



Active, durable bismuth oxide-manganite composite oxygen electrodes: Interface formation induced by cathodic polarization



Minle Chen^{a,b,1}, Yi Cheng^{c,1}, Shuai He^c, Na Ai^d, Jean-Pierre Veder^e, William D.A. Rickard^e, Martin Saunders^f, Kongfa Chen^{a,*}, Teng Zhang^{a,**}, San Ping Jiang^{c,***}

^a College of Materials Science and Engineering, Fuzhou University, Fuzhou, Fujian, 350108, China

^b Key Laboratory of Eco-materials Advanced Technology (Fuzhou University), Fujian Province University, Fuzhou, Fujian, 350108, China

^c Fuels and Energy Technology Institute and Department of Chemical Engineering, Curtin University, Perth, WA, 6102, Australia

^d Testing Center, Fuzhou University, Fuzhou, Fujian, 350108, China

^e John De Laeter Centre & Department of Physics and Astronomy, Curtin University, Perth, WA, 6102, Australia

^f Centre for Microscopy, Characterisation and Analysis, The University of Western Australia, Perth, WA, 6009, Australia

HIGHLIGHTS

- Outstanding performance for power generation and steam splitting.
- Excellent operating stability at 600 °C for 350 h.
- Unravelling the mechanism of forming a dense interfacial layer by cathodic polarization.

ARTICLE INFO

Keywords:

Solid oxide cells
Bismuth oxide
Manganite
In situ electrode/electrolyte interface formation

ABSTRACT

Bismuth oxide is as an active promoter in enhancing the ionic conductivity and electrocatalytic activity of manganite oxygen electrodes of solid oxide cells, but there are very limited reports on the formation and evolution of electrode/electrolyte interface of bismuth oxide-manganite composite electrode under the influence of electrochemical polarization. Herein, we report the effect of electrochemical polarization and direction of polarization current on the electrocatalytic performance and electrode/electrolyte interface of a $(\text{La}_{0.8}\text{Sr}_{0.2})_{0.95}\text{Mn}_{0.95}\text{Pt}_{0.05}\text{O}_{3+\delta}\text{-Er}_{0.4}\text{Bi}_{1.6}\text{O}_3$ (LSMPT-ESB) composite oxygen electrode assembled on zirconia electrolyte. The cell with the LSMPT-ESB electrode produces outstanding performance for power generation and steam splitting, and it is stable without noticeable degradation during operation at 600 °C for 350 h in the fuel cell mode. The cathodic polarization induces *in operando* formation of electrode/electrolyte interface with observation of an Er-deficient LSMPT-ESB dense layer and Er-rich $(\text{Er,Bi,Mn})\text{O}_x$ particles on the zirconia electrolyte surface. This is different to the case of dwell under open circuit and in particular under anodic polarization conditions. The present study gains insights into the development of high performance, reliable bismuth oxide-manganite composite oxygen electrode for reduced temperature solid oxide cells.

1. Introduction

Solid oxide cells (SOCs) are an all-solid device for efficient and environmentally friendly energy storage and conversion. Among the potential candidate electrolyte materials of SOC, cubic bismuth oxide possesses the highest ionic conductivity with remarkable surface exchange ability [1]. Bismuth oxide is not chemically stable upon

exposure to reducing environment at the hydrogen electrode side, but the fabrication of a doped bismuth oxide layer on $\text{Y}_2\text{O}_3\text{-ZrO}_2$ (YSZ) electrolyte significantly facilitates the oxygen incorporation at the electrode/electrolyte interface and electrocatalytic activity of most investigated $(\text{La,Sr})\text{MnO}_{3+\delta}$ (LSM) oxygen electrode [2,3]. The addition of Er and Y stabilized bismuth oxides (ESB and YSB) into the perovskite and noble metal oxygen electrodes such as LSM [4–10],

* Corresponding author.

** Corresponding author.

*** Corresponding author.

E-mail addresses: kongfa.chen@fzu.edu.cn (K. Chen), Teng_Zhang@fzu.edu.cn (T. Zhang), S.Jiang@curtin.edu.au (S.P. Jiang).

¹ These authors contributed equally.

$\text{La}_{0.6}\text{Sr}_{0.4}\text{Co}_{0.2}\text{Fe}_{0.8}\text{O}_{3-\delta}$ (LSCF) [11], $\text{Sm}_{0.95}\text{Co}_{0.05}\text{Pd}_{0.05}\text{O}_{3-\delta}$ (SmCPd) [12] and Ag [13–15] remarkably enhances the electrocatalytic activity for the oxygen reduction reaction (ORR) and oxygen evolution reaction (OER). Notably, the incorporation of stabilized bismuth oxide greatly reduces the operating temperature of LSM oxygen electrode [16,17], which is originally designated for high temperature SOCs [18]. On the other hand, bismuth oxide is highly reactive with the oxygen electrodes in particular the Co-based perovskite oxides. For example, LSCF and SmCPd tend to react with YSB and ESB at a low temperature of 600–650 °C [11,12]. On the contrary, LSM has a remarkably better chemical compatibility with ESB even after the ESB-LSM mixture is heat-treated at 900 °C for 50 h [2]. This is most likely the reason why a great number of studies have been concentrated on LSM-bismuth oxide composite oxygen electrodes.

Pristine LSM electrode is lack of ionic conductivity and thus the ORR and OER reactions are primarily limited at the electrode/electrolyte interface, where high potential and formation of oxygen vacancies are detected during operation using *in situ* probing approaches [19,20]. A number of independent studies have reported evidence for elemental redistribution and microstructural changes at the electrode/electrolyte interface of LSM electrodes under the influence of electrochemical polarization [21–31]. For example, Backhaus-Ricoult et al. [22] observed the rapid spreading of Mn^{2+} generated under high cathodic polarization from the LSM electrode/YSZ electrolyte interface to the whole electrolyte surface using *in situ* photoelectron microscopy. Haider and McIntosh [24] studied the activation effect of polarization on dense LSM film electrodes at 700 °C and concluded that a short duration of polarization for 5 min led to changes in surface chemistry of the LSM film, while a long duration of polarization for 16 h resulted in bulk pore formation.

In contrast, there are very limited reports on interface formation and evolution of stabilized bismuth oxide-LSM composite electrodes. There is evidence that the stabilized bismuth oxide is non-stationary at the electrode/electrolyte interface under the influence of electrochemical polarization. Lee et al. observed the formation of a 50 nm ESB thin layer on the YSZ surface after the electrochemical test [6]. Recently, we have reported that a $\sim 1 \mu\text{m}$ dense ESB-LSM layer was formed on the YSZ electrolyte surface after the nanostructured ESB decorated LSM electrode was operated in fuel cell mode [32]. However, the underlying mechanism for the polarization induced formation and evolution of electrode/electrolyte interface of ESB-LSM electrodes is largely unknown. Herein, we aim to unravel the effect of electrochemical polarization on the electrode/electrolyte interface, electrocatalytic activity and operating stability of $(\text{La}_{0.8}\text{Sr}_{0.2})_{0.95}\text{Mn}_{0.95}\text{Pt}_{0.05}\text{O}_{3+\delta}$ (LSMPt)-ESB composite oxygen electrodes.

2. Experimental

2.1. Fabrication of powder synthesis and electrode

$(\text{La}_{0.8}\text{Sr}_{0.2})_{0.95}\text{Mn}_{0.95}\text{Pt}_{0.05}\text{O}_{3+\delta}$ (LSMPt) and $\text{Er}_{0.4}\text{Bi}_{1.6}\text{O}_3$ (ESB) powders were synthesized via modified Pechini method. 5% Pt was added in the B-site of LSM to enhance the activity for ORR (Fig. S1, Supporting Information). Starting chemicals including reagent grade La $(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$, Sr $(\text{NO}_3)_2$, Mn $(\text{NO}_3)_2$, $\text{H}_2\text{Cl}_6\text{Pt} \cdot x\text{H}_2\text{O}$, Bi $(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$, Er $(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$, citric acid (CA), ethylenediaminetetraacetic acid (EDTA) and ammonia solution were dissolved in deionized water. The molar ratio of metal ions/CA/EDTA was 1:1.5:1. The aqueous solution was placed on a hot plate and stirred continuously till it became a viscous gel. The gel was dried at 180 °C in an oven for 12 h and ground in a mortar. The as obtained LSMPt and ESB powders were calcined at 900 °C and 600 °C in air for 2 h, respectively. The formation of desired phases was confirmed using a Bruker D8 Advance X-ray diffractometer with a Cu $\text{K}\alpha$ X-ray source (Fig. S2a, Supporting Information). The LSMPt and ESB powders were in an average size of 220 and 630 nm,

respectively (Fig. S2b and c, Supporting Information).

The LSMPt and ESB powders were mixed in a mass ratio of 60:40 and combined with an ink vehicle (Fuel Cell Materials) in a solid loading of 70 wt% using an agate mortar and pestle. The electrode ink was assembled on the YSZ electrolyte via screen printing and heat-treated in an oven at 150 °C for 2 h. Pt ink (Gwent Electronic Materials Ltd) was painted as the current collector and heat-treated at 150 °C for 2 h. In this process, the oxygen electrode was prepared without the additional sintering step at a high temperature [33].

2.2. Fabrication and testing of single cells

Hydrogen electrode-supported YSZ films were fabricated using slurry spin coating [34,35]. The hydrogen electrode support consisted of NiO (J.T. Baker), YSZ (TZ-8Y, Tosoh) and tapioca in a mass ratio of 40:40:20, and the hydrogen electrode functional layer (HEFL) of NiO and YSZ in a mass ratio of 50:50. The hydrogen electrode support/HEFL/YSZ film tri-layers were co-fired at 1450 °C in air for 5 h. The thickness of hydrogen electrode support, HEFL and YSZ film was 0.8 mm, 14 μm and 12 μm , respectively, the diameter of cell was 14.5 mm, and the geometric surface area of oxygen electrodes was 0.23 cm^2 .

Electrochemical polarization curves and impedance spectra of the cells were measured at 500–750 °C with an interval of 50 °C, using a Gamry Potentiostat (Reference 3000 and Interface 1000). Hydrogen at a rate of 50 ml min^{-1} was flowed to the hydrogen electrode, and the oxygen electrode was exposed to static surrounding air. To test the cell's electrolysis performance, wet H_2 was also flowed to the hydrogen electrode using a humidifier. The stability of cells was evaluated under 0.5 A cm^{-2} at 750 °C and 0.25 A cm^{-2} at 600 °C. The impedance spectra were collected at a frequency range of 100 kHz–0.1 Hz with an AC signal amplitude of 10 mV at open circuit.

2.3. Phase and microstructure characterizations

The microstructure of LSMPt-ESB electrodes was characterized by SEM (Zeiss Neon 40 EsB and Supra55 Sapphire). In order to examine the electrolyte surface, the oxygen electrode was removed from the electrolyte surface by acid treatment in 32% HCl solution at room temperature for 24 h. The topography of electrolyte surface was examined using a Bruker Dimension FastScan atomic force microscope (AFM) in tapping mode. To investigate the electrode/electrolyte interface, the LSMPt-ESB electrodes were separated by force or removed by acid treatment, and lamella samples were prepared using a focused ion beam (FIB)-SEM (FEI Helios Nanolab G3 CX DualBeam). Microstructural observation and elemental mapping analysis of the lamellae were performed using a high angle annular dark field scanning transmission electron microscope (HAADF-STEM, FEI Titan G2 80–200 TEM/STEM with ChemiSTEM Technology) at 200 kV. Near edge X-ray absorption fine structure spectroscopy (NEXAFS) measurements were conducted at the Soft X-Ray beamline of the Australian Synchrotron [36] to characterize the Mn cations on the YSZ electrolyte surface after the acid treatment. The NEXAFS spectra were recorded at the Mn L-edge (635–660 eV). All NEXAFS spectra were processed and normalized using the QANT software program developed at the Australian Synchrotron [37].

3. Results and discussion

3.1. Electrochemical performance and stability

The cell with a directly assembled LSMPt-ESB composite oxygen electrode was polarized at 0.5 A cm^{-2} and 750 °C in the fuel cell mode, and the polarization performance as a function of polarization time is shown in Fig. 1a and b. The cell produces an open circuit voltage of 1.11 V, close to the theoretical value, demonstrating that the YSZ

Download English Version:

<https://daneshyari.com/en/article/7724852>

Download Persian Version:

<https://daneshyari.com/article/7724852>

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