



Carbon deposition behaviour in metal-infiltrated gadolinia doped ceria electrodes for simulated biogas upgrading in solid oxide electrolysis cells



V. Duboviks^{a,*}, M. Lomberg^a, R.C. Maher^b, L.F. Cohen^b, N.P. Brandon^a, G.J. Offer^c

^a Department of Earth Science and Engineering, Imperial College, London SW7 2BP, United Kingdom

^b Department of Physics, Imperial College, London SW7 2BP, United Kingdom

^c Department of Mechanical Engineering, Imperial College, London SW7 2BP, United Kingdom

HIGHLIGHTS

- We examine carbon deposition on SOC fuel electrodes under bias and at open circuit.
- We perform *in situ* and *ex situ* Raman analysis of CGO-based electrodes.
- Electric bias facilitates deposition of carbon filaments under electrolysis.
- Amorphous carbon is deposited in Ni-CGO electrode due to dry reforming.
- Cu infiltrated CGO electrodes suppress carbon deposits in biogas.

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ABSTRACT

One of the attractive applications for reversible Solid Oxide Cells (SOCs) is to convert CO₂ into CO via high temperature electrolysis, which is particularly important for biogas upgrading. To improve biogas utility, the CO₂ component can be converted into fuel via electrolysis. A significant issue for SOC operation on biogas is carbon-induced catalyst deactivation. Nickel is widely used in SOC electrodes for reasons of cost and performance, but it has a low tolerance to carbon deposition. Two different modes of carbon formation on Ni-based electrodes are proposed in the present work based on *ex-situ* Raman measurements which are in agreement with previous studies. While copper is known to be resistant towards carbon formation, two significant issues have prevented its application in SOC electrodes – namely its relatively low melting temperature, inhibiting high temperature sintering, and low catalytic activity for hydrogen oxidation. In this study, the electrodes were prepared through a low temperature metal infiltration technique. Since the metal infiltration technique avoids high sintering temperatures, Cu–Ce_{0.9}Gd_{0.1}O_{2–δ} (Cu-CGO) electrodes were fabricated and tested as an alternative to Ni-CGO electrodes. We demonstrate that the performance of Cu-CGO electrodes is equivalent to Ni-CGO electrodes, whilst carbon formation is fully suppressed when operated on biogas mixture.

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1. Introduction

The EU has committed to a 20% reduction in greenhouse gas (GHG) emissions compared to 1990 levels by 2020. To reach this objective, the EU Council set a binding target for alternative energies of 20% and a target of 10% for substitution of fossil with biofuels at 2020 [1]. One promising renewable fuel is biogas which

has the potential to contribute considerably to greenhouse gas emission reduction if used as a biofuel [2]. Biogas production has been steadily growing since 2001 [3]. Currently, there is an increasing demand for biogas as a vehicle fuel or for injection to the natural gas grid [3].

Biogas can be sustainably produced by the anaerobic digestion of biodegradable materials such as cow manure, plant material and other green or animal waste [3]. Biogas from organic waste digesters usually contains from 60% to 70% CH₄, from 30% to 40% CO₂ and 1% N₂ [4]. However, the presence of CO₂ in fuel mixtures burned in internal combustion engines (ICEs) reduces the power

* Corresponding author.

E-mail address: dubovik.vladislav@gmail.com (V. Duboviks).

output, especially for lower compression ratios [5,6]. Biogas fuelled ICEs also suffer from high levels of hydrocarbon emissions as a result of incomplete fuel combustion [6]. To enable the efficient use of biogas in most applications the gas must be upgraded, i.e. carbon dioxide, which constitutes a large part of the raw biogas, must either be separated from methane or converted into useful fuel. Since both CH_4 and CO_2 are identified as the main GHGs, biogas upgrading can serve both to minimise GHG emissions and increase their utility. Catalytic reforming of CH_4 with CO_2 is a promising technology for utilization and upgrade of these GHGs [7,8]. The dry reforming reaction was first proposed by Fischer Tropsch in 1928 and results in a mixture of H_2 and CO , often referred as synthesis gas (syngas). It is a more energy efficient process compared to steam reforming of methane and has significant potential in energy conversion and storage applications. The resulting gas mixture also has a higher CO/H_2 ratio making it suitable for the synthesis of higher hydrocarbons [7,9].

For efficient biogas upgrading it is desirable to couple the process with the engine exhaust or another source of high grade heat [4,10]. The output gas composition of the reactor will depend on its temperature. Dry reforming is an endothermic reaction and when the fuel mix contains 70% CH_4 and 30% CO_2 , it will only reach full conversion above 900 °C (as calculated using the Gibbs energy minimization method with HSC Chemistry software.) [11] In many cases such high grade heat is not available and CO_2 is still present at the outlet of the reactor. Electrolysis has been shown to be economically viable and technologically feasible way of converting the CO_2 into useful fuel [12–14].

A major problem inhibiting large scale commercial application of biogas upgrading with Solid Oxide Cell (SOC) technology is catalyst deactivation due to carbon deposition [7,15]. Thermodynamic calculations have been carried out using the HSC Chemistry software to evaluate the risk of carbon formation depending on the gas composition on the electrode considered in this study. The points in Fig. 1 represent the gas compositions that are considered for testing, and the dashed red line separates the region where carbon formation is predicted thermodynamically. 12% CO – 14% CO_2 – 16% CH_4 – 58% H_2 gas composition is the thermodynamic equilibrium mixture in the gas phase at 600 °C. Again, the

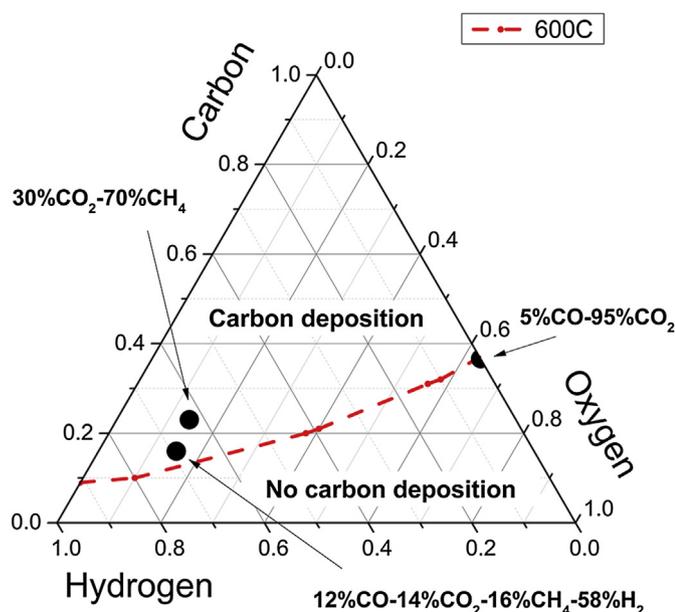


Fig. 1. Carbon deposition limits at 600 °C in C–H–O ternary diagram.

calculations have been performed using the Gibbs energy minimization method and do not take into account the presence of a catalyst or kinetic effects. It has been reported previously that no carbon formation occurs when operating cells in fuel cell mode in biogas mixtures contrary to the predictions of thermodynamic calculations [16]. Equally, it has been shown in the previous work, that kinetics may also cause an adverse effect [17]. Under polarisation in electrolysis mode, oxygen species are carried away from the fuel electrode to the air electrode through the electrolyte thus increasing the risk of carbon formation on the fuel electrode.

As shown in Fig. 1, a gas composition primarily consisting of CO_2 with only 5% of CO lies almost on the border between the two regimes, while still in the region where carbon formation is thermodynamically unfavourable. However, if the proportion of CO is even slightly increased, there is the potential for it to cause carbon formation. In this case, from the thermodynamic point of view, the main candidate for formation of surface carbon deposits is CO disproportionation. The presence of methane, on the other hand, introduces another potential mechanism of carbon formation – namely the dissociation of CH_4 into C and H [18,19]. As a result, for SOCs operating on biogas fuels two forms of morphologically different carbon deposits are possible – amorphous carbon causes less damage and is easier to remove from the catalyst compared to graphitic types of carbon. Tracer temperature programmed oxidation experiments (a catalytic test carried out under $^{13}\text{CH}_4/^{12}\text{CO}_2$) have indicated that amorphous forms of carbon in Ni_3C originates mostly from the methane dissociation reaction [20]. More stable carbon that is likely to encapsulate Ni particles or form graphitic whiskers arises from CO disproportionation (Boudouard reaction) [20].

Therefore, it is clear that it is necessary to prevent carbon deposits forming on the electrodes in order to enable SOCs to be successfully applied to biogas upgrade. Carbon formation on Ni-based electrodes can result in metal dusting – permanently damaging the electrode, whilst carbon deposition on Cu-based electrodes was reported to deactivate the cell by filling the pores without causing physical damage [21,22]. However, it should be noted that although not experimentally observed, filling the pores with carbon is likely to lead to cracking of the electrode eventually. At the same time, a major obstacle in developing Cu-based electrodes is the relatively low melting temperature of CuO – 1200 °C [23]. This is well below typical YSZ and CGO sintering temperatures.

Wet infiltration techniques avoid the need for elevated processing temperatures and offer a means to independently control the triple phase boundary (TPB) density and pore size. This fabrication technique is well described in the literature [24–26]. Briefly, a porous ceramic matrix is prepared by tape casting or screen-printing, and sintered without a metallic phase. The metallic phase is then introduced in a separate step which does not require high-temperature processing. Generally, the ceramic matrix is impregnated with the aqueous solution of a metal nitrate (e.g. $\text{Ni}(\text{NO}_3)_2$) and heated to ca. 500 °C to decompose the nitrate. Such low fabrication temperatures allow for a wide range of catalyst admixtures, including Cu, to be introduced to the matrix, while significantly lowering the metal content required to obtain a fully percolated metal network [27]. It was demonstrated that percolation occurs at only 9–14 vol% for impregnated electrodes, compared to ca. 30 vol% required for conventional electrodes [25,27,28]. Additionally, modelling studies and Focused Ion Beam (FIB) tomography have shown that the TPB density in infiltrated electrodes can be increased by an order of magnitude compared to conventional electrodes [29,30]. Another approach to the fabrication of Cu-based electrodes involves using refractory metal additives to promote sintering at lower temperatures [31].

In order to limit or even prevent the carbon-induced electrode

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