Solid State Ionics 323 (2018) 85–91

Contents lists available at ScienceDirect

Solid State Ionics

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

Effect of high-temperature ageing on (La,Sr)(Co,Fe)$O_{3-δ}$ cathodes in microtubular solid oxide fuel cells

Hongqian Wang[a], Hirofumi Sumi[b], Scott A. Barnett[a,*]

[a] Department of Materials Science and Engineering, Northwestern University, Evanston, IL 60208, USA
[b] Inorganic Functional Materials Research Institute, National Institute of Advanced Industrial Science and Technology (AIST), Nagoya 463-8560, Japan

ARTICLE INFO

Keywords:
Solid oxide fuel cell (SOFC)
Perovskite cathode
AC impedance
Distribution of relaxation time (DRT)
Focused ion beam-scanning electron microscopy (FIB-SEM)

ABSTRACT

Microtubular solid oxide fuel cells with $La_{0.6}Sr_{0.4}Co_{0.2}Fe_{0.8}O_{3-δ}$ (LSCF) cathodes were aged in ambient air at temperatures ranging from 700 to 1000 °C for up to 700 h. Distribution of relaxation time analysis of electrochemical impedance spectroscopy (EIS) measurements indicated an increase in the cathode resistance with increasing ageing temperature up to 900 °C. The cells aged at 1000 °C were not measurable. The degradation did not result from microstructural changes, as shown by focused ion beam-scanning electron microscopy (FIB-SEM) 3D tomography that showed no significant changes at ageing temperatures ≤900 °C. On the other hand, the amount of segregated Sr, present both on LSCF surfaces and in Sr-rich particles, increased with increasing ageing temperature and correlated well with the increase in cathode resistance. Analysis of the EIS and microstructural data using the Alder-Lane-Steele model indicates that the Sr surface segregation increases cathode resistance via a decreased oxygen surface exchange rate.

1. Introduction

(La,Sr)(Co,Fe)$O_{3-δ}$ (LSCF) is an important cathode material for solid oxide fuel cells (SOFCs), providing low polarization resistance R_P at temperatures well below 800 °C [1]. However, LSCF can be susceptible to degradation by mechanisms including reactions with YSZ electrolytes, Sr surface segregation [2], Cr poisoning from steel stack components [3–5], and microstructural coarsening [6,7]. In the present paper, the focus is on degradation mechanisms intrinsic to LSCF independent of the electrolyte type and the interconnect material [8], i.e., coarsening and Sr segregation. Coarsening and sintering of porous electrodes are expected at sufficiently high temperatures, long times, and small particle sizes. However, it is difficult to predict whether a given electrode will be susceptible to coarsening/sintering because of the strong dependence of coarsening rate on initial feature size. For example, coarsening of initially ~50-nm-diameter infiltrated LSCF to > 100 nm after ageing for ~1000 h at ≥700 °C has been shown to measurably increase R_P [6,7]. On the other hand, LSCF electrodes with larger feature sizes do not coarsen measurably: e.g., no coarsening was observed for LSCF with ~300 nm particle size aged for ~1000 h at up to 800 °C [2], or for LSCF with 550 nm feature size aged for 1000 h at 600–900 °C [9]. In the latter study, an increase in R_P was observed after ageing at 600 and 750 °C, despite no change in microstructure [9]; this may have been due to Sr segregation, which was not tested in that study. Indeed, Sr surface segregation and increased R_P have been observed on model thin-film LSCF electrodes [10] and on LSCF porous electrodes [2]. More results on LSCF electrodes with different feature sizes are needed to understand the respective roles of coarsening and Sr segregation on electrode stability.

Here we present results on LSCF cathodes on tubular SOFCs with ageing at 700–1000 °C for up to 700 h. Since these cells are projected to operate at temperature ≤600 °C [11], these higher temperatures are expected to accelerate degradation. The cells utilize GDC electrolytes, so there is no issue with LSCF/YSZ reactions. No Cr was present during the ageing experiments, in order to avoid Cr poisoning and thereby focus on the segregation and coarsening/sintering effects. Electrochemical Impedance Spectroscopy (EIS) data taken before and after ageing under various conditions is analyzed using distribution of relaxation time methods to isolate the cathode response. 3D tomographic measurements and Sr surface segregation measurements on as-prepared and aged cells are used to understand the effects of ageing on LSCF electrochemical performance.

2. Experimental

2.1. Sample preparation

Anode microtubes were made from NiO (Sumitomo Metal Mining),

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* Corresponding author.
E-mail address: s-barnett@northwestern.edu (S.A. Barnett).

https://doi.org/10.1016/j.ssi.2018.05.019
Received 21 March 2018; Received in revised form 21 April 2018; Accepted 16 May 2018

$(Ce_{0.9}Gd_{0.1})O_{1.95}$ (GDC; Anan Kasei), pore former (acrylic resin; Sekisui Plastic) and binder (Cellulose; Yuken Kogyo) powders. The weight ratio of NiO to GDC was 6:4. A pore former of acrylic resin with a grain size of ca. 5 μm was added before sintering to increase anode porosity. These powders were mixed mechanically for 2 h in a kneading machine with the proper amount of water added. The anode microtubes were extruded using a piston cylinder with a metal hole of 2.4 mm (outside diameter) and 2.0 mm (inside diameter). After extrusion, the tubes were dried overnight in air at room temperature. An electrolyte slurry was prepared by mixing GDC, a binder (polyvinyl butyral; Sekisui Chemical), a dispersant (tallow propylene diamine; Kao) and a plasticizer (dioctyl adipate; Wako Pure Chemical Industries) into ethanol and toluene solvents for 48 h. The GDC electrolyte was formed by dip-coating. The GDC thin-film electrolyte and NiO anode microtube were co-sintered in air 3 h at 1450 °C. The $La_{0.6}Sr_{0.4}Co_{0.2}Fe_{0.8}O_{3\text{-}\delta}$ (LSCF; Kusaka Rare Metal) cathode was coated by a similar manner. The cathode thin-film layers were sintered sequentially in air for 1 h at 1050 °C. The outside diameter of microtube was 1.8 mm, and the cathode length was 10 mm after sintering. The thickness of the anode, electrolyte and cathode were ca. 200, 5, and 20 μm, respectively.

2.2. Cell ageing and electrochemical evaluation

Cells were aged at 700, 800, 900 and 1000 °C in a tube furnace exposed to ambient air. Two ageing times, 300 and 700 h, were used at each temperature. An as-prepared cell was used as a reference sample, for comparison with the aged cells. The characteristics of power generation and AC impedance were evaluated with a potentiostat/galvanostat and an impedance analyzer (Bio-Logic Science Instruments VSP). A silver wire was used as a current collector on the LSCF cathode. A mixture of H_2:H_2O:N_2 = 20:3:77 was supplied as fuel at a flow rate of 100 mL/min to the anode side, and a mixture of O_2:N_2 = 21:79 was supplied as oxidant at 100 mL/min to the cathode side. The operating temperature was 550 °C. Current-voltage (i-V) characteristics were measured from open circuit voltage (OCV) to 0.4 V at a sweep rate of 5 mV/s. The AC impedance was measured at OCV in the frequency range from 1 MHz to 0.1 Hz with 20 steps per logarithmic decade. The distribution of relaxation time (DRT) analysis was done as described in detail in Refs. [11–14]. The polarization processes are considered as an equivalent circuit composing an infinite series connection of parallel RC elements. The inductance components were removed by the same method as described in Ref. [11] before DRT analysis for the impedance spectra in this study. The software package FTIKREG [15] was used to solve an ill-posed inverse problem in DRT analysis by Tikhonov regularization.

2.3. Microstructural measurements

In preparation for 3D tomography, the pores within the LSCF cathodes were infiltrated with a low-viscosity epoxy [16] prior to the observation. The serial sectioning and imaging was carried out using a FEI Helios system with 2 kV electron beam energy and backscattered electron (BSE) detector. The image resolution was 15 × 15 nm and the spacing between images was 30 nm. The area imaged was located close to the cathode/electrolyte interface and the milling direction was perpendicular to the tube axis. Image segmentation and 3D reconstruction were done as described elsewhere [17]. Macrohomogeneous morphological information including phase volume fraction, surface areas, particle size distributions and tortuosity were calculated based on the 3D data sets.

2.4. Chemical characterization

The as-prepared and aged cells were cut into three fragments using a diamond saw. The cell fragments were separately stirred in ultrapure H_2O for 10 min. Subsequently, the samples were transferred into a 12 mol·L^{-1} HCl solution and stirred until the cathodes were completely dissolved. The tubes with ultrapure H_2O solution were then centrifuged and only the upper part of the solution was used, in order to eliminate any loose particles. The ultrapure H_2O and the concentrated HCl solutions were mixed with the appropriate amounts of H_2O/HCl/HNO_3 to yield 0.36 mol·L^{-1} HCl/0.72 mol·L^{-1} HNO_3 solutions for ICP-OES analysis.

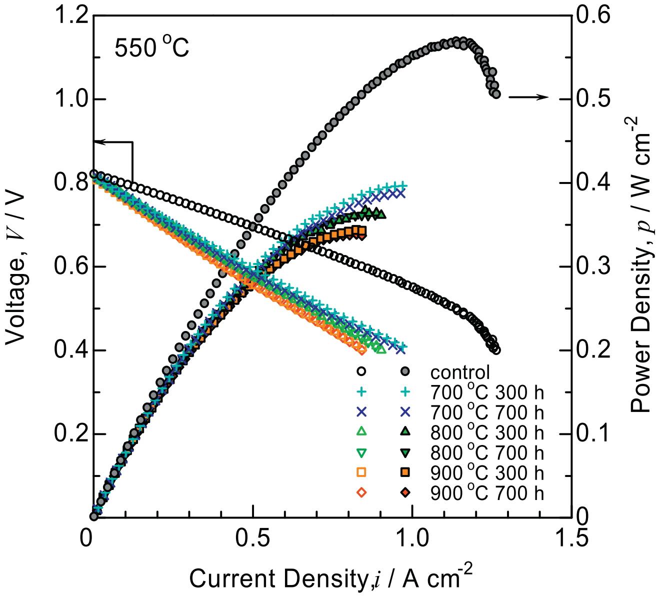

Fig. 1. Voltage and power density versus current density measured at 550 °C for the control and aged microtubular cells.

The chemical analysis of the solutions was done using a Thermo Scientific iCAP 7600 spectrometer. A certified stock solution (10.00 μg/mL from Inorganic Ventures) containing La, Sr, Co and Fe was used to prepare the calibration standards for quantification. The following background corrected emission lines were chosen for evaluation: La (379.478 nm; 412.323 nm), Sr (216.596 nm; 407.771 nm; 421.552 nm), Co (228.616 nm; 237.862 nm), Fe (238.204 nm; 239.562 nm; 240.488 nm).

3. Results and discussion

3.1. Electrochemical properties of LSCF cathodes

Fig. 1 shows the current-voltage and power characteristics at 550 °C for the control and aged microtubular cells. The open circuit voltage (OCV) was 0.82 V for all cells, lower than the theoretical values derived from Nernst equation due to current leakage in the GDC electrolyte. The maximum power density for the control cell, 0.57 Wcm^{-2}, decreased to 0.39, 0.36, and 0.34 Wcm^{-2} for the cells aged at 700, 800 and 900 °C, respectively. At each temperature, increasing the annealing time from 300 to 700 h yielded only a very small decrease in power density. There appears to be a limiting current for the control sample; the maximum currents for the aged samples were lower, and hence concentration polarization effects were not observed. The relatively low limiting current is due to testing under low H_2 partial pressure, i.e., 0.2 atm. Fig. 2 shows the Nyquist plot of AC impedance at 550 °C for the control and aged microtubular cells measured at OCV. The ohmic loss for the aged samples was slightly larger than that for the control sample. There was a substantial increase in the polarization resistance after ageing that increased with increasing ageing temperature. As shown in the Bode plot in Fig. 3a, this was due to significant increases in the impedance responses at frequencies < 10 Hz and at ~100 Hz after ageing. Note that ageing at 1000 °C damaged the cell structure to a point where