



Influence of lattice oxygen stoichiometry on the mechanism of methane oxidation in SOFC anodes

Steven McIntosh*, Michael van den Bossche

Department of Chemical Engineering, University of Virginia, Charlottesville, VA, USA, 22904-4741

ARTICLE INFO

Article history:

Received 1 September 2009
Received in revised form 7 July 2010
Accepted 22 July 2010
Available online 15 August 2010

Keywords:

Solid Oxide Fuel Cells (SOFC) anode
Direct hydrocarbon
Hydrocarbon oxidation
Perovskite
 $\text{La}_{0.75}\text{Sr}_{0.25}\text{Cr}_{1-x}\text{Mn}_x\text{O}_{3-\delta}$ (LSCM)
Oxygen stoichiometry

ABSTRACT

There is growing interest in developing oxide materials for direct hydrocarbon solid oxide fuel cell anodes. In addition to electronic and ionic conductivities, the electrocatalytic activity of these materials is a critical requirement for a high performance anode. In this paper, we present evidence for the important role of variable lattice oxygen stoichiometry and anode geometry in dictating the activity and reaction mechanism of $\text{La}_{0.75}\text{Sr}_{0.25}\text{Cr}_{1-x}\text{Mn}_x\text{O}_{3-\delta}$ -based anodes for CH_4 oxidation. Total oxidation of CH_4 is favored by low oxygen vacancy concentration and availability of reducible B-site cations. The non-linear dependence of electrode polarization resistance with current density is attributed to dynamic changes in lattice oxygen vacancy concentration. The relatively high open circuit potential of porous anodes compared with thin films is attributed to an increase in secondary reactions of the fuel within the porous anode.

© 2010 Elsevier B.V. All rights reserved.

1. Introduction

$\text{La}_{0.75}\text{Sr}_{0.25}\text{Cr}_{1-x}\text{Mn}_x\text{O}_{3-\delta}$ (LSCM) has recently been investigated as a promising anode material for the direct oxidation of methane fuel in Solid Oxide Fuel Cells (SOFCs) [1–7]. There are three primary requirements for a functional SOFC electrode: oxygen anion conductivity, electronic conductivity, and electrocatalytic activity towards the desired reaction. LSCM is typically utilized in a composite electrode with an electrolyte phase such as yttria-stabilized zirconia or cerium gadolinium oxide (CGO) providing ionic conductivity. The electronic conductivity of $\text{La}_{0.75}\text{Sr}_{0.25}\text{Cr}_{0.5}\text{Mn}_{0.5}\text{O}_{3-\delta}$ is ~ 0.6 S/cm at 800 °C in 5% H_2 [1], which is further reduced when placed in a porous composite electrode. As such, a number of authors have added a secondary metallic phase as an electronic conductor in composite electrodes [4,5,8]. While these efforts can lead to reasonable power densities for hydrogen fuel, the significantly lower power densities in hydrocarbon fuels [1,5] indicate that the electrocatalytic activity towards hydrocarbon oxidation limits performance. The addition of Pt or Pd not only enhances the power density in hydrocarbon fuels [4,6], but also increases cell cost.

A number of studies have sought to study the oxidation activity of oxide SOFC anode and related materials [3,9–15]; It has been shown that the activity is primarily dictated by the nature and oxidation state of the B-site cation [9,11,14], with strong dependence on oxygen

stoichiometry, and lattice oxygen anion mobility [10,12]. At lower temperatures, the reaction is thought to proceed via an Eley–Rideal mechanism with mobile adsorbed surface oxygen as the active species [16–19]. However, at higher temperatures it is indicated that a Mars–van Krevelen (MVK) mechanism dominates [20]. In the MVK mechanism, reaction occurs via the reduction and oxidation (redox) of lattice oxygen sites. The reduction step in the SOFC anode occurs via fuel oxidation at the active surface site, accompanied by a two-electron charge transfer. Re-oxidation occurs by bulk ion transport. Based on the observed strong influence of the B-site cations and using a point defect approach, we may hypothesize that the active site is likely a $\text{B}^{n+}\text{–O–B}^{n+}$ complex, which is reduced to form an oxygen vacancy, $\text{B}^{(n-1)+}\text{–}\square\text{–B}^{(n-1)+}$. One limitation of these previous studies is that both oxygen and fuel are co-fed to a flow reactor, representing a substantially different gas atmosphere from the SOFC anode compartment. The increased $p\text{O}_2$ will increase lattice oxygen stoichiometry and the reoxidation pathway may shift towards a gas phase rather than bulk pathway.

In addition to the electrocatalytic rate for hydrocarbon oxidation, the selectivity towards total and partial oxidation reactions has a strong influence on cell efficiency. It is desirable to promote total oxidation of the fuel, for example Eq. (1), over partial oxidation, for example Eq. (2), to maximize the theoretical cell open circuit potential. The mechanism inside a porous anode is further complicated by a number of potential side reactions, including gas-phase free-radical cracking and polymerization, coking, steam reforming, and dry (CO_2) reforming. It is also feasible that partial oxidation products may be further oxidized at another reaction site. This complexity requires that

* Corresponding author. Tel.: +1 434 982 2714; fax: +1 434 982 2658.
E-mail address: mcintosh@virginia.edu (S. McIntosh).

a variety of experimental approaches be combined to understand hydrocarbon oxidation in the SOFC anode.



In addition, the large potential gradients and resulting oxygen ion flux in the anode may have a significant influence on the reaction mechanism. It is generally accepted [21] that the SOFC cathode material $\text{La}_{0.8}\text{Sr}_{0.2}\text{MnO}_{3\pm\delta}$ (LSM) is partially reduced (with the concomitant formation of oxygen vacancies) by the cathodic potential gradients within an operating SOFC. This facilitates a mechanistic shift towards a bulk ion transport mechanism for oxygen incorporation. Takashi et al. have recently suggested that a similar, but reversed, mechanism operates within oxide anodes [22]. In this case, the oxide material is oxidized, with reduction in oxygen vacancy concentration, by the anodic potential within the SOFC anode.

This paper summarizes our recent work that seeks to measure the catalytic activity of LSCM as a function of oxygen non-stoichiometry under anode conditions and link this to the performance of LSCM-based SOFC anodes [5,7,15].

2. Experimental

$\text{La}_{0.75}\text{Sr}_{0.25}\text{Cr}_{0.75}\text{Mn}_{0.25}\text{O}_{3-\delta}$ (LSCM7525), $\text{La}_{0.75}\text{Sr}_{0.25}\text{Cr}_{0.50}\text{Mn}_{0.50}\text{O}_{3-\delta}$ (LSCM5050), $\text{La}_{0.75}\text{Sr}_{0.25}\text{Cr}_{0.25}\text{Mn}_{0.75}\text{O}_{3-\delta}$ (LSCM2575) and $\text{La}_{0.75}\text{Sr}_{0.25}\text{Mn}_{0.75}\text{O}_{3-\delta}$ (LSM) powders were fabricated by a sol-gel technique [15]. All of the resulting powders were X-ray pure after calcination at 1000 °C and had BET surface areas between 2.42 and 4.60 m²/g. 0.25 g of each powder was sieved to a size fraction between 100 and 200 nm and loaded into a 1/4" i.d. quartz reactor tube. Full details of the pulse reactor setup and procedure are available elsewhere [15]. In brief, the sample was equilibrated at reaction temperature in flowing 10 vol.% O₂/Ar prior to equilibration in flowing Ar, $p\text{O}_2 = 2 \times 10^{-6}$. The sample was then subjected to 6 second pulses of 20 vol.% CH₄/Ar interspersed with 120 second intervals of Ar while the reactor effluent was analyzed with an inline mass spectrometer (Omnistar GSD300, Pfeiffer Vacuum). A pulse technique is employed to allow the surface oxygen stoichiometry to re-equilibrate with the bulk between measurements. The total feed flowrate was constant at 50 ml/min. The reactor effluent composition was analyzed to calculate the rate of CO₂ (total oxidation) and CO (partial oxidation) production. Instantaneous selectivity was calculated as the ratio of these two rates. This total rate of O consumption was calculated from the production rate of CO₂ and CO assuming reactions 1 and 2 dominate. The change in sample lattice oxygen stoichiometry was tracked per pulse by subtracting the O content of the reactor effluent. The initial oxygen stoichiometry was determined by thermogravimetric analysis.

A dual layer tape casting technique was used to prepare an SOFC with a 180 μm thick Cu/LSCM5050/YSZ anode supporting a 50 μm thick YSZ electrolyte and a 20 μm thick LSM/YSZ cathode. As with the pulse system, a full description of the processing steps is available elsewhere [5]. A green bilayer tape with YSZ/graphite-based layer was cast on top of a thinner YSZ green tape. Sintering the dried tape at 1550 °C

resulted in a 180 μm thick porous YSZ layer supporting a 50 μm thick dense electrolyte layer. The LSM/YSZ cathode was attached to the electrolyte surface by sintering at 1200 °C. The anode was completed through repeated infiltration with metal nitrate salt precursor mixtures (LSCM5050 completed first, followed by Cu) and intermediate calcination at 450 °C. The cell was additionally calcined at 1000 °C after the addition of LSCM5050 to form the perovskite phase. The maximum calcination temperature during Cu addition was 450 °C. The final anode composition was 8 wt.% LSCM5050 and 35 wt.% Cu with the balance YSZ. Although this anode composition differs from the dense film anode, the Cu does not perform any electrocatalytic function in the anode [23], acting only as an electronic conductor. Cells with only LSCM in the anode (up to 30 wt.%) provided lower cell power density. This is most likely due to the thickness of the anode and the low electronic conductivity of LSCM at 700 °C. As such, the anode supported cell studies were performed with the addition of Cu to the anode. This LSCM/Cu/YSZ anode is thus analogous to the Ceria/Cu/YSZ anodes studied by Gorte, Vohs and coworkers at the University of Pennsylvania [23]. The chemical compatibility of Cu with LSCM in the LSCM/Cu/YSZ anode was investigated by recording XRD patterns of fired LSCM powder impregnated with Cu(NO₃)₂ solution in a 8:35 LSCM:Cu weight ratio and fired in air at 700 °C, both before and after reducing in humidified H₂ at 700 and 800 °C.

Electrical contacts were made with Au paste and Au wire on the anode and Pt paste and Pt wire at the cathode. Cell V-I and electrochemical impedance spectra (EIS) were measured using a Gamry Instruments Reference 600 potentiostat (Gamry Instruments, Warminster, PA, USA).

A second electrolyte supported cell with dense film electrodes was also studied as a simplified geometry. Dense thin LSCM5050 (600 nm thick) anode and LSM (300 nm thick) cathode film electrodes were symmetrically deposited on either side of an YSZ pellet electrolyte using ultrasonic spray pyrolysis. An LSM reference electrode was added to the free electrolyte surface on the cathode side by slurry painting. Au contacts were patterned onto the LSCM5050 surface utilizing lithography-based processing, while contacts on the cathode side were made using Pt paste and Pt wire. The free LSCM5050 surface of a nominally identical cell was doped with Pd using a Pd-nitrate salt solution. The cells were sealed onto alumina tubes and V-I curves collected at 700 °C in H₂, CH₄ and C₄H₁₀ fuels. Full details of the experimental procedure and extensive discussion of the results are available elsewhere [7].

3. Results and discussion

Table 1 lists the rate of oxygen consumption at 800 °C for the materials studied. Increasing Mn content increases the rate of oxidation (total rate of O consumption based on reaction stoichiometry) for all lattice oxygen stoichiometries. Note that reaction ceases for the LSCM7525 at $3-\delta = 2.68$ as the system equilibrates at the $p\text{O}_2$ of the CH₄ feed. The final oxygen stoichiometry decreases with increasing Mn content due to increased reduction of Mn compared to Cr under these conditions. We concur with literature reports that the B-site cation dominates activity and demonstrate that Mn provides a more active site for methane oxidation than Cr. Without knowledge of the rate

Table 1

Rate of oxygen consumption and instantaneous selectivity towards total methane oxidation as a function of oxygen stoichiometry and composition at 800 °C.

Material	$3-\delta$	Rate μmol/m ² s	Select. %	$3-\delta$	Rate μmol/m ² s	Select. %	$3-\delta$	Rate μmol/m ² s	Select. %
LSM	2.91	8.80	100	2.70	1.49	100	2.60	0.476	81
LSCM2575	2.88	2.50	100	2.70	0.434	88	2.60	0.088	15
LSCM5050	2.89	2.14	100	2.70	0.224	5	2.60	0.047	0
LSCM7525	2.89	1.18	100	2.70	0.262	0	2.60	N/A	N/A

Download English Version:

<https://daneshyari.com/en/article/1296499>

Download Persian Version:

<https://daneshyari.com/article/1296499>

[Daneshyari.com](https://daneshyari.com)