



# Efficient conversion of CO<sub>2</sub> in solid oxide electrolytic cells with Pd doped perovskite cathode on ceria nanofilm interlayer



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## ARTICLE INFO

### Article history:

Received 22 August 2016

Received in revised form 11 November 2016

Accepted 27 November 2016

Available online 21 December 2016

### Keywords:

Electrolysis

Nano ceria

Electrolyser

Energy storage

CO<sub>2</sub> conversion

## ABSTRACT

The conversion of CO<sub>2</sub> into high energy density fuels and chemicals using electricity generated from renewable sources in High Temperature Solid Oxide Electrolysers is one of the emerging energy storage technologies. By utilising waste heat from industrial processes or solar concentrators or nuclear reactors, HT-SOE devices can reduce the electrical energy input up to 30%. Thus such devices are attractive for utilising CO<sub>2</sub> as a renewable energy storage media when coupled with Solar Concentrator Photovoltaic systems. Application of traditional solid oxide fuel cell electrodes such as Ni-YSZ restricts the operation of the electrolyser to using CO<sub>2</sub> mixed with reducing gases such as hydrogen or CO to prevent re-oxidation of metallic Ni to NiO in the presence of CO<sub>2</sub>. Furthermore carbon deposition can occur at high current densities in dry CO<sub>2</sub>. New redox stable ceramic cathodes (CO<sub>2</sub> electrode) are promising alternatives to Ni-YSZ electrodes. In this work, we report electrochemical performance of Palladium (Pd) doped La<sub>0.6</sub>Sr<sub>0.4</sub>Co<sub>0.2</sub>Fe<sub>0.8</sub>O<sub>3- $\delta$</sub>  (LSCF-Pd) as potential cathode for these devices. Using LSCF-Pd as both anode and cathode, with nanocrystalline thin film doped ceria as an interlayer between the cathode and the electrolyte, current densities in excess of 360 mA cm<sup>-2</sup> were obtained at 800 °C in electrolyte supported tubular cells with high CO<sub>2</sub> and steam conversion to syngas. The electrochemical performance of the electrode was found to be stable during the 50 h testing of the cell on cyclic load. The cells and reactors used are modular and scalable.

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## 1. Introduction

Converting waste CO<sub>2</sub> from power plants and industrial processes into value added chemicals and fuels is one of the increasingly researched field of energy technology. In particular, there has been significant increase in research activities related to solid electrolyte membrane based electrochemical reactors for utilisation of CO<sub>2</sub> [1–3]. Excess or off-peak power from renewable energy sources (RESs) such as solar, wind and tidal power can be used as input along with CO<sub>2</sub> and water, and then can be stored in the form of gaseous or liquid hydrocarbons as these devices can be directly coupled to RES. These hydrocarbons can be stored and used in devices such as fuel cells, internal combustion engines or turbines to produce power on demand or to produce easily transportable fuels such as methanol. Amongst various electrochemical reactors, the high temperature solid oxide electrolysis (HT SOE) cells operating at temperatures between 500 and 800 °C are one of the most efficient and flexible systems for CO<sub>2</sub>

conversion [1,2]. Due to the endothermic nature of both CO<sub>2</sub> and water splitting, HT SOE, can absorb heat as energy input along with electricity, to reduce demand on electrical energy input making the technology ideal for coupling with Solar Concentrator Photovoltaic (SCPV) and Spectral beam splitting technology [4]. As utilisation of waste heat is possible, HT SOE could also be coupled with industrial plants such as cement factories where waste heat is also available along with sources of CO<sub>2</sub>. The operation of these electrolysers is the reverse of solid oxide fuel cells (SOFCs), with dry CO<sub>2</sub> electrochemically reduced to CO.

In HT SOE, if water (in the form of steam) is fed simultaneously on the cathode side, a mixture of hydrogen and CO can be produced by the so-called co-electrolysis process which can then be used to produce liquid fuels. The process is derived from solid oxide fuel cell (SOFC) technology; hence, many of the materials, fabrication processes and operating conditions are similar to those used in SOFCs [2,3]. However, key challenges are low conversion rates, degradation of electrocatalysts, and the long-term stability and electrochemical performance of electrodes.

Traditionally SOFC electrodes such as nickel mixed with yttria-zirconia electrolyte (Ni-YSZ cermet) or doped ceria (Ni-DC) have been used as the cathode (CO<sub>2</sub> electrode) in HT-SOE [5]. However,

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one of the issues with using Ni-YSZ as SOE cathode is requirement of the addition of hydrogen or CO along with CO<sub>2</sub> and/or H<sub>2</sub>O to prevent oxidation of Ni to NiO. Additionally, the redox stability of such an electrode is a concern during thermal cycling of the electrolysers. Application of HT SOE to conversion of CO<sub>2</sub> into chemicals is commercially viable only if the electrolyser can be coupled with a renewable energy supply. However, most renewable energy sources are inherently intermittent in nature. Thus the coupled device would undergo regular thermal and electrical load cycling, leading to rapid device degradation, and would require a complex thermal and electrical load management system.

One of the demonstrated strategies to avoid electrode degradation and delamination arising from redox stability of Ni based electrodes is to use ceramic electrodes without significant metal content that are stable in redox environments and do not require additional reducing feed gas. Several different ceramics, including various perovskites such as titanates and manganates have been investigated as electrodes on the reducing side of such systems [6]. Lanthanum strontium cobalt ferrite (LSCF) is one such material which has been investigated as the anode for various hydrocarbon and solid carbon fuels [7,8]. LSCF is susceptible to partial reduction in a strongly reducing atmosphere but it has been demonstrated that the reduced phases are catalytically active and the LSCF electrode can be structurally stable in mildly reducing atmospheres such as CO<sub>2</sub>/CO mixture [9]. The application of LSCF in HT SOE systems is particularly interesting because the materials can be used as an air electrode (oxygen evolution electrode) at the same time as the CO<sub>2</sub>/H<sub>2</sub>O reduction electrode. This can potentially lead to significantly simpler cell fabrication process enabling cathode and anode coatings and heat treatments in a single step. LSCF is known to react with YSZ electrolyte forming insulating interfacial phases when sintered above 900 °C, however, this issue can be resolved with the application of ceria (CeO<sub>2</sub>) based interlayers between the LSCF electrode and the YSZ electrolyte [10]. Furthermore, it has recently been demonstrated that partial substitution of Fe with Pd increases vacancy concentration, oxygen uptake and catalytic activity [11].

In this work we report the electrochemical performance of Pd doped LSCF as a cathode in a scalable tubular HT SOE design for electrolysis of dry CO<sub>2</sub>, as well co-electrolysis of steam and CO<sub>2</sub> to produce syngas. The same material is also used as the anode (oxygen evolution electrode) making it symmetrical tubular HT SOE. Results are also provided from short-term tests (50 h of operation) in co-electrolysis mode with a cyclic electrical loading. Also demonstrated is, fabrication of ceria thin film as a barrier layer between the Pd doped LSCF electrode and YSZ electrolyte with a simple and scalable dip coating method.

## 2. Experimental

Palladium doped LSCF (La<sub>0.6</sub>Sr<sub>0.4</sub>Co<sub>0.2</sub>Fe<sub>0.77</sub>Pd<sub>0.03</sub>O<sub>3- $\delta$</sub> ) powder (hereafter referred as LSCF-Pd) was prepared using citrate gel

processing. Analytical grade nitrates (Sigma Aldrich) of the corresponding metal cation were mixed in appropriate molar ratios and citric acid (Sigma Aldrich) was used as a fuel. The mixture was heated to 90 °C to form a gel which was subsequently burnt at 400 °C to decompose nitrates followed by heat treatment at 800 °C for 2 h. As-prepared powder was then used to make electrode ink. For comparison, LSCF (La<sub>0.6</sub>Sr<sub>0.4</sub>Co<sub>0.2</sub>Fe<sub>0.8</sub>O<sub>3- $\delta$</sub> ) powder without Pd doping was also prepared using the same synthesis method.

### 2.1. Deposition of ceria nanofilm interlayer

Closed end tubes of YSZ were prepared by isostatic pressing YSZ powder (Tosoh Corporation, Japan) and sintering at 1500 °C. The sintered tube had a nominal wall thickness of 0.8 mm and outer diameter of 10 mm. For preparation of the ceria interlayer on the cathode side (the outer side of the tube), the YSZ tube was cleaned thoroughly, treated with surfactants and dipped into a Sm<sub>0.2</sub>Ce<sub>0.8</sub>O<sub>1.9</sub> (SDC) polymeric precursor. The polymeric precursor was prepared by dissolving analytical grade Ce-Nitrate and Sm-Nitrate mixed (Sigma Aldrich, Australia) in appropriate molar ratios along with ethylene glycol as a plasticiser and glycine (Sigma Aldrich, Australia) as the fuel to obtain a clear, precipitate free solution. Nitric acid was used to adjust the pH. Details of such precursor preparation process was reported in reference [12]. After ageing of the precursor, the tube was dipped in the solution kept in sonicated bath and slowly removed from the bath while drying with heat gun at approximately 85 °C temperature. This coating process was repeated two times, followed by heat treatment at 800 °C for 2 h in air with a heating rate of 60 °C h<sup>-1</sup>. For all tested tube cells, a similar method was followed to deposit the ceria nanofilm interlayer.

### 2.2. Tube cell preparation

After deposition of the ceria nanofilm, the cells were coated with electrodes using brush coating both inside and outside of the tube with the electrode inks prepared using a terpinol based ink vehicle (Fuel Cell Materials, USA). Three different tube cells were prepared for testing with three different cathodes keeping anode material same for all cells. For the anode (oxygen evolution electrode), the LSCF-Pd material prepared in this work was used for all the cells tested. Also, ceria nanofilm coated YSZ tubes with a similar nominal thickness (0.8 mm) were used for all cells. Table 1 lists the electrode coatings and heat treatment program used.

### 2.3. Materials characterisation

The X-ray diffraction (XRD) patterns of the synthesized cathode powder before and after treatment in 4% H<sub>2</sub>/CO<sub>2</sub> mixture for 4 h were obtained using benchtop XRD (Bruker D2 Phaser). The lattice parameters of the compositions were determined with

**Table 1**  
Materials and heat treatment cycles for cells.

	Cathode (outer side of tube)	Anode
Cell #1 <sup>a</sup>	La <sub>0.6</sub> Sr <sub>0.4</sub> Co <sub>0.2</sub> Fe <sub>0.77</sub> Pd <sub>0.03</sub> O <sub>3-<math>\delta</math></sub> on Ceria nanofilm layer with silver paste current collection layer	LSCF-Pd with Ag-YSZ paste current collection layer
Cell #2 <sup>a</sup>	La <sub>0.6</sub> Sr <sub>0.4</sub> Co <sub>0.2</sub> Fe <sub>0.8</sub> O <sub>3-<math>\delta</math></sub> on Ceria nanofilm layer with silver paste current collection layer	LSCF-Pd with Ag-YSZ paste current collection layer
Cell #3 <sup>b</sup>	Ag-YSZ electrode as well as Paste current collection layer only on Ceria nanofilm layer	LSCF-Pd with Ag-YSZ paste current collection layer

<sup>a</sup> Cathode heat treated at 950 °C for 2 h and anode and current collection layers heat treated at 800 °C for 2 h.

<sup>b</sup> Both cathode and anode heat treated at 800 °C for 2 h.

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