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Technical Communication

# Silver modified cathode for a micro-tubular, single-chamber solid oxide fuel cell

*Naveed Akhtar*, Kevin Kendall*

*Department of Chemical Engineering, University of Birmingham, Birmingham B15 2TT, UK*

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ABSTRACT

Micro-tubular, solid oxide fuel cells consisting of nickel, yttria-stabilized zirconia (Ni–YSZ) anode, yttria-stabilized zirconia (YSZ) electrolyte and lanthanum strontium cobaltite ferrite–gadolinium doped ceria (LSCF–GDC) cathode have been developed and operated under single-chamber conditions, utilizing methane/air mixture. The cell performance was compared with a silver modified cathode by the addition of 10wt% silver-paste in LSCF–GDC cathode. The cells with and without silver addition yielded maximum power densities of 118.75 mW $cm^{-2}$ and 61.53 mW $cm^{-2}$ at 700 °C, respectively. The results demonstrate that silver is a good candidate for enhancing the oxidation reduction kinetics via improved adsorption, desorption, dissociation and subsequent diffusion. However, long term performance of the silver modified cathode is not guaranteed under single-chamber conditions.



## 1. Introduction

In recent years there has been an increasing interest in the research and development of single-chamber, solid oxide fuel cells (SC-SOFCs) [1–4]. Though, SC-SOFCs are an ideal candidate for portable type applications where normally low power densities are demanded, they offer compact design due to elimination of gas-separating channels and are very simple to fabricate [2,3]. Furthermore, gas-tight sealing is not required because the reactants are already pre-mixed. Besides these advantages, they still have to suffer many challenges such as, low fuel-utilization/electrical efficiencies, high catalytic/electro-catalytic activity and selectivity of the electrodes for their respective reactions (e.g. anode must maintain high activity for partial oxidation followed by electrochemical oxidation of the produced species such as carbon monoxide and hydrogen; cathode must be inert towards fuel combustion). Moreover, all of the components (i.e. the anode, cathode, electrolyte and interconnects) must be durable enough to work properly in a dual-atmospheric environment. Not only this, the extremely low power densities of SC-SOFCs put further restrictions on their use, as such, at present they are suitable for miniaturized portable power generations, only [3,5–12].

The purpose of this study is to focus on one of the above listed challenges, i.e. to suggest possible ways to improve the power densities of SC-SOFCs. In this respect, cathode side improvement was opted due to the well-established reason that the cathode overpotential accounts for the major power loss in a solid oxide fuel cell (SOFC) operation [13]. The state of the art, conventional cathode (i.e. lanthanum strontium

* *Corresponding author. Present address:* Department of Chemical Engineering and Chemistry, Technical University Eindhoven, 5600 MB, Eindhoven, The Netherlands.
E-mail address: navtar433@yahoo.com (N. Akhtar).
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manganate, LSM) is limited to high-temperature applications (>800 °C), at which an acceptable performance can be realized. Also, being as an electronic conductor, the active region in LSM electrode is limited to the cathode–electrolyte interface. In recent years, there has been a strong motivation to reduce the operating temperature of SOFCs, and therefore "Intermediate Temperature Solid Oxide Fuel Cells (IT-SOFCs)" are gaining more and more interest. For IT-SOFC applications, mixed ionic electronic conductors (MIEC) are considered to be an ideal candidate because of their extended triple phase boundaries (TPBs). Among various MIECs for cathode applications, lanthanum strontium cobaltite ferrite–gadolinium doped ceria (LSCF–GDC) composite cathode has been widely used by many researchers [7,10,13]. It should be noted that the addition of GDC into LSCF to form a composite cathode is beneficial in reducing the polarization resistance of pure LSCF, especially at low temperatures (<650°C) [13]. In order to further promote the oxygen surface exchange kinetics, various additives have been previously reported such as palladium (Pd), platinum (Pt) and silver (Ag) etc. [1,14].

Uchida et al. [15] reported that the addition of small nm-size Pt catalyst in lanthanum strontium cobaltite (LSC) based cathode of a conventional SOFC improved the power density compared to non-Pt, LSC cathode. Sasaki et al. [16] investigated the cermetting effect of LSCF with Pt in order to develop a reduced temperature SOFC. They reported that the obtained cathode activity was far from satisfactory, mainly due to reduced activation overpotential of the modified cathode. With an objective of enhancing the catalytic activity of the LSM–YSZ cathode and thus to improve the electrochemical performance of a conventional SOFC, Hannappel et al. [17] added Pt, Pd and Ag to the cathode. They found that the addition of Pt did not result in any positive affect on the electrochemical performance. With respect to Pd containing cells, the only improvement in the electrochemical performance was seen with Pd on activated carbon. They attributed this performance enhancement due to enhanced cathode surface reactions. Cells prepared with Ag powder and Ag-oxide showed an improved electrochemical performance compared to Ag-free cells sintered at the same temperature. This shows that Ag is an electro-catalytically active element. Hwang et al. [18] studied the effect of Pt addition in LSCF cathode and found to be very effective in reducing the polarization resistance of the LSCF cathode. Liang et al. [19] prepared a novel nano-structured Pd–YSZ cathode for conventional IT-SOFC. Nano-sized Pd particles were impregnated onto the porous YSZ structure. Their results show that both the polarization resistance and the activation energy of such cathode are significantly lower than those for conventional perovskite-based cathodes. The addition of silver in LSCF [20], LSCF–GDC [21] and LSCF–SDC [22] cathodes has also been investigated and an improved performance has been reported. It was found that the main role of silver in performance enhancement is to improve the oxygen exchange reaction activity.

As inferred from above, the addition of Pd, Pt and Ag in the conventional SOFC cathodes show a similar effect in improving the electrochemical performance by reducing the polarization resistance and activation energy. The use of such noble metals in SC-SOFC may result in different outcome. For example, Pd and Pt have been reported to be active for methane oxidation [14]. The use of such additives may enhance parasitic loss on the cathode side of an SC-SOFC by consuming methane, which will result in lower electrical efficiency. The silver, on the other hand, is less reactive for methane oxidation and also cheaper than Pd and Pt. Therefore, Ag is opted as an additive for cathode in this study in order to investigate its role in performance enhancement.

In this study two different composite cathodes, i.e. LSCF–GDC and LSCF–GDC–Ag have been employed and their performance has been studied under single-chamber conditions.

## 2. Experimental

The micro-tubular cells consist of Ni–YSZ/YSZ, anode/electrolyte layers were purchased from Adaptive Materials Inc. (AMI), USA. The LSCF–GDC composite cathode paste was purchased from Fuel Cell Materials, USA. Two different cells with different cathode layers (1st cell: LSCF–GDC, 2nd cell: LSCF–GDC–Ag (10 wt %)) of approximately same thicknesses (50 micron) were paint brush and sintered at 1000°C (1st cell) and 850 °C (2nd cell), respectively. The sintering temperature for cell-2 has to be kept lower because of silver densification, agglomeration and vaporization at temperatures higher than this [14]. Silver-paste and current collecting wires (99.99% silver, Scientific Wire, UK) were used for both electrodes. The cells were operated using methane/air mixture of 25/60 mL $min^{-1}$. The geometry dimensions have been described in our earlier publication [1]. Fig. 1 shows the experimental setup used in this study.

## 3. Results and discussion

Fig. 2a and b shows the scanning electron microscope (SEM) photograph of two sintered cells containing different cathodes before operation. As can be seen all three layers (i.e. the anode, electrolyte and cathode) are well adhered in both of the cells. As can be seen from Fig. 2a, the dense microstructure of LSCF–GDC cathode is due to higher sintering temperature (1000°C). However, a slightly greater porosity has been observed in case of LSCF–GDC–Ag cathode (Fig. 2b) because of lower sintering temperature (850 °C). Fig. 2c and d shows the magnified view of Fig. 2a and b, respectively.

Fig. 3a shows the I–V and I–P characteristics of LSCF–GDC cathode based cell. As can be seen, the cell performance improves with increase in temperature until 700°C, afterwards, the open circuit voltage (OCV) drops to ~0.8V. This drop in OCV can be associated with lower Gibbs free energy with increasing temperature and methane parasitic combustion at the cathode consuming more oxygen at higher temperatures. The reduced oxygen partial pressure at this higher temperature may result in lower OCV and thereby in performance. Nevertheless, the highest power density of 61.53 mW $cm^{-2}$ is obtained at 700 °C as indicated by red curve in Fig. 3a.

In Fig. 3b, the I–V and I–P characteristic curves for LSCF–GDC–Ag cathode based cell have been shown. As can be seen, addition of silver greatly improves the power density and