

## Methane Oxidation via Lattice Oxygen under Solid Oxide Fuel Cell Conditions

Michael van den Bossche and Steven McIntosh\*

<sup>1</sup>Department of Chemical Engineering, The University of Virginia, Charlottesville, VA 22904 (USA)

\*mcintosh@virginia.edu

### Introduction

Solid Oxide Fuel Cells (SOFCs) are considered one of the leading technologies for efficient future power generation. Like all fuel cells, SOFCs consist of three main components: a cathode (air electrode), an anode (fuel electrode), and an electrolyte. Under operation, molecular oxygen is reduced to oxygen anions at the cathode, using electrons supplied from an external circuit. The generated anions then migrate to the anode through a dense ceramic electrolyte. Fuel oxidation occurs at the anode and the liberated electrons flow through an external circuit to the cathode, completing the process.

Since the transported ionic species is an oxygen anion, SOFC can theoretically operate directly on a range of hydrocarbons from methane to gasoline [1]. The primary challenge is the choice of SOFC anode materials. The anode must conduct oxygen anions and electrons and be catalytically active for fuel combustion. The perovskite structured oxide  $\text{La}_{0.75}\text{Sr}_{0.25}\text{Cr}_{0.5}\text{Mn}_{0.5}\text{O}_{3-\delta}$  [2,3], has recently been proposed as a potential anode material.  $\delta$  is the non-stoichiometry of the oxide lattice and is a function of cation reducibility, temperature and  $p\text{O}_2$ .

The SOFC anode environment is highly reducing with no gas-phase oxidant; the oxygen is supplied via lattice diffusion through the anode material. In order to investigate the catalytic properties of anode materials, it is necessary to reproduce these conditions. In this study, we utilize a pulse reactor system to probe the activity of  $\text{La}_{0.75}\text{Sr}_{0.25}\text{Cr}_x\text{Mn}_{1-x}\text{O}_{3-\delta}$  towards  $\text{CH}_4$  oxidation under SOFC anode conditions as a function of temperature,  $\delta$ , and  $x$ .

### Materials and Methods

Powder samples of the materials  $\text{La}_{0.75}\text{Sr}_{0.25}\text{Cr}_x\text{Mn}_{1-x}\text{O}_{3-\delta}$  ( $x=0,0.25,0.5,0.75,1$ ) were prepared from nitrate salts via a combined EDTA/citric acid complexometric route, followed by combustion of the resulting gel. The product powders were calcined at 1273K for 4 hours to produce the perovskite structure, as confirmed by XRD. 0.3g of powder, particle size 100-200  $\mu\text{m}$ , was loaded into a quartz reactor tube and heated in flowing Ar,  $p\text{O}_2=10^{-5}$  atm. Upon equilibration, 6 second pulses of 20%  $\text{CH}_4$  in Ar interrupted by 120 s periods of Ar were repeatedly applied to the sample. The reactor exit composition was analyzed via an online mass-spectrometer (Omnistar, Pfeiffer Vacuum, Nashua, NH).

### Results and Discussion

Figure 1 shows the  $\text{CO}_2$  production rate for  $\text{La}_{0.75}\text{Sr}_{0.25}\text{MnO}_{3-\delta}$  as a function of temperature and oxygen stoichiometry. The initial oxygen stoichiometry in flowing Ar,  $p\text{O}_2 = \text{O}(10^{-5})$  atm is close to 3.0 at all temperatures. Each pulse of  $\text{CH}_4$  consumes a fraction of this oxygen through the oxidation reaction. The difference between the lattice stoichiometry and that in equilibrium

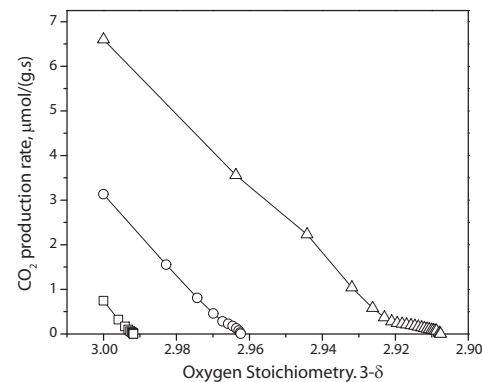
with the reactant gas is the chemical potential driving force for reduction of the oxide. The methane feed contains  $<10$  ppm  $\text{O}_2$  at room temperature yielding an equilibrium  $p\text{O}_2 = \text{O}(10^{-24})$  atm at 973K. At this low  $p\text{O}_2$  stability of the material is important; indeed, the deviation in linearity below  $3-\delta = 2.92$  at 1173K is attributed to decomposition of the material.

The  $\text{CO}_2$  production rate is a function of both the intrinsic surface reaction rate, which consumes surface oxygen, and the bulk oxygen anion conductivity, which replenishes the depleted surface sites. Both of these processes would be expected to show a strong dependence on temperature; however, the ionic conductivity of the material increases as  $3-\delta$  decreases (there are more vacancies on the oxygen sub-lattice for ion transport via site-hopping). It is suggested that the observed decrease in reaction rate with decreasing oxygen stoichiometry is due to decreasing lattice oxygen chemical potential. The reaction rate drops below detectable limits as the oxygen stoichiometry reaches equilibrium with the reactant gas stream. Selectivity towards  $\text{CO}_2$  decreases with decreasing lattice oxygen stoichiometry.

### Significance

Within the anode, the oxygen stoichiometry is determined by a balance between the rate of oxygen ion supply through the electrolyte and the surface reaction rate. Knowledge of the catalytic properties of anode materials is critical in determining the rate limiting process for future SOFC development and optimization. In addition, the selectivity towards  $\text{CO}_2$  or  $\text{CO}$  dictates the efficiency of the fuel cells system with  $\text{CO}_2$  production preferred. A full analysis as a function of Cr/Mn ratio will be presented.

**Figure 1.**  $\text{CO}_2$  production rate as a function of bulk oxygen stoichiometry for  $\text{La}_{0.75}\text{Sr}_{0.25}\text{MnO}_{3-\delta}$  at  $\square$  - 973K  $\circ$  - 1073K and  $\triangle$  - 1173K. Each symbol represents a single pulse of  $\text{CH}_4$ . The oxygen stoichiometry is that of the bulk at the beginning of the pulse.



### References

1. McIntosh, S., and Gorte, R.J. *Chem. Rev.* 104, 4845 (2004)
2. Tao, S.W., and Irvine, J.T.S. *Nat. Mater.* 2, 320 (2003)
3. Tao, S.W., and Irvine, J.T.S. *Chem. Rec.* 4, 83 (2004)