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ScienceDirect

Solid State Ionics 179 (2008) 1422 – 1426

SOLID STATE IONICS

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Electrochemical performance and degradation of $(La_{0.6}Sr_{0.4})_{0.99}CoO_{3-\delta}$ as porous SOFC-cathode

Per Hjalmarsson *, Martin Søgaard, Mogens Mogensen

Risø National Laboratory, Denmark

Received 8 July 2007; received in revised form 9 November 2007; accepted 14 November 2007

Abstract

This paper shows that measured impedance in porous $(La_{0.6}Sr_{0.4})_{0.99}CoO_{3-\delta}$ cathodes can be dependent on both gas diffusion and electrode kinetics at temperatures above 700 °C or below ambient pO_2s if electrode kinetics are fast. The reaction mechanism is discussed on the basis of measured temperature- and pO_2-dependences. The degradation was found to be related exclusively to the electrode kinetics and measured about 0.5–1.5 $m\Omega\ cm^2\ days^{-1}$ depending on temperature with a higher rate measured in moisturised air. We speculate on degradation mechanism that involves formation of strontium hydroxides at catalytically active oxygen vacancy sites at the electrode surface.

Keywords: Degradation; LSC; MIEC; Lanthanum strontium cobaltite

1. Introduction

Strontium substituted lanthanum cobaltite $(La_{1-x}Sr_x)_sCoO_{3-\delta}$ (LSC) is a perovskite-type oxide with high electronic and oxide ion conductivity at elevated temperatures and is therefore considered for use in high temperature devices such as ceramic membranes and fuel cells. The mixed conducting property of LSC is believed to account for the low overpotentials measured when used as a SOFC-cathode as it expands the catalytically active area of the electrode beyond the triple phase boundary. However the use of LSC as a cathode on Yttria Stabilised Zirconia (YSZ) is problematic due to its high thermal and stoichiometric expansion coefficient ($17–20 * 10^{-6}\ K^{-1}$ and 0.015–0.030 mol^{-1}[1]) when compared to that of YSZ ($10.3 * 10^{-6}\ K^{-1}$ [2]). Also ionic and electronic blocking reaction products ($SrZrO_3$, $La_2Zr_2O_7$ [3]) inhibit the direct use of LSC on YSZ electrolyte. These problems are partially circumvented when going to lower temperatures and to a ceria-based electrolyte/barrier, however the cathode still needs to remain stable. This paper will discuss the electrochemical performance and degradation based on a set of data measured on a porous cathode of $(La_{0.6}Sr_{0.4})_{0.99}CoO_{3-\delta}$ (LSC40).

2. Experimental

Powder of $(La_{0.6}Sr_{0.4})_{0.99}CoO_{3-\delta}$ (LSC40) was synthesised using the glycine–nitrate combustion route [4] and calcined at 1250 °C for 12 h. A cathode slurry of 11 g perovskite powder, 15 g ethanol and 1 g PVP was mixed and ball-milled overnight. The slurry was sprayed onto both sides of a 200 μm thick tape of $Ce_{0.9}Gd_{0.1}O_{1.95}$ (CGO) and sintered at 950 °C for 2 h. The spraying and sintering procedure was repeated in order to fabricate a symmetric cell with approx. 25 μm thick LSC40 electrodes. The cell was cut to dimensions of 4.0 by 4.0 mm and painted with platinum paste to serve as current collectors. Four identical cells were measured with Electrochemical Impedance Spectroscopy (EIS) under open circuit voltage with a Solartron-1260 frequency response analyzer at temperatures from 550 to 900 °C and oxygen partial pressures (pO_2) from 0.02 to 1 atm. The impedance response was further monitored over 3 to 5 days under humidified and ambient air. Data was treated with a linear least square fit program, ZsimpWin3.21 using an equivalent

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* Corresponding author.
E-mail address: per.hjalmarsson@risoe.dk (P. Hjalmarsson).

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doi:10.1016/j.ssi.2007.11.010

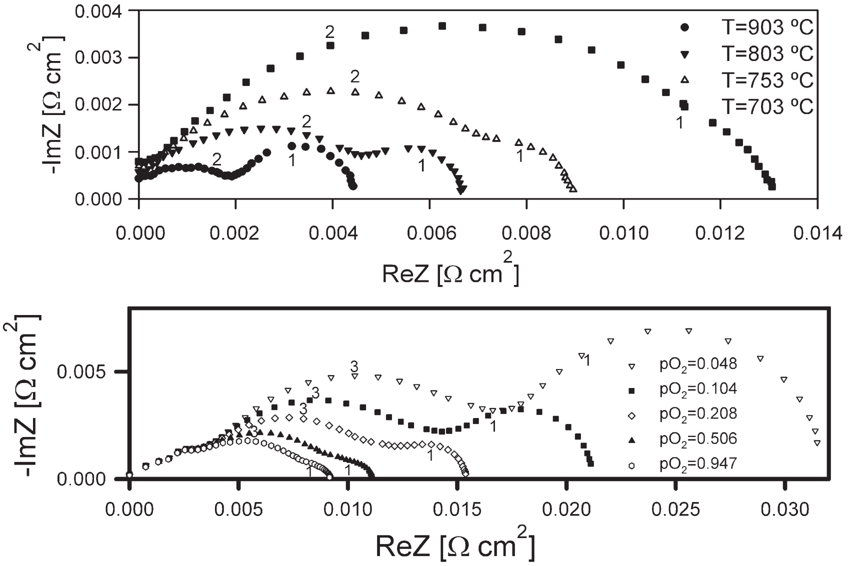

Fig. 1. Nyqvist plots of the electrode response at different temperatures (top) and pO_2s (bottom). Serial resistance and inductance was subtracted from all spectra for easy comparison. Numbers represent log-values of the frequencies.

circuit model of two RQ-circuits in series with a resistor and an inductor.

3. Results and discussion

3.1. Kinetics

Fig. 1 shows Nyqvist plots of prepared $(La_{0.6}Sr_{0.4})_{0.99}CoO_{3-\delta}$ electrodes in ambient air at different temperatures and pO_2s and clearly depicts the appearance of a low frequency semi-circle (summit frequency of ~10 Hz) at increasing temperatures and decreasing pO_2. This is due to the low frequency arc being relatively temperature independent while the thermally activated high frequency arc measured a surprisingly low resistance at high temperatures.

The low frequency arc appeared strongly dependent on pO_2 as depicted in Fig. 2 with a clear reciprocal pO_2-dependence. All data treatment of this arc showed γ-values (the exponent to which the constant phase element is raised) of 0.98–1, indicating that the process involved is ideally capacitive with a capacitance of about 50 mF cm^2. The reciprocal pO_2-dependence could point towards molecular adsorption but the relatively high capacitance and the fact that it is not a thermally activated process strongly suggest that the low frequency response originates from mass transport limitations [5].

The high frequency response (summit frequency of 0.5–5 kHz) proved to be thermally activated with an activation energy of 1.12±0.02 eV. The semi-circle was found to be slightly depressed, indicating a non-ideal capacitive process and, in order to be consistent, all fits were made with a γ-value of 0.65. Capacitances were measured to be about 0.2–0.3 mF cm^2, independently of temperature and pO_2.

Several reports have pointed towards dissociative adsorption as the rate limiting step for mixed conducting SOFC-cathodes, a process that has a theoretical pO_2-dependances, where plotting $\log R - n * \log(pO_2)$ yields a slope, $n=0.5$ ($1/2\ O_{2,ads} \rightarrow O_{ads}$) [6]. Fig. 2 shows measured resistances as function of pO_2 with $n=0.35$–0.37. The linearity was found to prevail over the entire, relatively large, temperature- and pO_2-region ($T=550$–750 °C and $pO_2=1$–0.02 atm), which indicate that no shift in reaction mechanism occurs within our experimental range. As our measured n-values are slightly lower than 0.5, this finding is indicative of a more complex reaction mechanism possibly involving more than one rate limiting process. It must be stressed that the porous cathode is non-ideal as compared to model electrodes used in fundamental electro-catalytic studies. More importantly the n-value is not a true reaction order as changes in pO_2 will also affect the defect structure of the electrode. A

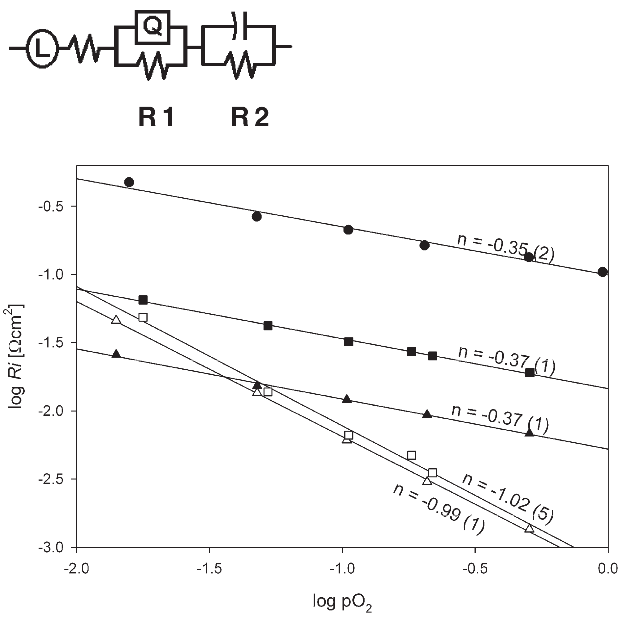

Fig. 2. Log–log plots showing the pO_2-dependence of the two equivalent circuit elements. Filled symbols represent R_1. Open symbols represent R_2. Δ,▲=750 °C; ■,□=650 °C; ●=550 °C.