

# Electrochemical Oxidation of Syngas on Nickel and Ceria Anodes



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## ABSTRACT

Fuel flexibility of solid oxide fuel cells enables the use of low cost and practical fuels like syngas. Understanding of the oxidation kinetics with syngas is essential for proper selection of anode material and its design optimization. Using nickel and ceria pattern anodes, we study the electrochemical oxidation of syngas in both dry and wet environments. In dry environment, the polarization resistance of CO oxidation drops drastically with the addition of small amounts of hydrogen to CO gas stream. In wet environment (4 % moisture), the polarization resistance of CO is only slightly higher than syngas and hydrogen. Observation in the first case is related to the hydrogen preferential oxidation whereas latter is a combined effect of water gas shift reaction and preferential oxidation of hydrogen. Kinetic modeling is also carried out to understand hydrogen and CO co-oxidation. Simulation suggests that CO, besides hydrogen, may also electrochemically oxidize depending upon its concentration in the syngas. At higher concentration, CO electrochemical oxidation may be non-negligible especially in case of ceria anodes.

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## 1. Introduction

Solid oxide fuel cells (SOFCs) are considered as promising candidates for next generation stationary power production because they are efficient and fuel flexible. Besides hydrogen, various hydrocarbon based fuels such as biomass and coal derived synthetic gas (syngas), natural gas, and biogas etc. are suggested as potential fuels for SOFC as they can be fed directly to the anode after necessary cleaning [1–4]. Syngas is mainly a mixture of hydrogen, CO and varying concentrations of CH<sub>4</sub>, H<sub>2</sub>O, CO<sub>2</sub>, N<sub>2</sub> and other impurities. Natural gas and biogas can also be reformed to produce a mixture of hydrogen and CO. Thus in all these fuels, a mixture of hydrogen and CO is ultimately expected to undergo electrochemical oxidation. When CO/H<sub>2</sub> mixture is fed to SOFC anode, overall (electro-)chemical reactions can be described using the Kroger-Vink notation:



Here  $\text{O}_\text{O}^{\times}$  is a regular oxide ion and has no effective charge ( $x$ ) and the oxide ion vacancy,  $\text{V}_{\text{O}}^{\bullet\bullet}$ , has an effective charge +2.

Total faradaic current is a result of charge transfer reactions (1) and (2). The relative contribution of both of these reactions is not very clear so far. Several experimental [5–9] and modeling [10–15] studies have been conducted to understand the effect of syngas composition on the cell performance. For example, at low CO concentrations, even up to equimolar CO/H<sub>2</sub> mixture, cell performance is almost the same as obtained by moist hydrogen [6]. Sasaki [8] reported only 4 % drop in the cell voltage for CO/H<sub>2</sub> = 7:3 (at 1000 °C and 0.32 A. cm<sup>-2</sup>) indicating only insignificant effect on the cell performance. Sukeshini [9] observed monotonous decrease in the maximum power density with increase in CO/H<sub>2</sub> ratio, and the degradation was not more than 25 % for CO/H<sub>2</sub> = 3:1. For very high CO fractions, CO/H<sub>2</sub> = 9:1, significant drop in the cell performance at 950 °C is reported [7]. These studies are conducted for short term operation and proved good performance for a wide range of CO/H<sub>2</sub> ratios.

It is known that the rate of electrochemical oxidation of CO is 2–3 times slower than that of hydrogen [5]. Thus, hydrogen is expected to oxidize preferentially in syngas mixtures [16]. It is worthwhile remembering that steam is the product of hydrogen oxidation which in turn promotes CO conversion via water-gas-shift (WGS) reaction (reaction (3)) thus producing hydrogen. Whether CO electrochemically oxidizes as well, is very uncertain. In modeling studies, two different approaches are considered to address this concern. Firstly, it is commonly assumed that only hydrogen participates in electrochemical oxidation while CO is converted to hydrogen via WGS reaction. So total current density is solely

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attributed to electrochemical oxidation of hydrogen. Secondly, some authors [10,12] have taken care of the current fraction from both CO and hydrogen oxidation on the basis of their electrochemical oxidation rates in CO/CO<sub>2</sub> and H<sub>2</sub>/H<sub>2</sub>O environments. Both of these approaches have their own limitations because of non-electrochemical oxidation of CO in first approach and linear coupling between hydrogen and CO electrochemistry in the latter. Recently, Bao et al. [11,17] proposed a non-linear coupling of hydrogen and CO electrochemistry in order to correlate total current output with syngas composition. They developed a model based on macroscopic electrochemistry and species transport in complex microporous structure. Their study concludes that as CO/H<sub>2</sub> ratio increases, hydrogen current fraction decreases which they associated to the contribution of electrochemical oxidation of CO. However, as their work did not take into account the elementary reactions explicitly, further work is required to understand possible electrochemical oxidation of CO in syngas mixtures.

Using syngas as an SOFC fuel requires electromechanically stable anode materials besides high electrocatalytic activity. Practically viable anodes are expected to maximize the (electro-)chemical oxidation (reactions (1–3)) and suppress coke formation and the influence of syngas contaminants like H<sub>2</sub>S and HCl. The state-of-the-art Ni/YSZ anode fulfills most of the requirements related to catalysis and thus widely used in pure hydrogen feed. However, inherited poor redox stability of nickel [18] and carbon intolerance [19] make Ni/YSZ anodes less suitable for use in syngas. Recently ceria-based materials have gained considerable attention as possible alternative anodes for hydrocarbon feeds [20,21]. In non-electrochemical applications, ceria has been extensively investigated as a support material for various reactions like hydrocarbon oxidation, WGS conversion, and CO preferential oxidation (CO-PROX) [22]. As an anode material, ceria has shown even better catalytic activity for hydrogen and CO oxidation compared to nickel [23,16]. This superior activity of ceria is a result of extended reaction sites on ceria surface that are limited to geometrical interface between ionic and electronic phases in case of nickel anode. Conversely, the electronic conductivity and WGS catalytic activity of pure ceria is too low to be used as an anode in syngas environment [24,25]. Electronic conductivity of ceria (0.2–2.0 S. cm<sup>-1</sup>) is 3–4 orders of magnitude lower than that for nickel (21.4 × 10<sup>3</sup> S. cm<sup>-1</sup>) at 1000 °C [26]. Thus the added advantages of both of these materials have been combined and tested for syngas applications with promising results compared to Ni/YSZ [27,28]. Besides nickel/ceria cermet, copper/ceria cermet has also been tested in syngas with better performance than Ni/YSZ [29]. In copper/ceria cermet, copper primarily provides electronic conductivity to the anode and is otherwise catalytically inert [30]. While major focus of these studies was the development of better performing anode, very little attention has been paid on understanding the electrochemistry of fuel oxidation on ceria. Available knowledge of possible reaction mechanism(s), rate-limiting processes and WGS catalytic activity of ceria at cell operating temperature is very limited [16,26,31–34]. Therefore, it is essential to investigate the reaction kinetics on nickel and ceria separately in order to realize the commercialization of nickel/ceria cermet anodes.

Studying reaction kinetics with porous and cermet structures has their own inherent disadvantages. For example, the gas diffusion impedance in case of symmetrical cells can be significant at low frequencies [35]. Since the objective of this work is to study the kinetics, all such effects arising out of geometrical parameters need to be avoided. Hence we use pattern cells where the geometry is well defined and the reactions can be localized. Since the current drawn is very small, the gas diffusion impedance is not expected to play any significant part in determining the response [23]. The spectra obtained are expected to be easier to analyze as well.

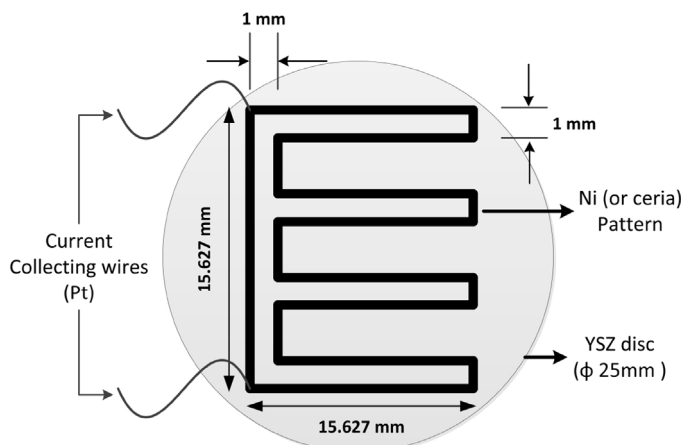


Fig. 1. Schematic of Ni and ceria pattern cells.

Previously, using nickel and ceria pattern cells, we mainly focused on the oxidation of CO/H<sub>2</sub> dry mixtures [36]. Results with pure hydrogen and CO [16] were also included for comparison. From these studies we concluded that hydrogen is preferentially oxidized in CO/H<sub>2</sub> mixtures. This conclusion was based on the observation that while adding small amounts of hydrogen to CO feed stream, impedance spectra were very close to that of pure hydrogen. In this work, we intend to extend the discussion using humidified syngas environment (4 % moisture). The results in humidified environment are compared with those obtained in dry environment. This sort of comparison between nickel and ceria anodes has not been reported before. Further, we developed an elementary kinetic model for CO/H<sub>2</sub> mixtures based on the previous models for pure hydrogen and CO oxidation in order to study the effect of WGS conversion and syngas compositions.

## 2. Experimental and modeling methodology

### 2.1. Cell preparation

Electrolyte supported, nickel and ceria pattern electrode cells are used in this study. Symmetrical cell configuration was chosen to study the anode processes. 8 % YSZ substrates (25 mm diameter and 250 μm thick) were obtained from Fuel cell materials ([www.fuelcellmaterials.com](http://www.fuelcellmaterials.com)). Nickel and ceria were deposited on to the substrates through a stainless steel mask using DC magnetron sputtering (AJA International, ATC 2600 UHV). Thickness of nickel and ceria patterns was 1.780 μm and 500 nm, respectively. Details of the sputtering process are reported previously [16,37]. Fig. 1 shows the schematic of the pattern cells. Area specific triple-phase-boundary (TPB) length of the cells is 0.203 m. cm<sup>-2</sup>.

### 2.2. Cell test station

A schematic representation of quartz reactor tube containing ceramic cell holder is shown in Fig. 2. Cell was placed between two macro-porous ceramic supports also working as gas distributors. Gold mesh was applied on both sides of the cell for current collection. A small weight was placed on the top distributor to ensure a good contact between gold mesh and the cell. Quartz tube was placed inside a temperature controlled furnace for testing at desired temperature. For humidified experiments, the gas mixtures were saturated in a temperature controlled humidifier.

Electrochemical impedance spectroscopy was carried out to identify different processes affecting the cell operation using Gamry Potentiostat (R600). EIS measurements were conducted with AC perturbation of 10 mV, between 700 °C to 850 °C and in

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