for SCFC’s operation.

III.3. Thermodynamic calculations

In order to better understand the formation of NiO below the limiting temperature, we have looked to the thermodynamics of the Ni / NiO system in a gaseous atmosphere containing oxidising (O$_2$, H$_2$O, CO$_2$) and reducing (C$_3$H$_8$, CO, H$_2$) gases. Five independent reactions may be proposed:

\[
\begin{align*}
H_2 + NiO & \rightarrow Ni + H_2O \\
CO + NiO & \rightarrow Ni + CO_2 \\
\frac{1}{3}C_3H_8 + NiO & \rightarrow 6CO + \frac{4}{5}H_2 + Ni \\
Ni + \frac{1}{2}O_2 & \rightarrow NiO \\
\frac{1}{10}C_3H_8 + NiO & \rightarrow Ni + \frac{3}{10}CO_2 + \frac{2}{5}H_2O
\end{align*}
\]

For each of these reactions, the reaction Gibbs energy has been calculated considering the composition of the real gas very close to 530°C, namely 535°C. As previously done, the amount of water was estimated according to the mass balance equation for oxygen. Hence, \( \Delta G^\circ(T) \) could be obtained according to the general equation (10):

\[
\Delta_r G(T) = \Delta G^\circ(T) + RT \ln \left( \prod \frac{p^r(products)}{p^r(reactant)} \right)
\]
where \( \Delta G^\circ(T) \) is the standard free enthalpy, \( R \) the ideal gas constant, \( T \) the temperature, \( P \) the partial pressures of the gaseous products and reactants with \( v_i \) and \( v_j \) the stoichiometric coefficients, respectively. The results are presented in Figure 10 which shows the variations of \( \Delta G^\circ(T) \) as a function of temperature. Considering minimum \( \Delta G^\circ(T) \) Gibbs Energy, two reactions are expected to control the chemical state of nickel: the oxidation of Ni by oxygen (8) and the reduction of NiO by propane (7) It can be seen that below 520°C (as indicated by the arrow), reaction (8) is the most favored reaction, whereas above 520°C, reaction (7) is the most favored. This is in very good agreement with the observed phenomenon since metallic Ni was found to oxidize at temperatures lower than 530°C.

![Figure 10: Thermodynamic considerations: free enthalpy variation as a function of temperature for the different reactions involving nickel](image)

**IV. Conclusions**

To better understand the behaviour of a Ni-GDC cermet anode working in a single chamber fuel cell under \( O_2 / C_3H_8 \) mixtures, the catalytic properties of GDC and nickel powders were studied separately as a function of the oxygen to propane ratio and of temperature. The GDC powder was found to catalyze the total oxidation of propane [2] in the range 400-600°C. However, even at high temperatures, the catalytic activity was not very high compared to that of nickel in similar conditions.

Nickel was found to catalyze also partial oxidation of propane [1]. The maximal amounts in CO and \( H_2 \) were obtained for \( O_2 / C_3H_8 \) ratios close to the stoechiometric proportions.

The catalytic activity versus temperature showed three domains which temperature limits way depend on the \( O_2 / C_3H_8 \) ratio. For a ratio equal to 6/4:
- above 565°C, the water gas shift equilibrium controls the gaseous composition, between 535°C and 565°C, simultaneous total and partial oxidation occurred, below 535°C, only total oxidation took place due to oxidation of nickel into NiO in agreement with thermodynamic prediction.

This study not only clarifies the nature of the reactions involved in the SCFC’s operated with \( O_2 / C_3H_8 \), but also points out the existence of a limiting temperature. Above this limiting temperature, metallic nickel is stable and the anode is able to provide \( CO \) and \( H_2 \) at sufficient rates. However, the temperature must not exceed too high values since once the water gas shift equilibrium is reached, the gas composition does not vary too much. Studying the catalytic activity of nickel for \( CO \) and \( H_2 \) production allows to determine the best compromise with respect to temperature.
References