Journal of Power Sources 258 (2014) 98–107

Contents lists available at ScienceDirect

Journal of Power Sources

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

Development and understanding of $La_{0.85}Sr_{0.15}Cr_{1-x}Ni_xO_{3-\delta}$ anodes for $La_{5.6}WO_{11.4-\delta}$-based Proton Conducting Solid Oxide Fuel Cells

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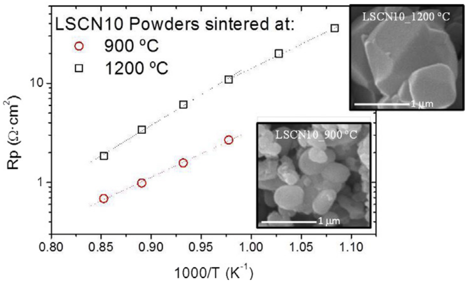
HIGHLIGHTS

- $La_{0.85}Sr_{0.15}Cr_{1-x}Ni_xO_{3-\delta}$ (x = 0.1, 0.2) is compatible with the protonic conductor $La_{5.6}WO_{11.4-\delta}$.
- The microstructure of anodes for proton conducting SOFC was optimized in symmetrical cells.
- Chromite anode performance improves with increasing Ni content.
- Decreasing the size of Ni nanoparticles improves anode performance.
- Langmuir–Hinshelwood mechanism describes the dissociative adsorption rate of H_2.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:
Received 11 October 2013
Received in revised form
23 January 2014
Accepted 4 February 2014
Available online 14 February 2014

Keywords:
SOFC anode
Chromite
Ni nanoparticles
Proton conductor
Lanthanum tungstate

ABSTRACT

Porous electrodes based on the system $La_{0.85}Sr_{0.15}Cr_{1-x}Ni_xO_{3-\delta}$ (x = 0.1 and 0.2) have been investigated as anodes for proton conducting solid oxide fuel cells based on the $La_{5.6}WO_{11.4-\delta}$ (LWO) electrolyte material. The microstructure of the anodes was optimized by varying both the starting powder morphology and the final anode sintering temperature. Two different electrode thicknesses were studied, i.e. 15 and 30 μm. The importance of the catalytic role of Ni was also studied by using different concentrations of Ni (10% and 20%) in the chromite and by tuning the Ni particle sizes through the control of the reduction temperature. Additionally, a ceramic–ceramic (cer–cer) composite electrode comprising a physical mixture of the optimized chromite and LWO phase was also considered. Finally, a kinetics study and modeling based on Langmuir–Hinshelwood mechanism was carried out in order to quantitatively describe the rate of dissociative adsorption of H_2 on the Ni particles spread on the chromite surface.

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1. Introduction

The high protonic conductivity of the $La_{6-x}WO_y$ (LWO, with $0.4 < x < 0.7$) and its stability in CO_2 containing atmospheres make this material a promising candidate as electrolyte for proton conducting solid oxide fuel cells (PC-SOFCs) [1–6]. Although this material exhibits mixed electronic–protonic conductivity under reducing conditions, its electronic conductivity is negligible when used as electrolyte subjected to a large pO_2 gradient (Air/H_2), i.e. the cell voltage approaches the Nernst potential [7,8]. The increasing interest in these PC-SOFCs resides in the possibility of reducing the operation temperature and avoiding the fuel dilution. Therefore, new electrodes, both cathodes and anodes, compatible with LWO electrolyte are demanded.

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http://dx.doi.org/10.1016/j.jpowsour.2014.02.015
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The high reactivity of the LWO phase with the widely used NiO [9] prioritizes the search of new anode materials compatible with LWO electrolyte. $LaCrO_{3-\delta}$ based materials have been broadly investigated as (i) interconnector for SOFC despite the extreme sensitivity to oxygen partial pressure and high manufacturing costs [10,11] and (ii) anode materials due to the redox stability and high ability to inhibit carbon coking [12,13] in CH_4-fueled SOFCs. Indeed, Ni doped $La_{0.85}Sr_{0.15}CrO_{3-\delta}$ (LSC) has been tested as promising anode for conventional SOFC, since it combines sufficient electronic and oxygen-ion conductivity under anode operation conditions and catalytic activity by incorporating a catalyst in the electrode, e.g. ruthenium or nickel [14–16]. It has been reported that these Ni doped chromites split metallic Ni nanoparticles under reducing atmospheres and these catalytic particles enhance the anode performance [17]. Furthermore, chromites present mixed electronic and protonic conductivity in reducing atmospheres and they are compatible with LWO electrolyte phase, which make them promising anode materials for LWO based PC-SOFC [8,9]. Regarding the nature of the ionic transport though LWO electrolyte, at 900 °C the oxygen transport is twice the proton transport, although at lower temperatures (800 °C and below), proton transport is prevailing over oxygen ionic and electronic conduction. Indeed, the final application of this cell is in the temperature range below 800 °C [1,18].

The present work focuses on the study and optimization of $La_{0.85}Sr_{0.15}Cr_{1-x}Ni_xO_{3-\delta}$ (LSCN, with $x = 0.1$ and 0.2) as anode for LWO based PC-SOFCs. Firstly, the anode performance was improved by changing the microstructure of the electrode, i.e. by varying the sintering temperatures of both the starting powder and the screen printed porous electrode. The catalytic role of Ni was analyzed by incorporating different amounts of Ni in the chromite and by varying the Ni particles sizes (using different reducing temperatures). LSCN-LWO cer–cer composites were also studied by mixing the best chromite composition with the LWO protonic phase. Finally, a kinetics analysis based on Langmuir–Hinshelwood mechanism was carried out. The obtained model allowed describing the rate of dissociative adsorption of H_2 on the Ni particles spread on the chromite surface.

2. Experimental

$La_{0.85}Sr_{0.15}Cr_{0.9}Ni_{0.1}O_{3-\delta}$ (LSCN10) and $La_{0.85}Sr_{0.15}Cr_{0.8}Ni_{0.2}O_{3-\delta}$ (LSCN20) powders were prepared by citrate reaction route, and two different pre-sintering temperatures of the powders (1200 and 900 °C) were studied [17]. The $La_{5.5}WO_{11.25-\delta}$ used as protonic phase for the composite cathode was prepared by Pechini method [19] following the experimental procedure explained elsewhere [6]. Screen printing inks were prepared by mixing the ball-milled powders with a solution of ethylcellulose in terpineol (6%-wt.) and subsequently refined using a three roller mill (Exakt). $La_{5.6}WO_{11.4-\delta}$ (LWO) electrolyte powder was commercially provided by Cerpotech.

Crystalline phase of the different materials was characterized by X-ray diffraction (XRD) by a PANalytical CubiX X'Pert PRO diffractometer, using $CuK\alpha_{1,2}$ radiation and a X'Celerator detector in Bragg–Brentano geometry. XRD patterns were recorded in the 2θ range from 10° to 90° and analyzed using X'Pert Highscore Plus software.

Dense ~1 mm-thick LWO disks were obtained by uniaxially pressing the ball-milled LWO powder at ~120 MPa and final firing at 1500 °C for 5 h. Porous ~30 and 15 μm-thick electrodes were obtained by screen-printing the inks on both sides of LWO electrolyte disks. The standard electrode thickness was 30 μm. Firing temperature of the screen-printed anodes cells was 950, 1050, 1150 and 1250 °C for 2 h. Finally, the anodes were reduced at two different temperatures, 900 and 800 °C. A summary of the different tested anodes (powder sintering temperature, anode sintering temperature and the final anode reduction temperature) is shown in Supporting Fig. 1. The final size of symmetrical cells was 15.5 mm in diameter, whereas anodes were ~9 mm in diameter.

LSCN/LWO/LSCN symmetrical cells were tested by electrochemical impedance spectroscopy (EIS) in two-point configuration. Input signal was 0 V DC – 20 mV AC in the $0.01–3\cdot10^5$ Hz frequency range. This signal was generated by a Solartron 1470E and a 1455A FRA module equipment. EIS measurements were performed in the 900–650 °C range, under moistened atmospheres (2.5% vol. H_2O) at different pH_2 (by using fluxes of 100% H_2 and 50% and 5% of H_2 in He). Wet 5% D_2 in He (2.5% vol. D_2O) was also used in order to identify protonic processes expecting H/D isotopic effects. In all the cases, the total flow remained constant (100 mL min^{-1}). Raw impedance data were fitted to an equivalent circuit using Z-plot software.

The microstructure was investigated using scanning electron microscopy (SEM) (Zeiss Ultra 55), and elemental analysis was carried out with energy-dispersive X-ray spectroscopy (EDS) (INCA, Oxford). The porosity of the anodes was calculated by analyzing SEM images.

3. Results and discussion

3.1. Structural characterization of $La_{0.85}Sr_{0.15}Cr_{1-x}Ni_xO_{3-\delta}$ ($x = 0.1$ and 0.2) powders and compatibility with LWO material

XRD patterns of $La_{0.85}Sr_{0.15}Cr_{1-x}Ni_xO_{3-\delta}$ ($x = 0.1$ and 0.2) powders prepared by Pechini method and sintered at 900, 1050 and 1150 °C, are represented in Fig. 1a and b. It can be observed that at 900 °C, besides the chromite structure peaks, there is some amount of $SrCrO_4$ (diffraction peaks labeled with * in the graphs). These small traces of $SrCrO_4$ are in agreement with previously reported studies [20] and disappear when the sintering temperature is increased, i.e. above 1050 °C. No changes in cell parameter are induced through the sintering at higher temperatures, as inferred from the peaks position.

SEM images (Fig. 2) show grain size distribution of the different LSCN powders at two different magnifications (top and bottom). Important differences in the grain size distribution and their homogeneity are observed as a function of sintering temperature, i.e. the grains remain smaller and more homogenous when the powder is sintered at lower temperatures. LSCN10 sintered at 1200 °C (Fig. 2a) presents grains ranging from 800 nm to 1.6 μm, while LSCN10 sintered at 900 °C (Fig. 2b) shows a well distributed microstructure with grains of around 150 nm. These differences in the morphology of the powders affect the anode performance, as it will be discussed latter. When comparing different Ni-content powders, LSCN10 and LSCN20, both sintered at 900 °C, (Fig. 2b and c, respectively) no major differences in the grain morphology are observed although LSCN20 grain sizes are slightly smaller.

Chemical compatibility of LSCN10 and LSCN20 anode materials with LWO electrolyte was also tested at high temperature, imitating the electrode sintering process. Fig. 3 shows XRD patterns of a mixture of 50 vol.% of LSCN10 (sintered at 1200 °C) and LSCN20 (sintered at 900 °C) and 50 vol.% of LWO (sintered at 800 °C) before and after being commonly sintered in air at 1150 °C for 5 h. From the patterns it can be inferred that there is no reaction between the Ni-doped chromites, LSCN10 and LSCN20, and LWO since all diffraction peaks can be assigned to both chromite and LWO phases. The small changes in intensities and widths of the structural peaks are merely attributed to the different initial calcination temperature of each powder. Regarding the preparation of cer–cer composites, LSCN20 and LWO powders (SEM images showed in

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