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Short communication

Effects of water on oxygen surface exchange and degradation of mixed conducting perovskites

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ABSTRACT

The effects of water on oxygen surface exchange kinetics and its degradation of dense $La_{0.6}Sr_{0.4}CoO_{3-\delta}$ (LSC) thin films on yttria-stabilized zirconia (YSZ) are investigated by impedance spectroscopy and X-ray photoelectron spectroscopy (XPS). Two distinguishable effects of water on oxygen surface exchange are identified. While humidification of the oxidant accelerates the oxygen incorporation in the short-term range, the long-term stability of the cathode decreases substantially. XPS analysis indicates that the accelerated LSC degradation rate under wet conditions originated from an increased change of the surface cation composition.

1. Introduction

Oxygen ion mixed conducting perovskites such as strontium-doped lanthanum cobaltite (LSC) are promising candidates as cathode materials in solid oxide fuel cells (SOFCs) at intermediate temperature because of their high catalytic activity for the oxygen incorporation reaction [1–3]. So far, quite a number of investigations have been published on the mechanism of the oxygen incorporation into oxygen ion mixed conductors [4–8]. However, very few studies deal with the effect of humidity on the oxygen incorporation reaction. This is surprising as water is part of the real operating conditions. Our previous study showed that OH groups at the $La_{0.6}Sr_{0.4}CoO_{3-\delta}$ surface are difficult to remove under nominally dry atmosphere at intermediate temperature ($T = 300\,^{\circ}C$) [9]. Thus, the effect of water on the cathode cannot be excluded in realistic fuel cell conditions. Reports about humidity effects on the cathode performance are contradictory. In Ref. [10], the overpotential of $Sm_{0.5}Sr_{0.5}CoO_{3-\delta}$ and $Ba_{0.6}La_{0.4}CoO_{3-\delta}$ cathode was reported to decrease on addition of H_2O to oxygen, while a decrease of the oxygen surface exchange coefficient in H_2O containing atmospheres was found in Refs. [11–14]. Obviously, further study is required to explain the apparently different observations. In this study, we report the effects of water on the oxygen surface exchange and the degradation of oxygen exchange kinetics on dense $La_{0.6}Sr_{0.4}CoO_{3-\delta}$ (LSC) thin films deposited by pulsed laser deposition (PLD). In Ref. [15] it is speculated that the protonic conductivity is very low in strontium-doped lanthanum cobaltite. Therefore, it is highly interesting to consider the water effects on the oxygen surface exchange in LSC. In this study, pore-free thin film electrodes have been used to avoid the morphological uncertainties and ambiguities in the interpretation of impedance spectra which can occur for porous thick films. To the best of our knowledge, no reports on the effect of water on pore-free film electrodes have been presented so far.

2. Experimental

Dense $La_{0.6}Sr_{0.4}CoO_{3-\delta}$ thin films of 100 nm thickness were deposited on both sides of polished (1 0 0) oriented yttria-stabilized zirconia single-crystals (YSZ, 9.5 mol% Y_2O_3, 5 mm × 5 mm × 0.5 mm, CrysTec GmbH, Germany) by PLD at a substrate temperature of 650 °C and an oxygen pressure of 0.4 mbar. The LSC films were deposited uniformly with 100 nm thickness. The films exhibited columnar growth as shown in Fig. 1. According to X-ray diffraction, these LSC films exhibit the rhombohedral perovskite structure and no second phase was detected in dry- (24 h at 600 °C in dry O_2) or wet- (24 h at 600 °C in humidified O_2, $P_{H2O} \approx 30$ mbar) aged films. YSZ substrates covered on both sides by LSC films were spring-loaded between platinum foils in a sample holder. The gas was humidified by bubbling O_2 (100 ml min^{-1}) through a water flask at 24 °C. Impedance spectra were recorded in the frequency range of 10^{6}–10^{-2} Hz with an amplitude of 20 mV using an impedance analyzer (SI 1260, Solartron, UK). The surface composition of LSC before and after hydration was determined by X-ray photoelectron spectroscopy (XPS, Axis Ultra, Kratos Analytical, Ltd., UK) with a monochromatized Al K_{α} X-ray source of 1486.58 eV and a small spot focusing hemispherical

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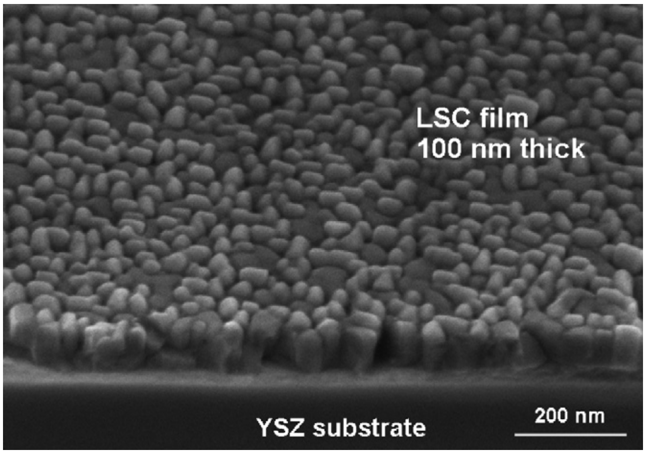

Fig. 1. High resolution scanning electron microscopy (SEM) image of a fractured sample with a 100 nm LSC film on YSZ substrate, measured from a 45° perspective.

electron energy analyzer. The inelastic mean free path from the Tanuma–Penn–Powell method (TPP-2M) [16] is ≈2.2 nm for La and Sr (photoelectron kinetic energy ≈1350 eV) and ≈1.3 nm for Co (kinetic energy ≈ 650 eV) in $La_{0.6}Sr_{0.4}CoO_{3-\delta}$. This difference has to be kept in mind when discussing cation ratios. The surface cation composition was estimated using the sensitivity factors provided by the instrument software and peak fitting with mixed 70% Gaussian–30% Lorentzian functions after Shirley background subtraction. In the case of Co 2p, the shape was fitted to a Voigt function, which is widely used to fit the asymmetric shape of the peak [17]. Peak positions were calibrated using the C 1s peak at 284.6 eV from hydrocarbon contamination.

3. Results and discussion

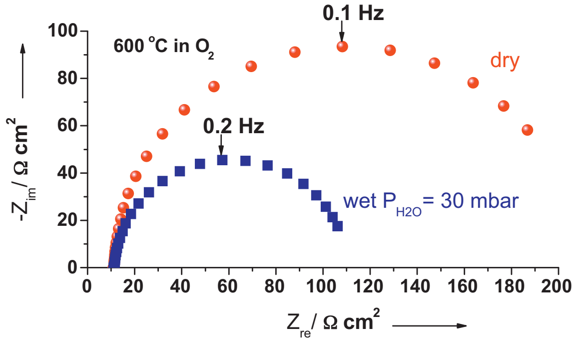

Fig. 2. Impedance spectra of LSC thin film deposited on both sides of YSZ substrate measured at 600 °C in dry or humidified O_2 atmosphere.

Fig. 2 shows representative impedance spectra of LSC films measured at 600 °C in dry or humidified O_2. The spectra show one dominating semicircle at low frequencies, as well as a non-zero axis intercept at high frequencies. The two resistances associated with high and low frequency features are assigned to a bulk resistance (R_b, originating from the ionic conductivity of YSZ) and surface exchange resistance (R_s, related to the oxygen exchange surface reaction) respectively, in agreement with previous measurements [3,5,18]. The activation energy (E_a) of R_b (0.96 ± 0.03 eV) in the temperature range from 400 °C to 600 °C is similar to the reported value (0.94 ± 0.03 eV) for a 9.5 mol% Y_2O_3-doped ZrO_2 single crystal [5]. The YSZ ionic conductivity calculated from R_b is $\approx 6.3 \times 10^{-4}$ S cm^{-1} at 500 °C, slightly lower than that of single crystal of 9.5 mol% Y_2O_3–ZrO_2 ($\approx 1.1 \times 10^{-3}$ S cm^{-1}) [19]. Thus, the R_b value mainly consists of the resistance of the YSZ electrolyte. The oxygen surface exchange reaction at a mixed conducting electrode consists of several elementary steps including adsorption, dissociation and incorporation on the surface of the electrode. The resistance R_s is directly related to the effective rate constant k of the oxygen surface exchange reaction: [20]

$$k = \frac{k_B T}{4e^2 R_s c_O} \tag{1}$$

k_B: Boltzmann constant; T: temperature; e: elementary charge; R_s: area specific surface resistance; c_O: total concentration of lattice

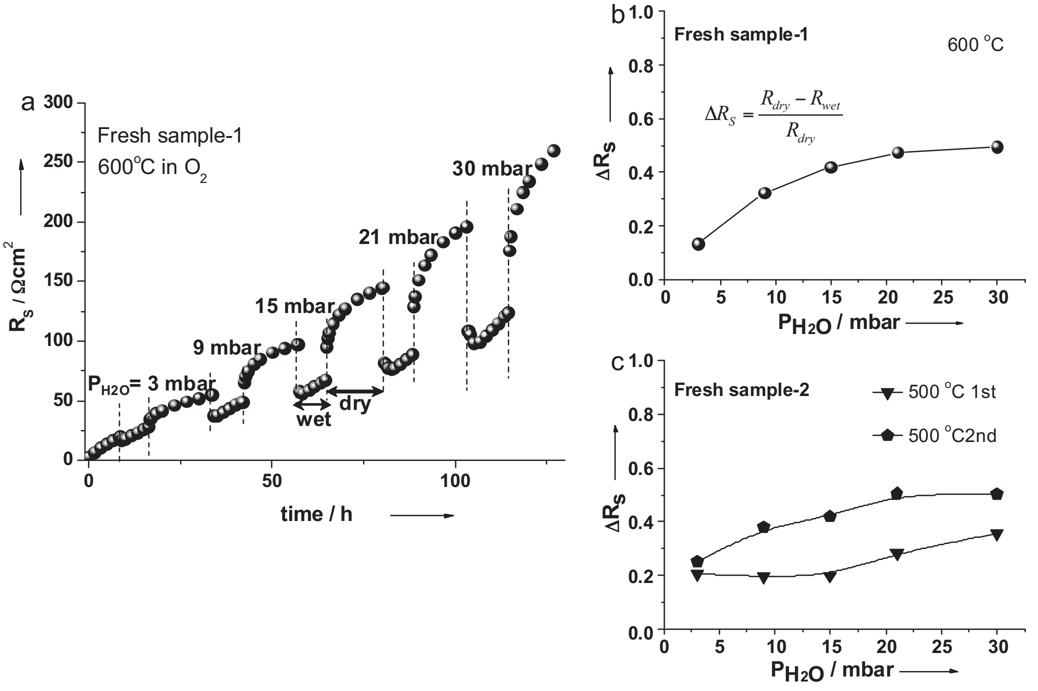

Fig. 3. Decrease of R_s upon hydration as a function of water partial pressure for the fresh sample-1 and 2 at 600 and 500 °C respectively.