

Calculation of a Standard Reformed Biogas Composition and Testing on SOFC Anode Powders

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A standard reformed biogas composition, based on a 63% CH₄ 37% CO₂ input biogas, was defined by calculation. It is designed to resemble the composition of biogas that would enter a real SOFC stack, assuming 80% fuel utilization, and 25% recirculation of the anode off-gas. It is thermodynamically impervious to coking above 720°C. This gas composition was then used to test the catalytic reforming performance of nickel powder and La_{0.8}Ce_{0.1}Ni_{0.4}Ti_{0.6}O_{3-δ} at 900°C in the standard reformed biogas. No coking was seen on the powder samples by visual inspection after this test. The La_{0.8}Ce_{0.1}Ni_{0.4}Ti_{0.6}O_{3-δ} is designed to exsolve Ni nanoparticles when reduced. SEM pictures of the post-test sample show some small particles that may be exsolved nanoparticles, but further investigation is needed to confirm this. Ni powder was the better reforming catalyst, but sintered extensively in the 3 h test. The La_{0.8}Ce_{0.1}Ni_{0.4}Ti_{0.6}O_{3-δ} also showed reforming capability, and much better microstructural stability in the standard reformed biogas.

Introduction

The world faces a challenge of how to provide more affordable, clean electricity that does not increase carbon dioxide emissions. In order to do this, the use of renewable fuels and increasing the conversion efficiency of fuel to electricity will be key. Biogas is a renewable fuel, currently utilized in gas turbines at an electrical efficiency of 40%. However, solid oxide fuel cells offer potentially higher efficiencies, up to 60-70%. In order to accomplish this, the challenges of coking and sulphur poisoning in fuel cells running on biogas must be addressed. New anode materials must be synthesized that are not as susceptible to these problems, as the current state of the art Ni-YSZ anode.

Calculation of Standard Reformed Biogas

In order to prevent coking when using biogas in an SOFC, it is necessary to change the C-H-O ratio in the gas stream, reducing the mol.% of carbon relative to oxygen and hydrogen. There are two main ways to accomplish this; firstly, by catalytic partial oxidation by adding air. However, this lowers fuel efficiency as some of the fuel is combusted before the SOFC. Secondly, by recirculating the anode off-gas, which adds more steam and carbon dioxide to the input biogas to the SOFC. These are also reforming agents for the biogas. Fig. 1 shows a schematic of an SOFC system running on biogas.

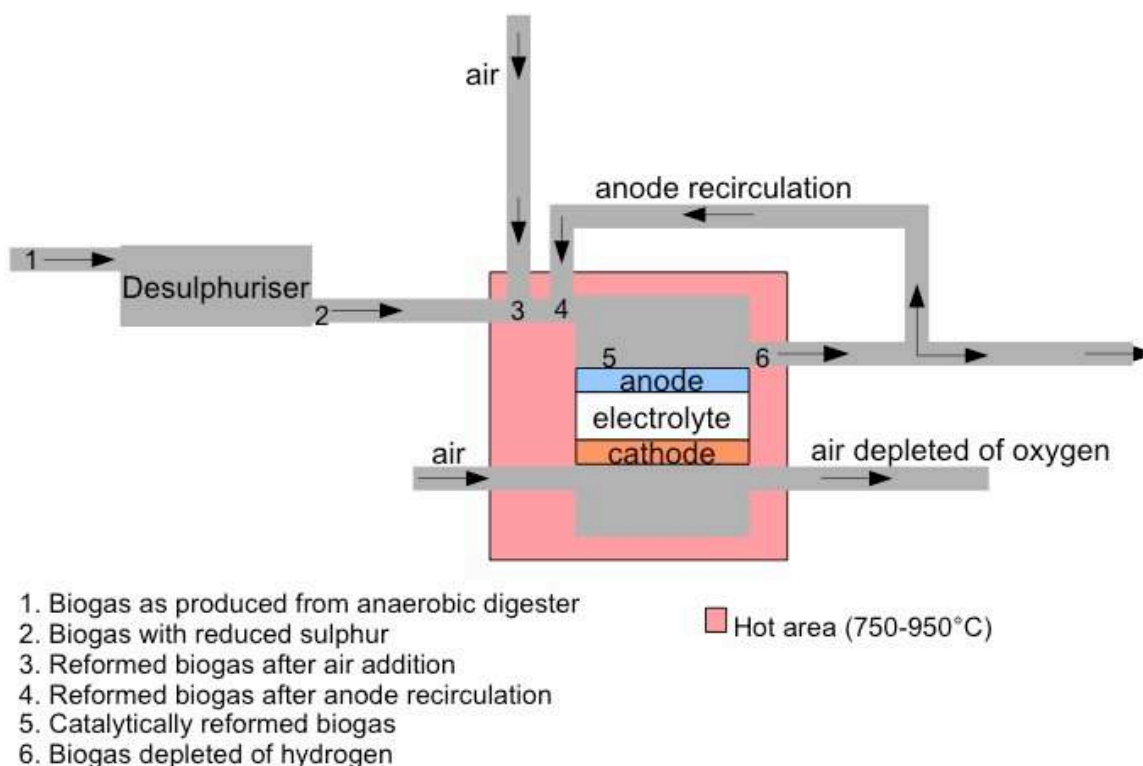


Figure 1. Simple schematic of an SOFC running on biogas. The numbers denote various compositions at different points in the system.

In this paper, a standard reformed biogas, composition at no.4 in Fig. 1 is defined, assuming that no air is added, but rather a fraction of the anode off-gas is recirculated. In order to do this, composition at no. 2 in Fig. 1, the input biogas, must be defined, as well as the fuel utilization in the SOFC, and the recirculation ratio, which is the fraction of the anode off-gas that is recirculated.

The input biogas composition was determined by taking an average and median across a range of methane levels in biogas, reported for different feedstocks (1,2). These were both close to 63% methane, so this was chosen as the methane level, and the balance was assumed to be carbon dioxide. The fuel utilization was determined by considering a variety of SOFC systems running on methane or biogas (3-9), and a fuel utilization of 80% was chosen as a representative value. A figure of 25% was chosen for the recirculation ratio. This is lower than for a methane-based system, because the carbon dioxide in the biogas acts as a reforming agent, for dry reforming of methane according to eq. 1. Therefore, the input biogas composition was set as 63% methane, 37% carbon dioxide, corresponding to composition at no. 2 in Fig. 1.



In order to calculate the standard reformed biogas composition at no. 4 in Fig. 1, an iterative approach was used to calculate a steady state composition. It was assumed that the biogas was input to the system at a steady rate, and that no air was added to the anode compartment, and that the stack was operating at 900°C. It was assumed that the methane in the biogas was utilized by the SOFC stack according to eq. 2, at a fuel utilization of

73.3%. The single pass utilization for the biogas is 73.3%, and the overall fuel utilization is 80%.



Thermodynamic modeling was carried out on the output gases from the stack, composition no. 6 in Fig. 1. This showed that at thermodynamic equilibrium at 900°C, the unused fuel would be almost totally converted to carbon monoxide and hydrogen. It was assumed that the gases coming out of the stack would be at thermodynamic equilibrium. 25% of the anode off-gas was then recirculated and added to the input biogas. Then the cycle described above was repeated, by assuming 73.3% fuel utilization of the input biogas, plus the recirculated 25% of the anode off-gas. Since this contained carbon monoxide and hydrogen, these were included as fuels to be used by the stack, and it was assumed that these were oxidized to carbon dioxide and steam at a fuel utilization of 73.3%, as well as the methane from the input biogas. Therefore, a second output gas composition was determined, and this process was modeled through repeated cycles, until a steady-state composition of gases was obtained. These figures were adjusted slightly and rounded, to give the standard reformed biogas composition. This is shown, together with the input biogas composition, in Fig. 2.

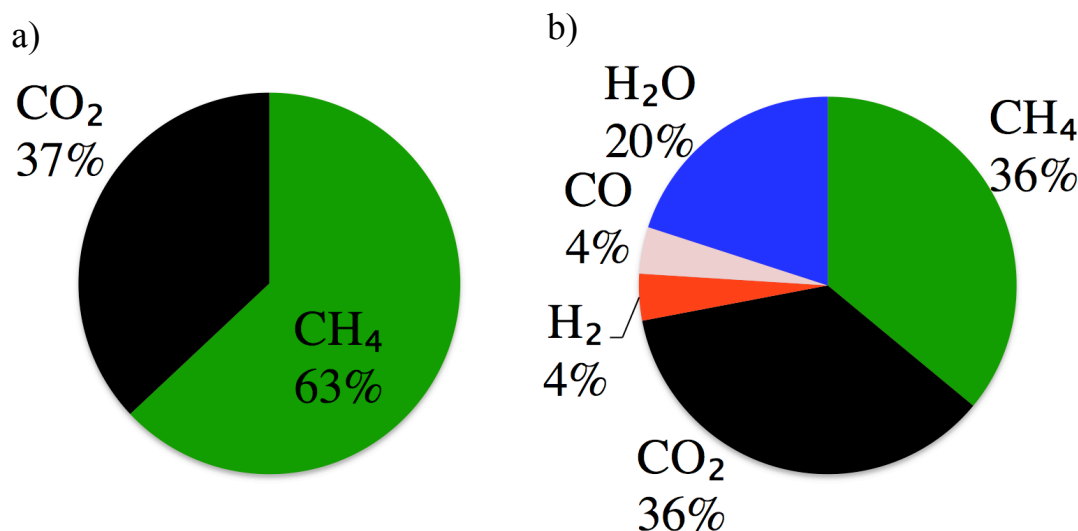


Figure 2. a) Composition of input biogas and b) standard reformed biogas

The gas composition at thermodynamic equilibrium for the standard reformed biogas composition at no. 4 Fig.1 was calculated as a function of temperature. This showed that above 720°C, there was no solid carbon, or coke in the equilibrium composition. Therefore this gas composition should not produce coking in the SOFC operating temperature range 750°C - 900°C.

Experimental

The catalytic activity of two powder samples was compared at 900°C in 300 ml/min of gas; consisting of 285 ml/min of the standard biogas composition, with the balance argon. The gases were mixed to the correct ratio using mass flow controllers (Bronkhorst).

The samples were placed on a sintered quartz frit inside a quartz reactor. Nickel oxide (0.636 g, nickel mass 0.5 g, Pi-Kem) and the perovskite $\text{La}_{0.8}\text{Ce}_{0.1}\text{Ni}_{0.4}\text{Ti}_{0.6}\text{O}_{3-\delta}$ (0.5 g, University of St Andrews) were tested. Each sample was reduced in 5% H_2/N_2 for 30 min, then switched to standard reformed biogas for 3 h. The outlet gases were analysed by GC (HP) MS-RGA (MKS Instruments), and a dewpoint sensor (Vaisala).

Results and Discussion

The outlet gas compositions from the catalytic reforming tests on the powder samples are in Fig. 3. A C-H-O balance was calculated for the amount of gases going in and coming out. The maximum error was 20% on the values in Fig. 3; this is mainly due to inherent error in quantifying precisely the levels of hydrogen on the MS-RGA. It can be seen that the LCNT sample partially reforms the standard reformed biogas, and the nickel reforms it much more.

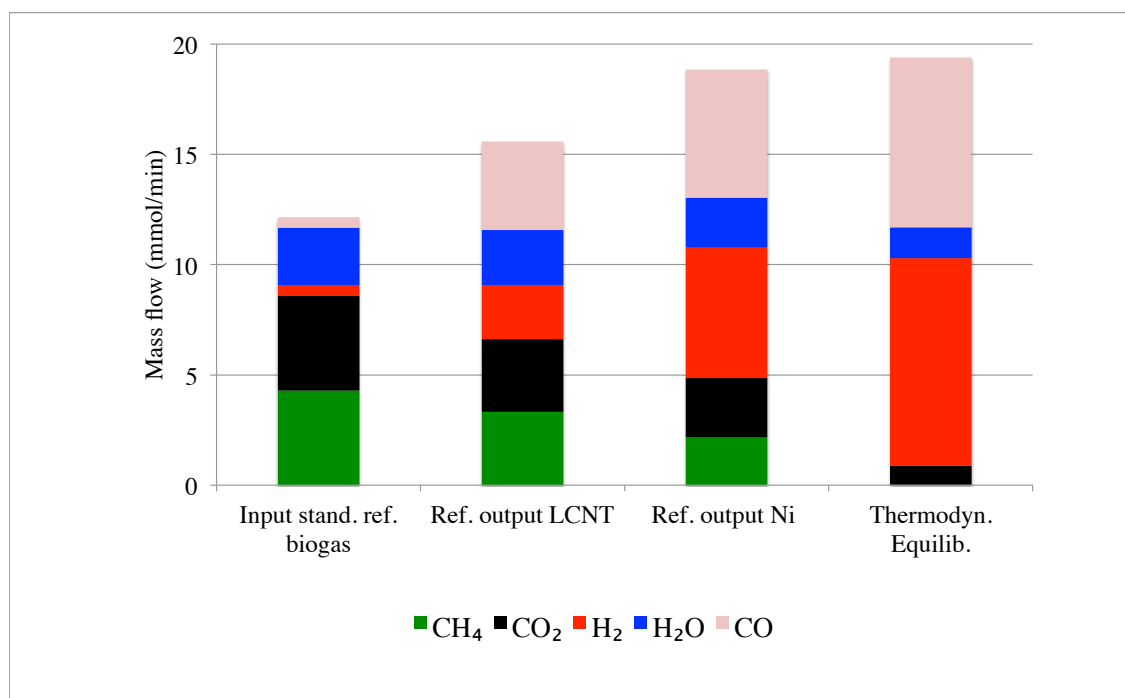


Figure 3. Outlet gas compositions from catalytic reforming tests, with the standard reformed biogas composition, and the composition at thermodynamic equilibrium for comparison. LCNT = $\text{La}_{0.8}\text{Ce}_{0.1}\text{Ni}_{0.4}\text{Ti}_{0.6}\text{O}_{3-\delta}$.

However, BET analysis of the powders before and after testing shows that the NiO has a BET surface area of $3.7 \text{ m}^2.\text{g}^{-1}$ before testing, and $0.5 \text{ m}^2.\text{g}^{-1}$ after testing, and the LCNT had a surface area of $1.4 \text{ m}^2.\text{g}^{-1}$ before, and $1.0 \text{ m}^2.\text{g}^{-1}$ after testing. Fig. 4 shows SEM images of a) LCNT and b) Ni powders after testing at 900°C in the standard reformed biogas. The Ni powder coarsens and sinters quite severely in the biogas during the test, whereas the LCNT does not coarsen as much. No coking was apparent on either sample after testing by visual inspection. LCNT is an A-site deficient perovskite that was designed to exsolve B-site cations upon reduction in hydrogen, producing nanoparticles

of Ni. Nanoparticles such as these can enhance the catalytic activity of perovskites, according to the principles outlined in (10).

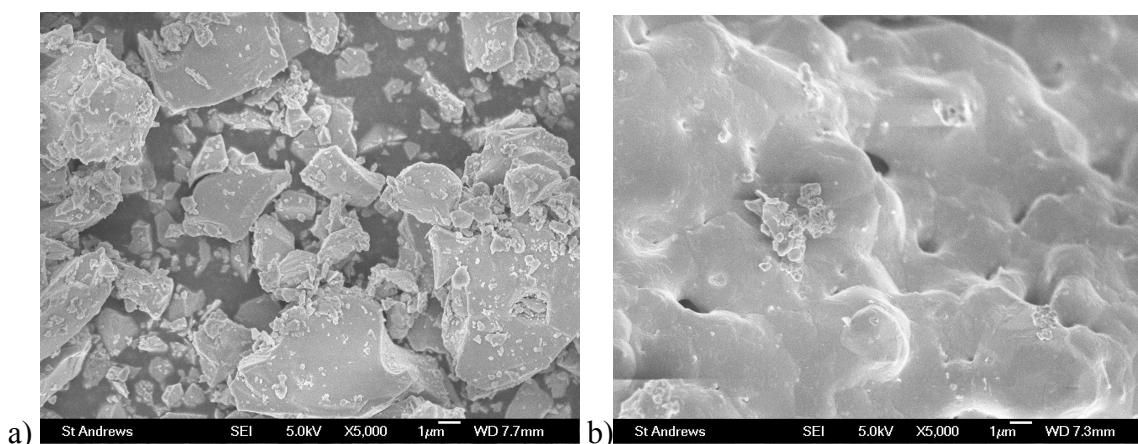


Figure 4. SEM images of powders after testing at 900°C in the standard reformed biogas for 3 h, a) $\text{La}_{0.8}\text{Ce}_{0.1}\text{Ni}_{0.4}\text{Ti}_{0.6}\text{O}_{3-\delta}$ (LCNT), and b) Ni

Fig. 5 compares a pellet sample of LCNT after reduction in 5% H_2/N_2 at 900°C, to the LCNT powder sample tested in standard reformed biogas. It can be clearly seen that Ni nanoparticles are present on the surface of the sample reduced in 5% H_2/N_2 . However, it is unclear from Fig. 5 whether there are any nanoparticles present. The nanoparticle formation may have been inhibited due to either the different gas mixture of the standard reformed biogas, or the different $p(\text{O}_2)$ compared to the 5% H_2/N_2 . A further experiment will be carried out to investigate whether nanoparticles can be produced in biogas or not.

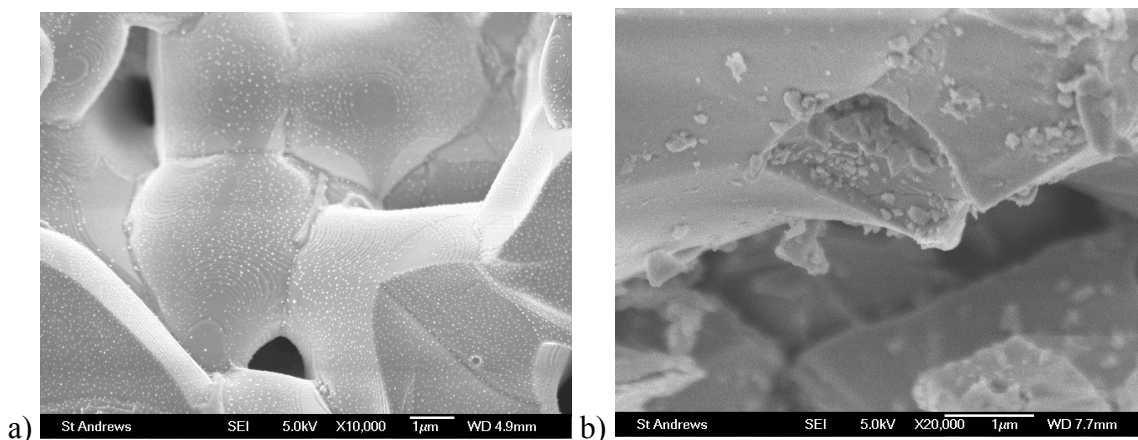


Figure 5. a) Surface of a pellet of $\text{La}_{0.8}\text{Ce}_{0.1}\text{Ni}_{0.4}\text{Ti}_{0.6}\text{O}_{3-\delta}$ with Ni nanoparticles produced after reduction in 5% H_2/N_2 at 900°C, b) surface of $\text{La}_{0.8}\text{Ce}_{0.1}\text{Ni}_{0.4}\text{Ti}_{0.6}\text{O}_{3-\delta}$ powder after 3 h test in standard reformed biogas at 900°C.

Conclusions and Further Work

A standard reformed biogas composition has been defined, by defining an input biogas from literature, assuming 80% fuel utilization in the SOFC stack, with 25% recirculation

of the anode off-gas, and calculating the steady state gas input to the SOFC stack. Determination of this gas composition allows catalytic reforming tests of potential anode powders, and fuel cell testing to be carried out in a gas composition representative of that which would be encountered in a real SOFC stack.

Ni powder and $\text{La}_{0.8}\text{Ce}_{0.1}\text{Ni}_{0.4}\text{Ti}_{0.6}\text{O}_{3-\delta}$ powder have been tested as reforming catalysts in the standard reformed biogas composition, and although Ni performs better as a reforming catalyst, it undergoes significant sintering during a 3 h test at 900°C compared to the $\text{La}_{0.8}\text{Ce}_{0.1}\text{Ni}_{0.4}\text{Ti}_{0.6}\text{O}_{3-\delta}$. Further testing will be done using the standard reformed biogas composition to test SOFC anodes, and to investigate whether the nanoparticles expected to form in biogas or not.

Acknowledgments

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