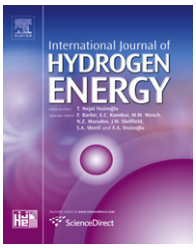
Available at www.sciencedirect.com

ScienceDirect

journal homepage: www.elsevier.com/locate/he



$La_{0.75}Sr_{0.25}Cr_{0.5}Mn_{0.5}O_3$ as hydrogen electrode for solid oxide electrolysis cells

*Chao Jin, Chenghao Yang, Fei Zhao, Daan Cui, Fanglin Chen**

Department of Mechanical Engineering, University of South Carolina, 300 Main Street, Columbia, SC 29208, USA

ARTICLE INFO

Article history:
Received 22 September 2010
Received in revised form
16 December 2010
Accepted 18 December 2010
Available online 21 January 2011

Keywords:
Solid oxide electrolysis cell
Hydrogen generation
$La_{0.75}Sr_{0.25}Cr_{0.5}Mn_{0.5}O_3$
Hydrogen electrode

ABSTRACT

$La_{0.75}Sr_{0.25}Cr_{0.5}Mn_{0.5}O_3$ (LSCM) has been applied as hydrogen electrode (cathode) material in solid oxide electrolysis cells operating with different steam concentrations (20, 40, 60 and 80 vol.% absolute humidity (AH)) using 40 sccm H_2 carrier gas at 800, 850 and 900 °C, respectively. Impedance spectra and voltage–current curves were measured as a function of cell electrolysis current density and steam concentration to characterize the cell performance. The cell resistance decreased with the increase in electrolysis current density while increased with the increase in steam concentration under the same electrolysis current density. At 1.6 V applied electrolysis voltage, the maximum consumed current density increased from 431 mA cm^{-2} for 20 vol.% AH to 593 mA cm^{-2} for 80 vol.% AH at 850 °C. Polarization and impedance spectra experiments revealed that LSCM–YSZ hydrogen electrode played a major role in the electrolysis reaction.

1. Introduction

Recently, there has been a strong interest in the large-scale production of secondary energy carrier for the nonelectrical market due to finite fossil fuel sources, increasing oil prices and environmental concerns [1–3]. Hydrogen is considered as one of important secondary energy carriers because it is storable, transportable and environmentally benign, and can be used as a fuel for heating and electrical production in fuel cells. Fossil fuel, biomass and some electrochemical means can be utilized to produce hydrogen. Water electrolysis for hydrogen production can play an important role in the hydrogen economy since it is a simple, reliable, and carbon-free process, producing high purity hydrogen. Compared with the ordinary alkaline water electrolysis explored during the early 1980s, steam electrolysis in solid oxide electrolysis cells (SOECs) operating at high temperature consumes less electrical energy and is more efficient for hydrogen production [4,5]. Moreover, the power and heat generated by nuclear power systems and renewable energy sources, and waste heat from high temperature industrial processes can be utilized for steam electrolysis in SOECs [6].

In principle, an SOEC is essentially a reverse process of a solid oxide fuel cell (SOFC). Consequently, SOEC technology can be built on the SOFC technology which has been received significant research and development in recent years [7]. In reality, the reported study about SOECs is mainly based on the research in SOFCs, including cell fabrication methods, stack and system designs as well as electrode and electrolyte materials [7–11]. In particular, Ni/yttria-stabilized zirconia (YSZ) cermet, a conventional SOFC anode material, is the most commonly used hydrogen electrode material for study in the high temperature steam electrolysis. However, nickel in the cermet tends to agglomerate after prolonged operation, especially under high steam concentration environment, leading to reduced three-phase boundary sites and increased electrical resistance. Further, Ni–based electrode is easily oxidized in high steam concentration causing redox cycling

* *Corresponding author*. Tel.: +1 803 777 4875; fax: +1 803 777 0106.
E-mail address: chenfa@cec.sc.edu (F. Chen).

0360-3199/$ – see front matter
doi:10.1016/j.ijhydene.2010.12.085

instability of the Ni/YSZ cermet hydrogen electrode [12]. Recently, perovskite $La_{0.75}Sr_{0.25}Cr_{0.5}Mn_{0.5}O_3$ (LSCM) has been reported to be an electrochemically active and redox stable SOFC anode material [12–14]. Although Yang and Irvine have investigated the possibility of using LSCM as hydrogen electrode (cathode) material in high temperature steam electrolysis cells, only very low steam concentration (3 vol.% H_2O) was used in their study [15]. Such a low steam concentration has insignificant practical value. Bidrawn and co-workers have demonstrated high temperature steam (10% H_2O) and CO_2 electrolysis using LSCM cathode with Pd catalyst [16]. However, there has been no report of SOEC cell performance using LSCM-based hydrogen electrode operating at high steam concentrations (>10 vol.% H_2O).

In the present work, SOECs based on LSCM hydrogen electrode were prepared on YSZ electrolyte membranes. Various steam concentrations were used to characterize the cell performance in high temperature electrolysis. Further, a three-electrode configuration was applied to the cell to separate the contributions to the cell electrochemical performances associated with the hydrogen electrode and the oxygen electrode in the electrolysis process.

2. Experimental

$La_{0.75}Sr_{0.25}Cr_{0.5}Mn_{0.5}O_3$ (LSCM) material was prepared through a sol–gel method [17]. Stoichiometric amounts of lanthanum nitrate ($La(NO_3)_3\cdot 6H_2O$, Alfa Aesar, 99.9%), strontium nitrate ($Sr(NO_3)_2$, Alfa Aesar, 99.0%), chromium nitrate ($Cr(NO_3)_3\cdot 9H_2O$, Alfa Aesar, 98.5%) and manganese nitrate ($Mn(NO_3)_2\cdot 4H_2O$, Alfa Aesar, 98.0%) were dissolved in deionized water with constant stirring at room temperature. A stoichiometric amount of citric acid ($C_6H_8O_7\cdot H_2O$, Alfa Aesar, 99.0%), used as a chelating agent and fuel, was subsequently added in the above nitrate solution. The mole ratio of the total metal ions:citric acid was controlled at 1:1.5. Ammonium hydroxide (NH_3 content 28.0–30.0%, Sigma–Aldrich) was added to adjust the pH value to about 6.0. A gel was formed upon continuous stirring at 80 °C. The gel was dried at room temperature overnight and then fired in air at 350 °C for 2 h. The resulting powders were ground with an agate mortar and pestle, and subsequently calcinated in air at 1100 °C for 5 h. The crystallization of the LSCM powder was monitored by X-ray diffraction (XRD) (Philips Model PW1830 diffractometer, Cu $K\alpha$).

LSCM–yttria-stabilized zirconia (YSZ) (50:50 weight ratio) hydrogen electrode was prepared by mixing proper amounts of LSCM and YSZ (TZ-8Y, TOSOH Corporation, Japan) powders with a suitable amount of binder (ethyl cellulose and α-terpineol), followed by screen-printing on one side of YSZ pellet (20 mm diameter and 0.3 mm thickness, Fuel Cell Materials, USA), and then sintered at 1250 °C for 4 h $La_{0.8}Sr_{0.2}MnO_3$ (LSM, Fuel Cell materials, USA) was selected as oxygen electrode (anode) material, and LSM–YSZ (50:50 weight ratio) ink was symmetrically screen-printed on the other side of the YSZ pellet, opposite to the LSCM–YSZ electrode, and then sintered at 1200 °C for 2 h. The effective areas for both the LSCM–YSZ hydrogen electrode and the LSM–YSZ oxygen electrode were 0.5 cm^2. Pt meshes were attached on the surface of the hydrogen and oxygen electrodes using Pt paste as current collectors. Pt reference electrode was deposited on the YSZ pellet to the oxygen electrode side, 3.9 mm away from the LSM–YSZ oxygen electrode. Both Pt meshes and Pt reference electrode were fired at 1000 °C for 1 h. Pt leads were used to connect the electrodes to electrochemical testing equipment. The fabricated button cells were sealed to one end of an alumina tube with a ceramic paste (Aremco-552 high temperature ceramic adhesive paste). The ceramic paste was cured during the heating up of the cell electrochemical testing to form a gas tight sealing. Electrochemical performances of the SOEC cells were studied using a conventional two-electrode method while the overpotential of the hydrogen and oxygen electrodes in high temperature steam electrolysis process was determined using a three-electrode method, as schematically shown in Fig. 1.

A dedicated high temperature steam electrolysis measurement system was shown in Fig. 2 and testing procedure was described in detail in our previous publication [18]. Polarization curves (V–I curves) and electrochemical impedance spectra (EIS) were performed through a multi-channel VersaSTAT (Princeton Applied Research) in both fuel cell and electrolysis modes. For EIS measurement, the frequency range was from 100 kHz to 0.1 Hz and the AC amplitude was 10 mV. After the electrochemical testing, the cells were cooled down and the cell microstructures were analyzed using scanning electron microscopy (SEM, FEI Quanta 200).

3. Results and discussion

3.1. XRD and cell microstructure characterization

Fig. 3 shows X-ray diffraction patterns of LSCM powders at different conditions. Fig. 3(a) shows the XRD result of the final LSCM powders after calcinated in air at 1100 °C for 5 h, indicating the formation of a single perovskite phase. Fig. 3(b) is the XRD for the LSCM powders heat-treated by flowing 40 sccm H_2 with 80 vol.% AH at 900 °C for 24 h. Compared with the XRD pattern of pure perovskite phase LSCM powders shown in Fig. 3(a), there is no second phase or peak splitting for the XRD pattern shown in Fig. 3(b), suggesting that LSCM is chemically stable in reducing atmosphere with high steam concentration, the typical operating conditions in the hydrogen electrode of the high temperature electrolysis cells.

Fig. 4 presents the microstructure of the LSM–YSZ/YSZ/LSCM–YSZ SOECs after electrolysis testing. As shown in Fig. 4 (a), the obtained SOEC has a 300 μm thick YSZ electrolyte,

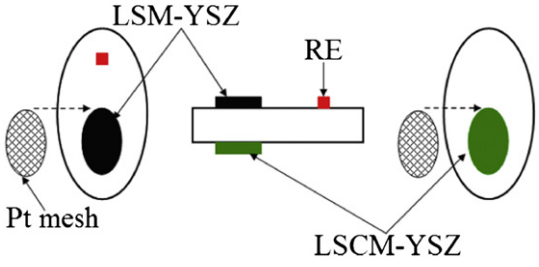


Fig. 1 – Schematic diagram of the cell configuration used in this study.