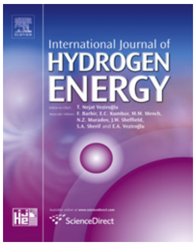
INTERNATIONAL JOURNAL OF HYDROGEN ENERGY 36 (2011) 14643–14647

Available at www.sciencedirect.com

ScienceDirect

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



An intermediate temperature solid oxide fuel cell fabricated by one step co-press-sintering

Lei Zhang [a,b], *Shanwen Tao* [a,*]

[a] *Department of Chemical and Process Engineering, University of Strathclyde, Glasgow G1 1XJ, UK*
[b] *Department of Chemistry, Heriot-Watt University, Edinburgh EH14 4AS, UK*

ARTICLE INFO

Article history:
Received 5 June 2011
Received in revised form
2 August 2011
Accepted 15 August 2011
Available online 15 September 2011

Keywords:
Lithiated NiO
Doped-ceria
Stability
Intermediate temperature
Solid oxide fuel cell

ABSTRACT

Lithiated NiO was adopted as electrodes for doped-ceria based IT-SOFCs. $Li_{0.3}Ni_{0.7}O_y$ electrode is chemically compatible with $Ce_{0.8}Gd_{0.05}Y_{0.15}O_{1.9}$ (GYDC) electrolyte in air. Single cell with configuration $Li_{0.3}Ni_{0.7}O|GYDC|Li_{0.3}Ni_{0.7}O$ was fabricated by one step dry-pressing and sintering at 1200 °C. Maximum power density of 503 $mWcm^{-2}$ at 0.5 V was achieved at 600 °C with H_2 as fuel and air as oxidant. Cell stability test was carried out at 575 °C under a constant voltage of 0.3 V and a current output of 380 $mAcm^{-2}$ was continually generated after an initial performance decrease. A stable anode is required for symmetrical IT-SOFCs.

1. Introduction

Solid oxide fuel cells (SOFCs) are promising green energy devices as they convert chemical energy directly into electricity at high efficiency. A single SOFC is normally fabricated by sandwiching a dense electrolyte between two porous electrodes with subsequent several sintering steps. Materials with different electrocatalytic activities are required for anode and cathode as they operate in reducing and oxidizing conditions respectively. However, anode and cathode also share some common demands for the properties such as good material stability, suitable thermal expansion coefficients (TECs), desired chemical compatibility and high electronic/ionic conductivity [1,2]. Therefore, a new concept to use the same material for both anode and cathode has been proposed [3,4]. The fabrication of SOFCs will also benefit from this simplified structure as same composition of electrodes enable the cell to be sintered at one step and therefore cost-effective. Bastidas et al. first proposed a perovskite oxide $La_{0.75}Sr_{0.25}Cr_{0.5}Mn_{0.5}O_3$ (LSCM) as symmetrical electrode and investigated the LSCM|YSZ|LSCM cell performance under H_2 and CH_4 where they achieved maximum power densities of 300 and 230 $mWcm^{-2}$ at 900 °C respectively [3]. Limited materials have so far been successfully demonstrated as symmetrical electrode for SOFCs, which are most perovskite-type oxides such as $Pr_{0.7}Ca_{0.3}Cr_{1-y}Mn_yO_{3-\delta}$ [5], $La_{0.8}Sr_{0.2}Sc_{0.2}Mn_{0.8}O_{3-\delta}$ [6] and $(La,Sr)TiO_3$ [7]. Zhang et al. studied $La_{0.7}Ca_{0.3}CrO_3$–$Ce_{0.8}Gd_{0.2}O_{1.9}$ composites as symmetrical electrode for SOFC on $La_{0.9}Sr_{0.1}Ga_{0.8}Mg_{0.2}O_{3-\delta}$ (LSGM) electrolyte and obtained maximum power densities of 573 $mWcm^{-2}$ in H_2 and 333 $mWcm^{-2}$ in commercial city gas at 900 °C [8]. Lithiated nickel oxides ($Li_xNi_{1-x}O_y$) have been extensively studied and used for lithium ion batteries [9–11] and molten carbonate fuel cells (MCFCs) [12–14] as cathodic materials. The pure NiO is a green colored insulator with rock

---

[*] *Corresponding author.* Tel.: +44 (0) 141 548 2361; fax: +44 (0) 141 548 2539.
E-mail address: shanwen.tao@strath.ac.uk (S.W. Tao).

0360-3199/$ – see front matter Copyright © 2011, Hydrogen Energy Publications, LLC. Published by Elsevier Ltd. All rights reserved.
doi:10.1016/j.ijhydene.2011.08.054

salt structure. The partially substitutions of Ni^{2+} by Li^{+} will introduce holes of Ni^{3+} or Vö for charge compensation and the oxide becomes a black semiconductor [15]. We have previously developed a cost-effective co-pressing-firing SOFCs fabrication process using $Li_{0.3}Ni_{0.7}O_y$ as cathode and demonstrated it is a promising cathode material for intermediate temperature SOFCs (IT-SOFCs) [16].

In this work, to extend our research, lithiated NiO was also adopted as anode for IT-SOFCs. Single cell was prepared by co-pressing-firing method and good cell performance was obtained under humidified H_2 as fuel and air as oxidant. The cell stability was investigated at 575 °C and a stable current density of ∼380 $mAcm^{-2}$ was continually generated.

2. Experimental

Electrolyte $Ce_{0.8}Gd_{0.05}Y_{0.15}O_{1.9}$ (GYDC) and symmetrical electrode lithiated NiO were synthesized according to refs [16] and [17]. Briefly, calculated amounts of $Ce(NO_3)_3 \cdot 6H_2O$, $Y(NO_3)_3 \cdot 6H_2O$ and Gd_2O_3 were mixed in deionized water. Nitric acid was added to form gadolinium nitrate. The cation concentration of the nitrates solution is controlled at 0.1 mol/L and dropwise added into a 0.2 mol/L ammonium carbonate solution under continuous stirring to form carbonate precipitates. The precipitates were washed with deionized water several times and subsequently with ethanol. The obtained precursor was heated at 600 °C to obtain GYDC powders.

$Li_{0.3}Ni_{0.7}O_y$ was prepared by glycine-nitrate combustion method. Nickel nitrate hexahydrate and lithium carbonate were dissolved in deionized water and heated at about 80 °C. Glycine (NH_2CH_2COOH) was added to the solution at a glycine/nitrate molar ratio of 0.5. With continually stirring, all the residual water evaporated and spontaneous ignition occurred eventually. The as-collected black ash was further heated at 800 °C for 20 h to obtain the $Li_{0.3}Ni_{0.7}O_y$. X-ray diffraction (XRD) data were conducted at room temperature using a Panalytical X'Pert Pro diffractometer with Ni-filtered CuKα radiation using 40 kV and 40 mA ($\lambda = 1.5405$ Å), fitted with a X'Celerator detector. Absolute scans were recorded in the 2θ range 5–100° with a step size of 0.0167°.

Single cell was fabricated by dry-pressing anode (50/50wt% $Li_{0.3}Ni_{0.7}O_y$/electrolyte with starch), electrolyte and cathode (50/50wt% $Li_{0.3}Ni_{0.7}O_y$/electrolyte with starch) at simple one-step under 300 MPa. The cell was sintered at 1200 °C for 4 h with an effective working area 0.4 cm^2. Silver paste was used on each side of the electrodes to improve electrical contact. The thickness of the electrolyte was around 60 μm. Fuel cell performance and stability test was carried out by a Solartron 1250 Frequency Response Analyser coupled to a 1287 Electrochemical Interface [17].

3. Results and discussion

The XRD patterns of single phase GYDC and $Li_{0.3}Ni_{0.7}O_y$ were shown in Fig. 1a and (b) with cubic structure. For comparison, the standard peaks on the background are associated with JCPDS file 77-2023 of $Li_{0.28}Ni_{0.72}O$ in the space group of Fm-3m. The chemical stability of $Li_{0.3}Ni_{0.7}O_y$-GYDC composite electrode was investigated by calcining the mixture of $Li_{0.3}Ni_{0.7}O_y$ and GYDC powders (50:50 at wt%) at 600 °C in air and pure H_2 for 20 h, respectively. As shown in Fig. 1c, only peaks of GYDC and $Li_{0.3}Ni_{0.7}O_y$ can be observed and no other phase in the composite electrode after calcination in air, indicating $Li_{0.3}Ni_{0.7}O_y$ is chemically compatible with GYDC in air at 600 °C.

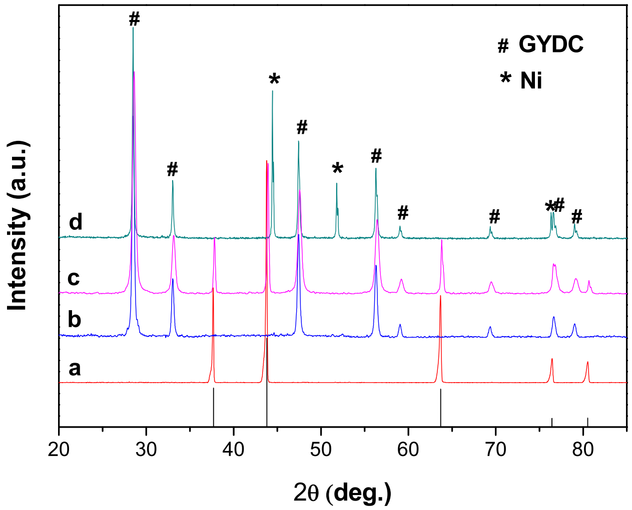


Fig. 1 – XRD of (a) $Li_{0.3}Ni_{0.7}O$, (b) GYDC, (c) $Li_{0.3}Ni_{0.7}O$-GYDC composite electrode calcined in air at 600 °C for 20 h and (d) $Li_{0.3}Ni_{0.7}O$-GYDC composite electrode calcined in H_2 at 600 °C for 20 h (The standard is JCPDS powder diffraction File No. 77-2023.).

Pure $Li_{0.3}Ni_{0.7}O_y$ and the mixture of $Li_{0.3}Ni_{0.7}O_y$ and GYDC at 50:50 weight ratio was reduced in H_2 at 600 °C for 10 h then re-oxidised in air at 600 °C for 10 h. After cooling down to room temperature in air, it was found that some Ni phase retained for pure $Li_{0.3}Ni_{0.7}O_y$ (Fig. 2c) while no Ni was observed in the $Li_{0.3}Ni_{0.7}O_y$/GYDC mixture (Fig. 2d). For pure $Li_{0.3}Ni_{0.7}O_y$, the re-oxidation of Ni may form a thin layer of NiO on the Ni particles which may stop further oxidization. In the mixture of $Li_{0.3}Ni_{0.7}O_y$ and GYDC, Ni is separated by DYDC and the oxygen vacancies in GYDC may help the diffusion of oxygen therefore facilitate the oxidation of formed Ni next to it. The $Li_{0.3}Ni_{0.7}O_y$ phase was not regenerated during the re-oxidization process. In both samples, no Li_2O was peak was detected. Possibly it is in amorphous state. The sublimation of Li_2O at high temperature cannot be ruled out.

Single cell was fabricated with $Li_{0.3}Ni_{0.7}O_y$ as both anode and cathode and tested using H_2 (∼3 vol. % H_2O) as fuel and air as oxidant. Fig. 3 shows the *I–V* and *I–P* curves of the cell performance. Open-circuit voltages (OCVs) of 0.88, 0.88 and 0.86 V were obtained at 550, 575 and 600 °C. The deviated OCVs from the theoretical value could attribute to the electronic conductivity of doped-ceria induced by the reduction of Ce^{4+} to Ce^{3+} in reducing atmospheres [18]. The lower OCV will decrease the power density of the cell. At around 0.5 V, maximum power densities of 156, 242 and 503 $mWcm^{-2}$ were achieved at 550, 575 and 600 °C, respectively. Fig. 4 shows the impedance spectra of the cell measured at temperature 550–600 °C under open circuit conditions. The series resistance R_s (high frequency intercept on real-axis) decreases