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# DIRECT-BIOGAS SOLID OXIDE FUEL CELL (SOFC) – A THEORETICAL ANALYSIS[1]

*Aline Lima da Silva*[2]
*Nestor Cezar Heck*[3]

**Abstract**
The present work is aimed at analyzing the direct feeding of biogas to SOFC anodes. SOFCs are suitable for electricity generation from biogas, and it is possible to run SOFCs even on biogas compositions richer in $CO_2$ – under such conditions, conventional heat engines would not work, due to difficulty in maintaining ignition. By means of a thermodynamic analysis, it is possible to show that SOFCs can be operated on gas mixtures with $CH_4/CO_2$ molar ratios ranging from 0.1:1 ($CO_2$ rich mixture) to 2:1 ($CH_4$ rich mixture). The effect of operating temperature and current on the composition of the anode atmosphere, efficiency and carbon deposition is discussed. The influence of biogas contaminants – $NH_3$ and $H_2S$ – on SOFC performance is evaluated. Under certain operating conditions, it is demonstrated that $CeO_2$ addition on Ni/YSZ can increase the resistance of the catalyst against sulfur poisoning by the $H_2S$. The effect of operating current on Ni poisoning by $H_2S$ is also investigated.
**Key words**: $H_2S$; Biogas; SOFC; Thermodynamic simulation.

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[2] *Dr., Postdoctoral researcher, Núcleo de Termodinâmica Computacional para a Metalurgia, NTCm PPGE3M, UFRGS, Porto Alegre, RS, Brasil; adasilva26@gmail.com.*
[3] *Metalurgical Engineer. Dr., Professor, Núcleo de Termodinâmica Computacional para a Metalurgia, NTCm; Depto. de Metalurgia, PPGE3M,UFRGS, Porto Alegre, RS, Brasil; heck@ufrgs.br.*

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## 1 INTRODUCTION

Biogas is a highly variable mixture of gases predominantly consisting of methane and carbon dioxide, besides other gases, including ammonia ($NH_3$) and $H_2S$.[1] One of the principal limitations of biogas is its variability of composition, not only in different locations but also over time, and often low level of methane which presents difficulties in its use in conventional power systems.[2] According to Staniforth and Ormerod,[3] as the proportion of $CO_2$ in the biogas increases, the fuel becomes progressively more difficult to ignite, and eventually the proportion of $CO_2$ becomes such that ignition can no longer be maintained. In practice, conventional heat engines are not operated at methane levels below 50%. Due to this limitation, large quantities of biogas are simply vented to atmosphere, wasting a potentially clean, renewable energy source.

The most attractive feature of SOFCs is their fuel flexibility due to the high operating temperature (973-1273K).[4] Biogas can therefore be considered as a possible fuel source for the SOFC.[3] It has been reported that SOFCs can generate considerable power even at 20% methane to carbon dioxide while the combustion engines cannot be applicable under this condition.[3] Direct feeding of real biogas generated in a methane fermentation reactor to SOFC would represent an environmental-friendly, compact and cost-effective energy conversion system in which dry reforming of $CH_4$ (R1) proceeds on Ni-based anode using the $CO_2$ intrinsically contained in biogas, with no need of external reformer. The produced $H_2$ and CO are electrochemically oxidized to produce electricity (R2 and R3). For $CH_4/CO_2$ molar ratios >1, electrochemical oxidation of $CH_4$ occurs (R4).[5]

$$CH_4+CO_2 \rightarrow 2CO+2H_2 \quad \text{(R1)}$$

$$H_2+O^{2-} \rightarrow H_2O+2e^- \quad \text{(R2)}$$

$$CO+O^{2-} \rightarrow CO_2+2e^- \quad \text{(R3)}$$

$$CH_4+O^{2-} \rightarrow CO+2H_2+2e^- \quad \text{(R4)}$$

Direct feeding of biogas would be possible for high temperature SOFC, however, Ni/YSZ anode has a tendency toward carbon deposition and is deactivated drastically by $H_2S$ poisoning.[5]

In the present work, the effect of operating temperature and current on the composition of the anode atmosphere and carbon deposition is discussed. By means of a thermodynamic analysis, it is shown that SOFCs can be operated on gas mixtures with $CH_4/CO_2$ molar ratios ranging from 0.1:1 ($CO_2$ rich mixture) to 2:1 ($CH_4$ rich mixture). The influence of biogas contaminants – $NH_3$ and $H_2S$ – on SOFC performance is evaluated. Under certain operating conditions, it is demonstrated that $CeO_2$ addition on Ni/YSZ can increase the resistance of the catalyst against sulfur poisoning by the $H_2S$. The effect of operating current on Ni poisoning by $H_2S$ is also investigated.

## 2 METHODOLOGY

Thermodynamic equilibrium calculations using the Gibbs energy minimization approach were carried out using the commercial software FactSage 6.3.

The selected databases were SGPS and FactPS, which include thermodynamic data for compounds only. The species considered for describing the ideal gas phase were: $H_2$, $H_2O$, $H_2S$, CO, $CO_2$, $CH_4$, $O_2$, $S_2$, COS, CS, $CS_2$, $SO_2$, $SO_3$, $S_2O$, $NH_3$, NO,

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$N_2O$, $NO_2$, $NO_3$, $N_2O_3$, $N_2O_4$, $N_2O_5$. The solid phase graphite was considered in the compounds data set to predict carbon deposition over the catalyst. The solid phases selected to describe the Ce-O-S system were the following: $CeO_{1.72}$, $CeO_{1.83}$, $CeO_2$, $Ce_2O_2S$, $Ce_2(SO_4)_3$, CeS, $Ce_3S_4$, $Ce_2S_3$, $Ce_2O_3$. The solid phases selected to describe the Ni-S-O system were the following: Ni, $Ni_3S_2$, $Ni_3S_4$, $Ni_6S_5$, NiS, $NiS_2$, $NiSO_4$, NiO.

With respect to sulfur poisoning mechanism for Ni-based catalysts used in anodes of SOFCs (typically Ni-YSZ cermet anodes), it would be interesting to pause here and discuss it briefly based on the experimental results reported for electrochemical measurements in SOFCs. According to Ashrafi et al.,[6] the poisoning of the nickel catalyst may occur even when the concentration of hydrogen sulfide ought not to cause the formation of a bulk nickel sulfide. Therefore, hydrogen sulfide may be assumed to be retained by a chemisorption process. The loss of activity of Ni-based catalysts through sulfur compounds could be due to strong sulfur chemisorption on the nickel surface, which prevents the further adsorption of reactant molecules. In a Ni-YSZ cermet anode, sulfur poisoning is characterized by a rapid initial drop in power output upon exposure to sulfur-containing fuels.[7] For describing sulfur chemisorption, Rostrup-Nielsen Jr.[8] used a Temkin-like isotherm:

$$\frac{pH_2S}{pH_2} = \exp\left(\frac{\Delta H_0^0(1-\alpha\theta)}{RT} - \frac{\Delta S_0^0}{R}\right) \quad (1)$$

Based on Equation 1, the equilibrium surface coverage (θ) will be calculated, in the present work, as:

$$\theta = \frac{\ln\left(\frac{pH_2S}{pH_2}\right) + \frac{\Delta H_0^0}{RT} + \frac{\Delta S^0}{R}}{\frac{\alpha\Delta H_0^0}{RT}} \quad (2)$$

With a $\Delta H_0^0$ of 289 kJ mol$^{-1}$, a $\Delta S^0$ of −19 J mol$^{-1}$ K$^{-1}$, and a $\alpha$ of 0.69.

After each equilibrium calculation carried out using the Gibbs energy minimization approach, the obtained $pH_2S/pH_2$ ratio is replaced in Equation 2, and the surface coverage value can be known. Operating conditions under which θ value can be diminished are determined in the present research. $CeO_2$ is added to the system to evaluate its beneficial effects on the reduction of θ value. The lower the Ni surface coverage, the lower the catalyst poisoning. Consequently, the drop in power output due to $H_2S$ poisoning will be reduced.

Biogas inlet feed ratio considered in calculations is of 1.9L/h. Total mass of catalyst is assumed to be 0.83 g (85mol% Ni, 5mol% CeO2, remaining YSZ; Ni/$CeO_2$ molar ratio of 20:1). In this way, it is supposed a space velocity of 2.3L/$hg_{catalyst}$, which can be reached during SOFC operation. In the section 3.3, ammonia feed ratio was also assumed to be 1.9 L/h. However, it is worth pointing out here that, for Figures 2 and 3 shown in the results section, different values of biogas inlet feed ratio were considered in order to compare with experimental results. Such values are indicated in figure captions.

When an SOFC is producing a current, there is a net input of oxygen ions ($O^{2-}$) to the anodic compartment that changes the equilibrium conditions of the system. Thus, moles of oxygen ($n_O$) must be added to the system, as shown in Equation 3.

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$$n_o\,(mol\cdot h^{-1}) = \left(\frac{I}{2F}\right)\times 3600 \qquad (3)$$

*I* is the current (A) and *F* is the Faraday constant (96485.34 C $mol^{-1}$).
The reversible electrical potential difference across the electrolyte of an SOFC is related to the difference in chemical potentials.[9] The electrode reactions involving oxygen gas ($O_2$) at anode and cathode are, respectively:

- $2O^{2-} = O_2(p_{O_2}^{an.}) + 4e^-$
- $O_2(p_{O_2}^{cat.}) + 4e^- = 2O^{2-}$

Hence, the virtual cell reaction is:

$$O_2(p_{O_2}^{cat.}) = O_2(p_{O_2}^{an.}) \qquad (R5)$$

Therefore, oxygen is transferred from a higher chemical potential (cathode) to a lower chemical potential (anode). The Gibbs free energy change for this cell reaction, $\Delta G_{R5}$, is equal to the difference between the chemical potentials on opposite sides of the electrolyte:

$$\Delta G_{R5} = \mu_{O_2}^{an.} - \mu_{O_2}^{cat.} = RT\ln\left(p_{O_2}^{an.}/p_{O_2}^{cat.}\right) = -4FE \qquad (4)$$

Thus, EMF (E) – electromotive force of a cell (V) for reversible conditions – is given by the following equation:

$$E = \frac{RT}{4F}\ln\frac{p_{O_2}^{cat.}}{p_{O_2}^{an.}} \qquad (5)$$

In Equation 5, the value of $p_{O_2}^{cat.}$ is 0.21 atm, and $p_{O_2}^{an.}$ is known from the equilibrium calculation. When no current is drawn (unloaded SOFC), EMF is referred as OCV (open circuit voltage).

## 3 RESULTS AND DISCUSSION

### 3.1 Biogas Conversion in SOFC Anodes

Figure 1a depicts equilibrium composition for exit gas from an unloaded SOFC along with experimental values from Staniforth e Ormerod.[3] Theoretical analysis shows that, as biogas becomes richer in $CH_4$, concentration of $H_2$ in biogas increases, while the concentration of $CO_2$ decreases continuously. With respect to CO, one can see that its concentration increases until reaching a maximum value, at ~47% methane in biogas. At higher contents of methane in biogas, solid carbon formation increases. These results suggest that dry reforming (R1) initially occurs and, when methane content in biogas is elevated (> 47%), methane decomposition takes place (R6). Thus, for methane content in biogas >47%, CO decreases while C(s) increases. Interestingly, as can be seen from Figure 1a, theoretical and experimental values for $H_2$ concentration agree until ~47% methane in biogas. At higher methane contents, experimental results show that the concentration of $H_2$ decreases. This discrepancy between theoretical and experimental values can be attributed to catalyst deactivation by carbon deposition, since theory predicts that the system is very prone

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to form solid carbon. Theoretical and experimental values agree perfectly for $CO_2$ concentration over the whole range of methane content in biogas. The maximum CO content obtained in experiments coincides with theoretical value. Figure 1b shows that $CH_4$ in exhaust gas increases abruptly with methane content in biogas. In fact, this can be due to deactivation of catalyst. Theoretical analysis shows a concentration much lower than experimental values, although thermodynamics also indicates that $CH_4$ concentration in exhaust gas increases with methane content in biogas. Figure 1c shows that high OCV values can be reached with biogas compositions richer in $CH_4$, since more reducing condition (lower $pO_2$ and higher $pH_2$) are achieved when % methane in biogas is elevated (Figure 1d).

Figure 2 shows the effect of methane content in biogas on the SOFC power. Results from thermodynamic analysis are compared with experimental results from Staniforth e Ormerod.[3] Obviously, current values predicted from thermodynamic analysis for a SOFC operating at 0.7V are higher than the current measured by a potentiostat. Irreversible losses are not included. SOFC efficiency can be estimated by dividing the experimental by the theoretical power. Interestingly, even for a biogas composition poor in $CH_4$ (only 10%) a power of ~200mWatts can be attained, with an efficiency of 60%. As biogas becomes richer in $CH_4$, SOFC power increases, even though the efficiency decreases. For an inlet mixture containing 41.63% of methane, the efficiency is of ~25%. However, this decreasing trend of efficiency with methane content in biogas is not a rule, since the value of power experimentally obtained will depend on the characteristics (composition, microstructure, etc.) of the SOFC anode material.

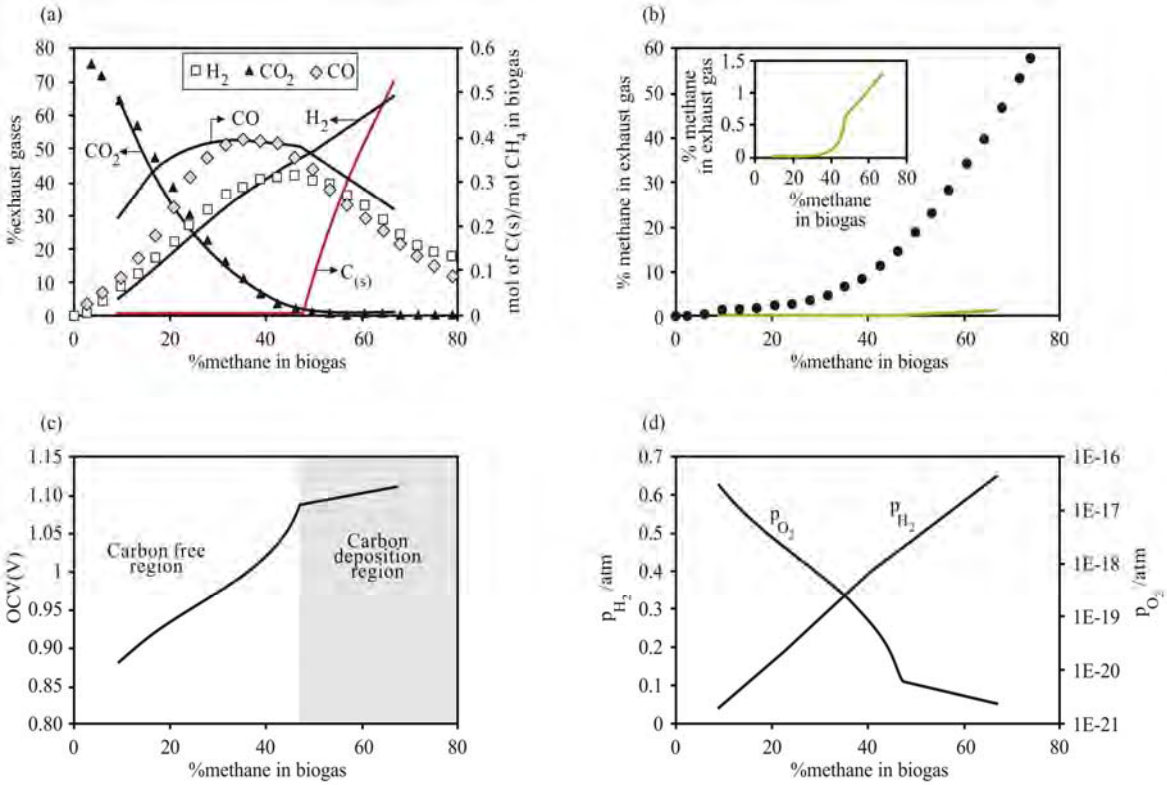


**Figure 1.** Effect of methane content in biogas on (a) exhaust gas composition ($H_2$, $CO_2$ and CO) and carbon deposition; (b) methane content in exhaust gas; (c) OCV; and (d) partial pressure of $H_2$ and $O_2$. Biogas flow rate = 6 ml/min, cell potential =0.7V. T=1.123K. Solid lines refer to theoretical values computed in the present work, and the markers are experimental values reported in Staniforth e Ormerod.[3]

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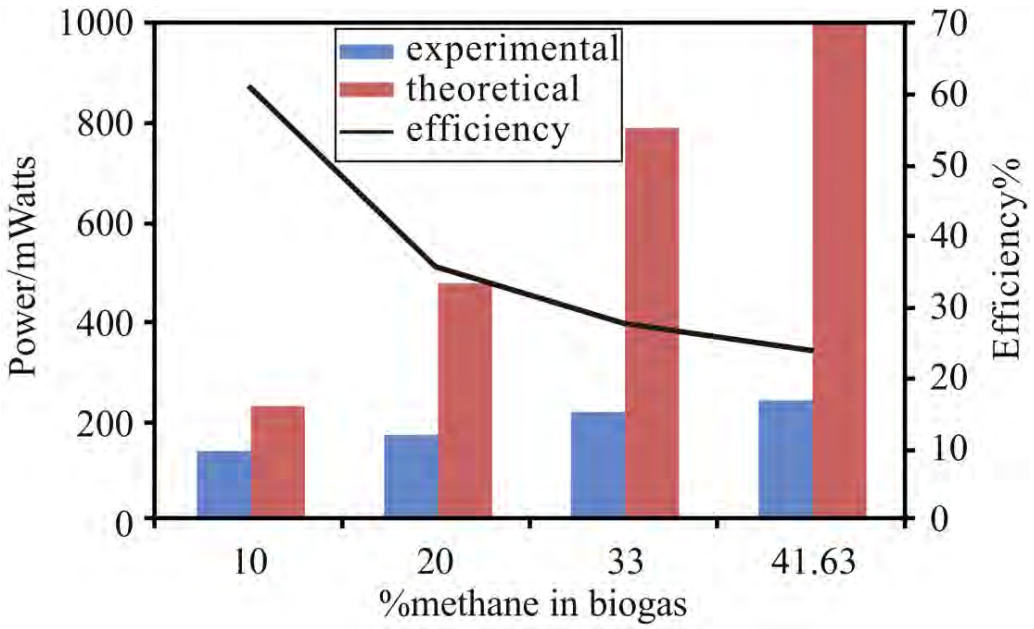


**Figure 2.** Effect of methane content in biogas on power and efficiency. Experimental values obtained from Staniforth e Ormerod.[3] Biogas flow rate = 6 ml/min, cell potential =0.7V. T=1.123K.

Figure 3a shows the equilibrium of the main species ($H_2$, CO, $H_2O$, $CO_2$, $CH_4$) and EMF as a function of current for an SOFC operating on biogas ($CH_4/CO_2$ molar ratio=2:1). Carbon deposition region disappears with increased load. CO concentration increases within the carbon deposition region. It should be noted that within carbon deposition region $H_2$ concentration and E change slightly, while $CH_4$ exists at a constant concentration. Only after the carbon deposition region $H_2O$ and $CO_2$ increase with significant consumption of $H_2$, resulting in lower values of E. Figure 3b depicts theoretical and experimental values of SOFC power operating on biogas and the efficiency. At the maximum value of power obtained experimentally, the efficiency is of ~50%. Thus, SOFCs operating on $CH_4$-rich biogas can achieve high efficiencies. Such performance will depend on optimization of anode material. While Figure 2 shows an efficiency of 25% for a methane rich biogas (41.63%), Figure 3b shows the possibility of achieving an efficiency of 50% for a biogas even richer in $CH_4$ (67%).

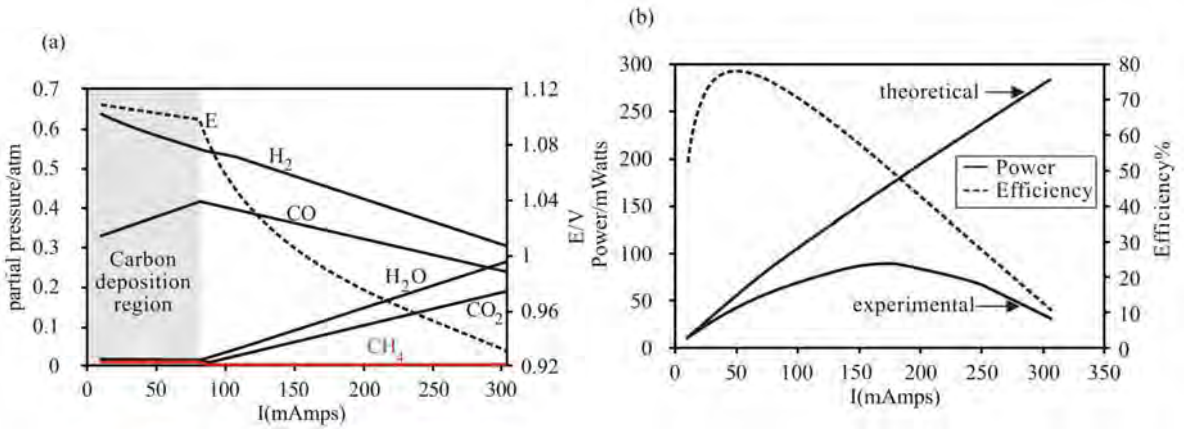


**Figure 3.** Effect of current on: (a) partial pressure ($H_2$, CO, $H_2O$, $CO_2$, $CH_4$), carbon deposition region and E; (b) power and efficiency. T=1123K. Feedstock: 1 $cm^3$ $min^{-1}$ $CH_4$ + 0.5$cm^3$ $min^{-1}$ $CO_2$. Experimental results from Laycock, Staniforth e Ormerod. [1]

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### 3.2 Effect of $CeO_2$ Addition on Prevention of Ni Poisoning by $H_2S$ During Biogas Conversion in SOFC Anodes

Figure 4 shows the effect of $CeO_2$ addition on Ni poisoning by $H_2S$. Figure 4a shows that within carbon deposition region $Ce_2O_2S$ phase can be formed, lowering $p_{H2S}$, which results in lower values of surface coverage (θ) of Ni catalyst when compared with a catalyst without addition of $CeO_2$ (Figure 4b). Within carbon deposition region, ceria assumes the reduced form ($CeO_{1.71}$). As current increases, ceria becomes more oxidized ($CeO_{1.83}$). The formation of $H_2O$ and $CO_2$, with the lowering of partial pressure of $H_2$, is unfavorable for formation of $Ce_2O_2S$ phase. Thus, there is a range of operating current at which $CeO_2$ can be effective in lowering θ values and, in this way, Ni poisoning. Even though $CeO_2$ can reduce θ values, it should be noted that Ni poisoning still occurs, since θ values fall in the region of diagram corresponding to chemisorption of S on Ni surface. However, the effects of Ni poisoning, e.g. reduction of SOFC power, will be lower in comparison with Ni catalyst without $CeO_2$ addition (Figure 4b). Clean Ni surface is observed only for θ values lower than 0.6 (such reference value was taken from diagram published in Wang e Liu[10]). Figure 4c shows the partial pressure of sulfur-containing species as a function of current. As can be seen, the partial pressure of $H_2S$ is much higher than that of other species. $SO_2$ is, from a practical point of view, not formed (partial pressure in the range of 1E-14-1E-12atm). This is reasonable to expect, due to extremely reducing anode atmosphere ($p_{O2}$ in the range of 1E-20-1E-18atm).

### 3.3 Ammonia Conversion in SOFC Anodes

Ammonia is a biogas contaminant. Typically, $NH_3$ is present at 100 ppm in biogas.[11] In this way, it is important to verify if SOFCs are tolerant to $NH_3$ and if it is possible to produce electricity from $NH_3$ with no formation of any undesirable nitrogen oxides. Figure 5a shows that, at 673K, $NH_3$ is totally converted into $N_2$ and $H_2$. Thus, at SOFC operating temperature, e.g. 1.123K, $NH_3$ is decomposed in $N_2$ and $H_2$. Figure 5b shows that, as current is drawn from the cell, $H_2$ is electrochemically oxidized to $H_2O$, while partial pressure of $N_2$ remains constant. In this way, $NH_3$ can be seen as fuel, not as contaminant. Figure 5c shows the partial pressure of nitrogen oxides as a function of current. From a practical point of view, nitrogen oxides are not formed during SOFC operation. This is reasonable to expect, due to extremely reducing anode atmosphere ($p_{O2}$ in the range of 1E-24-1E-17atm). Experimental reports for $NH_3$ utilization in SOFCs are in excellent agreement with theoretical findings of this work.

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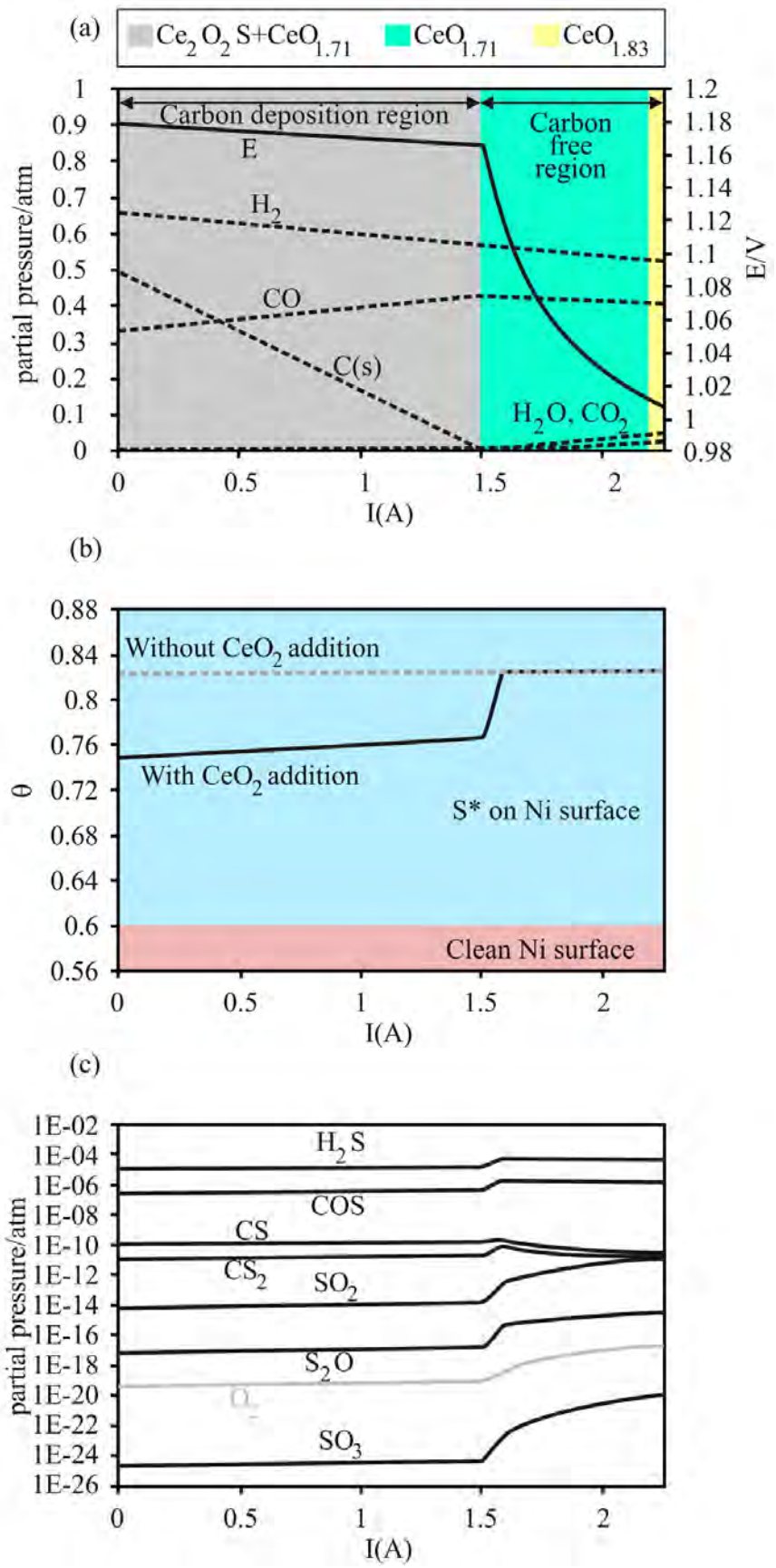


**Figure 4.** Effect of current on (a) Phase equilibria of Ce-O-S system, carbon deposition region, E and partial pressure of each species in the gas phase; (b) θ values; and (c) partial pressure of sulfur-containing species and $O_2$. $H_2S$ content=100 ppm; T=1.273K.

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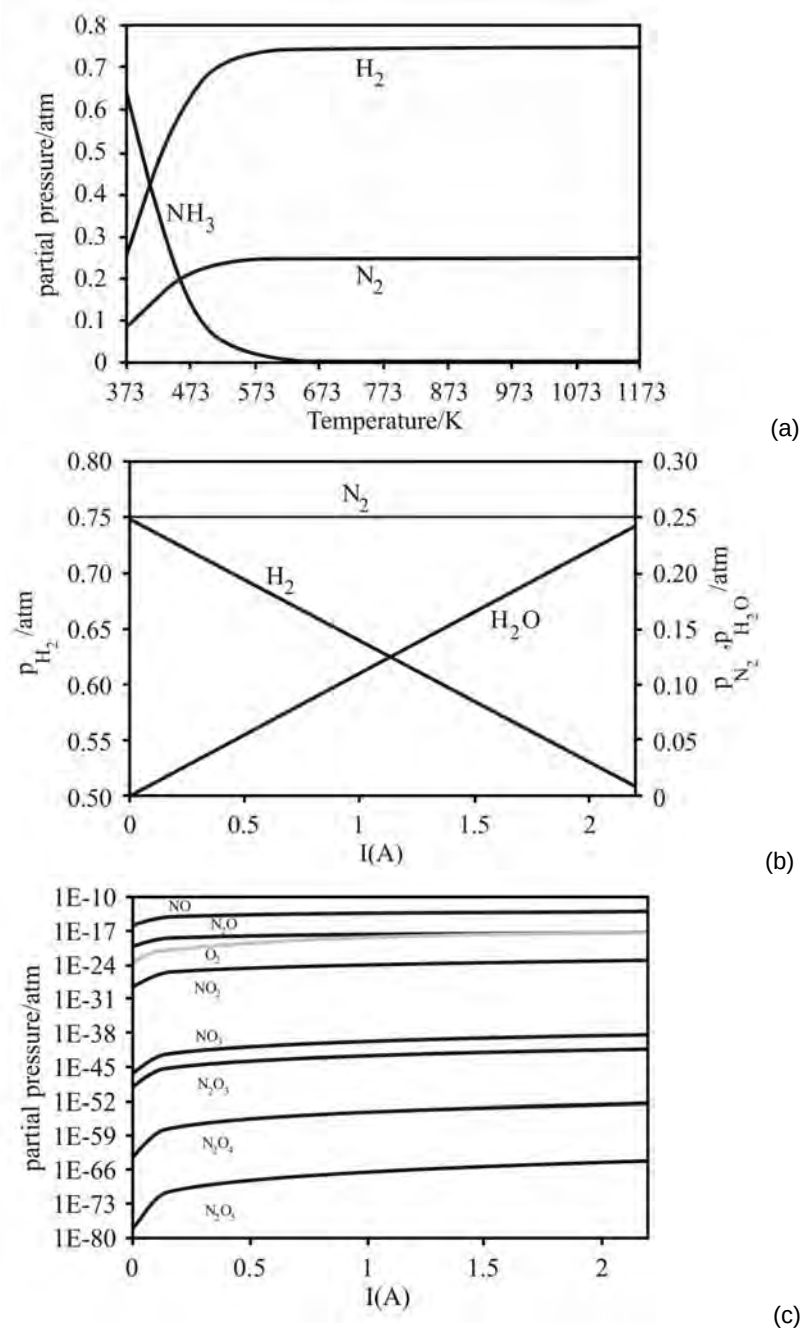


**Figure 5.** (a) Partial pressure of $NH_3$, $N_2$ and $H_2$ as a function of temperature; partial pressure, as a function of current, of; (b) $N_2$, $H_2$ and $H_2O$; and (c) nitrogen oxides, $O_2$. T=1123K for (b) and (c).

## 4 CONCLUSIONS

The present work was aimed at analyzing the direct feeding of biogas to SOFC anodes. The following conclusions can be drawn from the present study:

- it is theoretically demonstrated that SOFCs can run directly on biogas over a wide compositional range of methane. The results are experimentally validated. The electrical power varies with methane content of the biogas. The higher methane content in biogas, the higher the power. Methane is reformed by $CO_2$ producing $H_2$ and CO, which are electrochemically oxidized. High contents of methane result in significant carbon deposition, due to methane decomposition, forming graphite and $H_2$. Solid carbon can be gasified as

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current increases. At maximum power, an efficiency of 50% is achieved, as can be verified from experimental reports and theoretical results;

- under certain operating conditions, it is demonstrated that $CeO_2$ addition on Ni/YSZ can increase the resistance of the catalyst against sulfur poisoning by the $H_2S$. There is a range of operating current at which $CeO_2$ can be effective in lowering θ values and, in this way, Ni poisoning. Ceria becomes more oxidized as current increases. Sulfur oxides are not stable even when current is drawn from SOFCs;
- ammonia can be seen as a fuel. $NH_3$ is decomposed to $N_2$ and $H_2$, with subsequent electrochemical oxidation of $H_2$. Nitrogen oxides are not stable during SOFC operation.

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## REFERENCES

1 Laycock CJ, Staniforth JZ, Ormerod RM. Biogas as a fuel for solid oxide fuel cells and synthesis gas production: effects of ceria-doping and hydrogen sulfide on the performance of nickel-based anode materials. Dalton Transactions 2011;40: 5494−5504.
2 Huang J, Crookes RJ. Assessment of simulated biogas as a fuel for the spark ignition engine. Fuel 1998; 77: 1793-1801.
3 Staniforth J, Ormerod RM. Running Solid oxide Fuel Cells on Biogas. Ionics 2003; 9: 336- 341.
4 Steele BCH, Heinzel A. Materials for fuel-cell technologies. Nature 2001; 414:345-352.
5 Shiratori Y, Oshima T, Sasaki K. Feasibility of direct-biogas SOFC. Int J Hydrogen Energy 2008; 33: 6316-6321.
6 Ashrafi M, Pfeifer C, Pröll T, Hofbauer H. Experimental Study of Model Biogas Catalytic Steam Reforming: 2. Impact of Sulfur on the Deactivation and Regeneration of Ni-Based Catalysts. Energy & Fuels 2008; 22: 4190-4195.
7 Cheng Z, Wang JH, Choi YM, Yang L, Lin MC, Liu M. From Ni-YSZ to sulfur-tolerant anode materials for SOFCs: electrochemical behavior, in situ characterization, modeling, and future perspectives. Energy & Environmental Science 2011; 4: 4380-4409.
8 Rostrup-Nielsen JR. High temperature hydrogen sulfide chemisorption on nickel catalysts. Appl Catal 1981; 1: 303-314.
9 Rao YK. Stoichiometry and thermodynamics of metallurgical processes. Cambridge: Cambridge University Press; 1985.
10 Wang JH, Liu M. Computational study of sulfur–nickel interactions: A new S–Ni phase diagram. Electrochemistry communications 2007; 9: 2212-2217.
11 Kolbitsch P, Pfeifer C, Hofbauer H. Catalytic steam reforming of model biogas. Fuel 2008; 6: 701-706.