



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  $\text{La}_{0.6}\text{Sr}_{0.4}\text{CoO}_{3-\delta}$  (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.

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### 1. Introduction

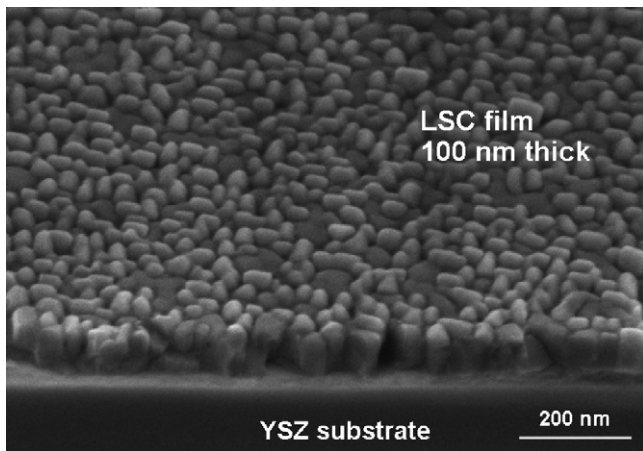
Oxygen ion mixed conducting perovskites such as strontium-doped lanthanum cobaltite (LSC) are promising candidates as cathode materials in solid oxide fuel cells (SOFCs) at intermediate temperature because of their high catalytic activity for the oxygen incorporation reaction [1–3]. So far, quite a number 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  $\text{La}_{0.6}\text{Sr}_{0.4}\text{CoO}_{3-\delta}$  surface are difficult to remove under nominally dry atmosphere at intermediate temperature ( $T = 300^\circ\text{C}$ ) [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  $\text{Sm}_{0.5}\text{Sr}_{0.5}\text{CoO}_{3-\delta}$  and  $\text{Ba}_{0.6}\text{La}_{0.4}\text{CoO}_{3-\delta}$  cathode was reported to decrease on addition of  $\text{H}_2\text{O}$  to oxygen, while a decrease of the oxygen surface exchange coefficient in  $\text{H}_2\text{O}$  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  $\text{La}_{0.6}\text{Sr}_{0.4}\text{CoO}_{3-\delta}$  (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  $\text{La}_{0.6}\text{Sr}_{0.4}\text{CoO}_{3-\delta}$  thin films of 100 nm thickness were deposited on both sides of polished (100) oriented yttria-stabilized zirconia single-crystals (YSZ, 9.5 mol%  $\text{Y}_2\text{O}_3$ , 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  $\text{O}_2$ ) or wet- (24 h at 600 °C in humidified  $\text{O}_2$ ,  $P_{\text{H}_2\text{O}} \approx 30$  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  $\text{O}_2$  (100 ml  $\text{min}^{-1}$ ) 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  $K_{\alpha}$  X-ray source of 1486.58 eV and a small spot focusing hemispherical

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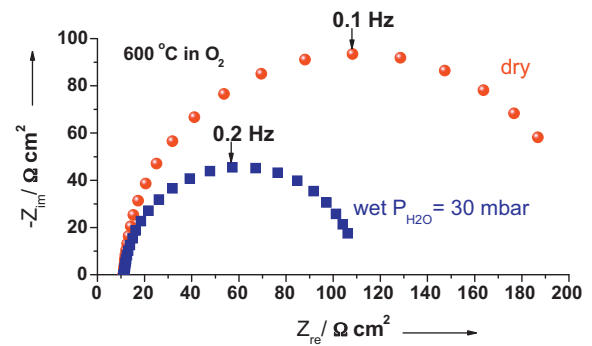


**Fig. 1.** High resolution scanning electron microscopy (SEM) image of a fractured sample with a 100 nm LSC film on YSZ substrate, measured from a 45° perspective.

electron energy analyzer. The inelastic mean free path from the Tanuma–Penn–Powell method (TPP-2M) [16] is  $\approx 2.2$  nm for La and Sr (photoelectron kinetic energy  $\approx 1350$  eV) and  $\approx 1.3$  nm for Co (kinetic energy  $\approx 650$  eV) in  $\text{La}_{0.6}\text{Sr}_{0.4}\text{CoO}_{3-\delta}$ . 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 shows representative impedance spectra of LSC films measured at 600 °C in dry or humidified  $\text{O}_2$ . The spectra show one dominating semicircle at low frequencies, as well as a non-zero axis

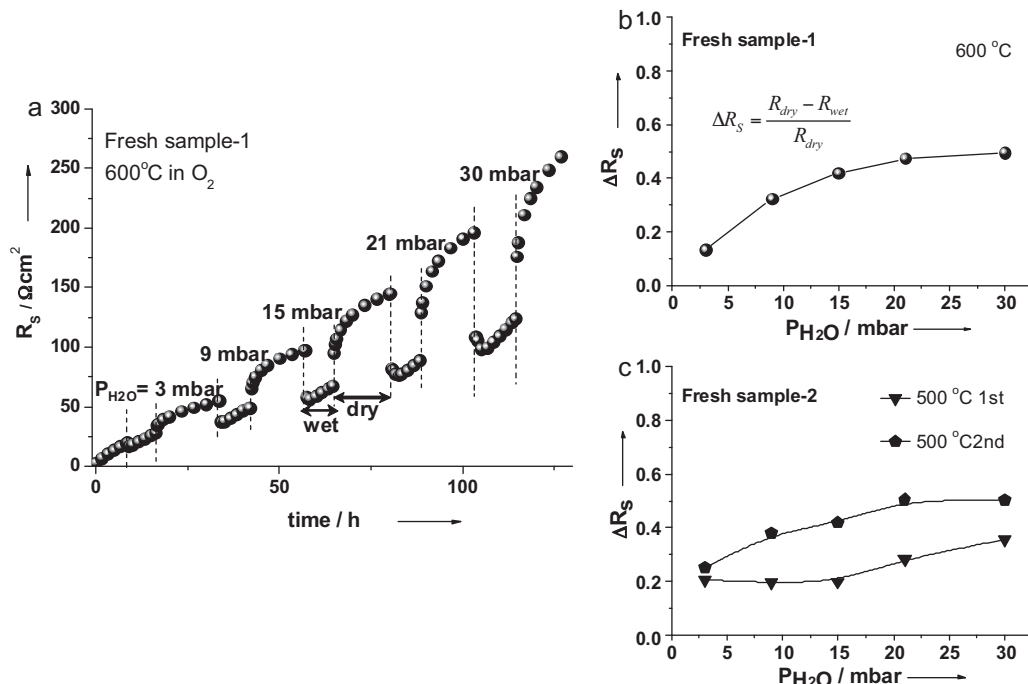


**Fig. 2.** Impedance spectra of LSC thin film deposited on both sides of YSZ substrate measured at 600 °C in dry or humidified  $\text{O}_2$  atmosphere.

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  $R_b$  ( $0.96 \pm 0.03$  eV) in the temperature range from 400 °C to 600 °C is similar to the reported value ( $0.94 \pm 0.03$  eV) for a 9.5 mol%  $\text{Y}_2\text{O}_3$ -doped  $\text{ZrO}_2$  single crystal [5]. The YSZ ionic conductivity calculated from  $R_b$  is  $\approx 6.3 \times 10^{-4} \text{ S cm}^{-1}$  at 500 °C, slightly lower than that of single crystal of 9.5 mol%  $\text{Y}_2\text{O}_3$ - $\text{ZrO}_2$  ( $\approx 1.1 \times 10^{-3} \text{ S cm}^{-1}$ ) [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]

$$k = \frac{k_B T}{4e^2 R_s c_0} \quad (1)$$

$k_B$ : Boltzmann constant;  $T$ : temperature;  $e$ : elementary charge;  $R_s$ : area specific surface resistance;  $c_0$ : 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.

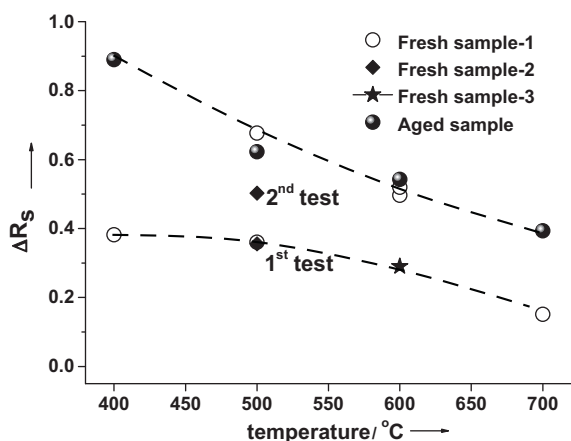


Fig. 4. Decrease of  $R_s$  upon hydration as a function of temperature for fresh and aged-samples ( $P_{\text{H}_2\text{O}} \approx 30$  mbar). Dash lines are also drawn as guide to the eye.

oxygen. At low temperatures (400–500 °C), a medium frequency arc appears that can be attributed to the transfer of oxide ions across the cathode/electrolyte interface [5]. However, this does not change upon hydration. Obviously, the water vapor affects only the oxygen exchange reaction, accelerating it by a factor of up to nine times at 400 °C. The chemical capacitance slightly increases from  $8.0 \times 10^2 \text{ F cm}^{-3}$  to  $8.7 \times 10^2 \text{ F cm}^{-3}$  at 600 °C upon hydration ( $P_{\text{H}_2\text{O}} \approx 30$  mbar). The chemical capacitance is proportional to the bulk quantity  $\partial c_{\text{O}}/\partial \mu_{\text{O}}$  ( $c_{\text{O}}$  is the oxygen concentration,  $\mu_{\text{O}}$  is the chemical potential of oxygen). Obviously, there is little change of the electrode's bulk composition upon hydration.

Fig. 3 shows the dependence of  $R_s$  on the water partial pressure for the fresh samples-1 and 2 at 600 °C and 500 °C.  $R_s$  steadily increased when the LSC film was kept under alternately dry and wet atmospheres. These degradation phenomena are in good qualitative and even quantitative agreement with previous reports on PLD-deposited LSC films [3]. In the fresh sample-2, the measurement for the  $P_{\text{H}_2\text{O}}$  dependence was performed twice to confirm the reproducibility of the results. Fig. 3 clearly shows that change of  $R_s$  ( $\Delta R_s = (R_{\text{dry}} - R_{\text{wet}})/R_{\text{dry}}$ ) becomes more pronounced with increasing water partial pressure, indicating that water vapor pressure is an important factor for controlling the oxygen surface exchange. These phenomena can be explained by a water adsorption isotherm since  $\Delta R_s$  increases with increasing the water partial pressure at constant temperature. Thus, it is expected that the adsorption of water is related to the enhancement of the surface exchange rate. The fresh sample-2 demonstrates that  $\Delta R_s$  increased more strongly for the second measurement indicating that the water effect depends on the starting condition of the  $R_s$  value because the film was aged during the measurement.

The temperature dependence of the  $\Delta R_s$  ( $P_{\text{H}_2\text{O}} \approx 30$  mbar) for four LSC films (fresh samples 1, 2, 3 and aged sample) is shown in Fig. 4. In the case of fresh sample-1, the film was heated from 400 °C to 700 °C and then cooled from 700 °C to 500 °C. The fresh sample-2 and -3 were measured directly at 500 °C and 600 °C. In order to observe the influence of previous aging, one LSC film had been aged at 600 °C in dry conditions for 2 h, which increased  $R_s$  at 400 °C by one order of magnitude. Fig. 4 displays that  $R_s$  under wet conditions decreased more strongly for the aged sample, which is in agreement with the already mentioned dependence of the water effect on the starting condition of the  $R_s$  value. In addition, the fresh sample-1 measured at 500 °C at the end of the thermal cycle also shows a stronger enhancement compared to the start of the thermal cycle. Although the experimental data at 600 °C in the fresh sample-1 is somewhat scattered, generally the enhancement of the surface exchange rate is stronger at lower temperatures, which suggests

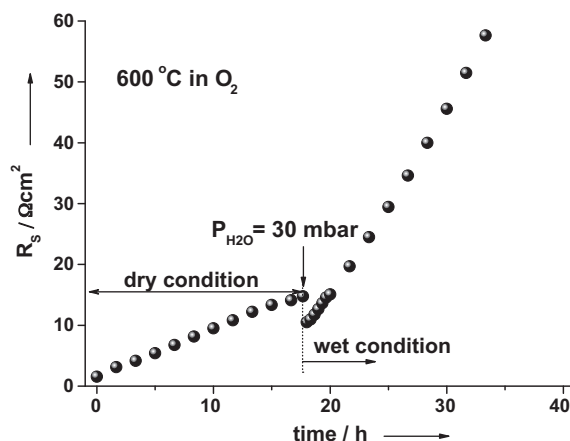


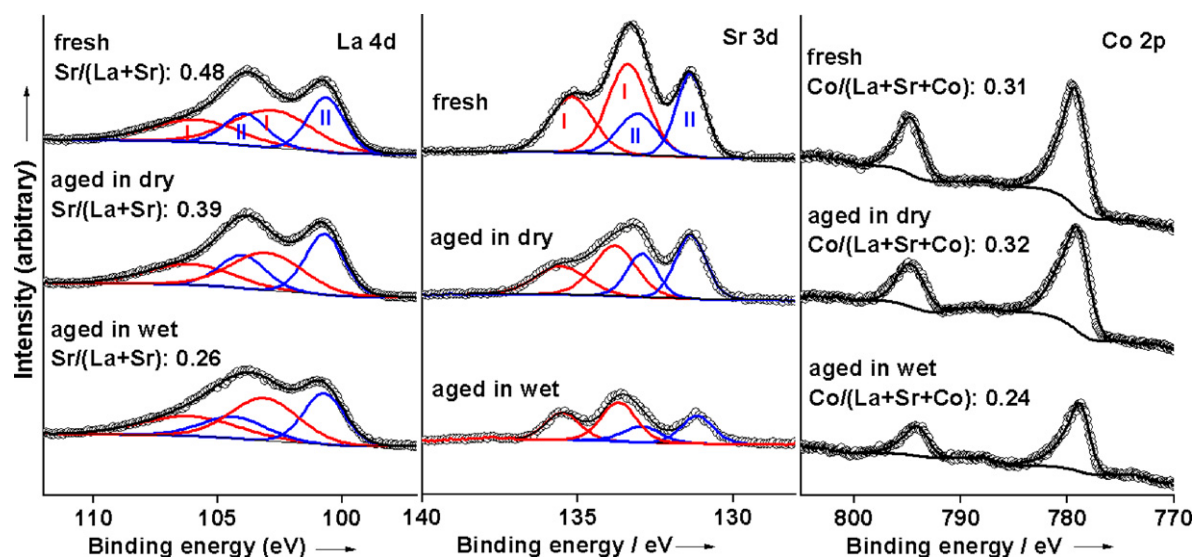
Fig. 5.  $R_s$  measured at 600 °C under dry and wet conditions showing the influence of water vapor in  $\text{O}_2$  on the surface exchange rate of the LSC (fresh sample-3).

that it may be the surface hydroxide coverage which affects the oxygen incorporation reaction.

The amount of adsorbed water increases for lower temperature and higher water partial pressure. For a hydroxylated lanthanum oxide surface temperatures of at least 427 °C are required to remove all hydroxide [21]. The water adsorbate coverage on a transition metal oxide such as  $\alpha\text{-Fe}_2\text{O}_3$  decreases exponentially with temperature above 400 °C and the remaining OH coverage is negligible at 800 °C: the OH coverage on  $\alpha\text{-Fe}_2\text{O}_3$  drops from 0.20 monolayer (ML) at 400 °C to 0.01 ML at 700 °C assuming that only one hydroxyl group is formed on each surface metal atom [22]. This tendency is in good agreement with our observation that the increase of surface exchange rate is more pronounced at lower temperature and higher water partial pressure. Thus, we suggest surface hydroxide species to play an important role in the oxygen surface exchange.

According to DFT calculations, the rate determining step for the oxygen incorporation into  $(\text{La,Sr})(\text{Fe,Co})\text{O}_{3-\delta}$  perovskite comprises the encounter of molecular oxygen adsorbates and surface oxygen vacancies [23]. In wet conditions, possibly protonated superoxide or peroxide adsorbates are formed which could increase the coverage with molecular oxygen intermediate species and also participate in the O incorporation reaction. Another possible explanation for the enhancement is that the oxygen vacancy concentration may be increased at the surface during hydration. It is reported that an interchange of oxygen XPS intensity occurs between the lattice and hydroxide species during hydration of a  $\text{La}_2\text{O}_3$  film, which supports some lattice oxide ions are being transformed into the hydroxide upon hydration [21,24]. However, further study is needed to elucidate the mechanism of exchange rate enhancement upon hydration.

A long-term measurement was performed to investigate the behavior of the oxygen exchange kinetics in dry and wet atmospheres. Fig. 5 shows the degradation of the exchange kinetics for the fresh sample-3 under dry and wet conditions at 600 °C. Two effects, enhanced of oxygen exchange rate upon hydration, and an accelerated degradation under wet atmosphere can be distinguished. The degradation rate of  $3.1 \Omega\text{cm}^2 \text{ h}^{-1}$  under wet conditions is much higher than that of  $0.75 \Omega\text{cm}^2 \text{ h}^{-1}$  under dry conditions. This degradation rate is in a good agreement with a previous report ( $\approx 0.7 \Omega\text{cm}^2 \text{ h}^{-1}$  in lab air) on 200 nm-thick LSC film PLD-deposited at 670 °C [3]. The degradation rate of fresh sample-1 shows a similar value ( $2.7 \Omega\text{cm}^2 \text{ h}^{-1}$  under  $P_{\text{H}_2\text{O}} \approx 30$  mbar at 600 °C) as also shown in Fig. 3. Thus, although we expect a variation of degradation rate due to different thermal history reproducibility was confirmed. While humidification of the oxidant is effective for enhancing the oxygen incorporation in the short-term range, the



**Fig. 6.** XP spectra of the La 4d, Sr 3d, and Co 2p core levels of three nominally identical LSC films with different aging processes: fresh, dry-aged (for 24 h at 600 °C in dry), and wet-aged (for 24 h at 600 °C in wet,  $P_{\text{H}_2\text{O}} \approx 30$  mbar) samples. Symbols: experimental data, Line: fit.

long-term stability of the cathode is substantially decreased. These two distinguishable effects of water on oxygen surface exchange may be the reason for the contradictory reports [10–14] about the water effects on cathode performance.

XPS has been used to study surface composition changes. Dry- (24 h at 600 °C in dry  $\text{O}_2$ ) or wet- (24 h at 600 °C in humidified  $\text{O}_2$ ,  $P_{\text{H}_2\text{O}} \approx 30$  mbar) aged films were compared to the fresh film. The surface composition was estimated from the relative peak areas of the La 4d, Sr 3d, and Co 2p core-level emission signals. Because the sensitivities for different elements are not precisely known, absolute concentrations could not be calculated. Fig. 6 shows the La 4d, Sr 3d, and Co 2p spectra and the fitting results for different LSC films, indicating that the aging process is accompanied by a significant cation composition change. All spectra are scaled to constant La area. The  $[\text{Sr}]/([\text{La}] + [\text{Sr}])$  ratios (based on peak areas and corresponding sensitivity factors) are also indicated in Fig. 6. The La 4d and Sr 3d spectra exhibit two components in addition to the  $J=3/2$ ,  $5/2$  splitting while the Co 2p spectra show only one doublet (multiple splitting  $\approx 15.4$  eV) with asymmetric peaks which is in agreement with the literature value for  $\text{Co}^{3+}$  in  $(\text{La},\text{Sr})\text{CoO}_{3-\delta}$  [25]. The high binding energy component I of La and Sr has previously been identified at the surface of a  $\text{La}_{0.6}\text{Sr}_{0.4}\text{Co}_{0.8}\text{Fe}_{0.2}\text{O}_{3-\delta}$  film [18]. The fresh LSC film exhibits a higher  $[\text{Sr}]/([\text{La}] + [\text{Sr}])$  ratio ( $\approx 0.48$ ) compared to the nominal bulk ratio of 0.4. Changes in the  $[\text{Sr}]/([\text{La}] + [\text{Sr}])$  ratio clearly show up for dry and wet aged samples. The dry-aged film not only exhibits a different Sr peak shape, but also a decrease of  $[\text{Sr}]/([\text{La}] + [\text{Sr}]) \approx 0.39$  compared to the fresh film. The area fraction of the high binding energy peak I decreased in the dry-aged film. This is consistent with an investigation of  $\text{La}_{0.6}\text{Sr}_{0.4}\text{Co}_{0.8}\text{Fe}_{0.2}\text{O}_{3-\delta}$  films, which concluded a strong increase of the high binding energy Sr peak after a cathodic polarization treatment which decreases  $R_s$  [18]. This result shows that the degradation process is related to the surface composition modification. It is reported in Ref. [26] that the degradation of the catalytic activity of  $(\text{La}_{0.6}\text{Sr}_{0.4})_{0.98}\text{Co}_{0.2}\text{Fe}_{0.8}\text{O}_{3-\delta}$  originates from Sr enrichment. The situation here is more complex because the degradation of LSC rather seems to be related to La enrichment in this study. The origin of the different observations for cation composition change is not clear at present. The wet-aged film shows a stronger decrease of Sr compared to the dry-aged film. Even though the area fraction of the high binding energy peak I in the wet-aged sample is similar to that of the fresh sample, the  $[\text{Sr}]/([\text{La}] + [\text{Sr}])$  ratio decreased to 0.26. As far as

the  $[\text{Co}]/([\text{La}] + [\text{Sr}] + [\text{Co}])$  ratios are concerned, there is little difference between fresh ( $[\text{Co}]/([\text{La}] + [\text{Sr}] + [\text{Co}]) \approx 0.31$ ) and dry-aged ( $\approx 0.32$ ) samples. However, this ratio decreased to  $\approx 0.24$  in the wet-aged sample. Using standard sensitivity factors, the Co content of mixed conducting perovskites is often underestimated [12]. Since the oxygen incorporation reaction is sensitive to the composition directly at the surface, the degradation process must be related to the cation rearrangement. XPS analysis indicates that the accelerated LSC degradation rate under wet conditions originated in an increased change of the surface cation composition. In addition, the degradation rate increases from  $1.6 \Omega\text{cm}^2 \text{h}^{-1}$  ( $P_{\text{H}_2\text{O}} \approx 3$  mbar) to  $2.7 \Omega\text{cm}^2 \text{h}^{-1}$  ( $P_{\text{H}_2\text{O}} \approx 30$  mbar) with increasing  $P_{\text{H}_2\text{O}}$  as shown in Fig. 3. Thus, it is expected that high water partial pressure causes more composition change at the surface. Our previous in situ XPS results measured at 300 °C also showed a decreased  $[\text{Sr}]/([\text{La}] + [\text{Sr}])$  ratio upon hydration, suggesting some cation rearrangements during hydration in LSC films [9]. According to X-ray diffraction, no second phase was detected in dry- or wet-aged films. XPS data only demonstrate the composition change at the surface (the inelastic mean free path is  $\approx 2.2$  nm for La and Sr and  $\approx 1.3$  nm for Co). Thus, it is difficult to say that a new phase is formed upon hydration. It can be assumed that the adsorbed OH induces cation rearrangements (in particular interchanging La and Sr) at the surface but keeping the overall mass balance. It is well known that Si poisoning can be a reason for the degradation of SOFC cathodes [27,28]. Bucher et al. reported that Si poisoning significantly contributes to the deterioration of the cathode performance in wet conditions [12]. For the samples in this study, according to XPS, surface Si concentrations are negligible. Thus, the Si-poisoning effect could be excluded here.

#### 4. Conclusions

In this study, we were able to clearly distinguish between two competing effects of water on oxygen surface exchange. The experimental results clearly show that at short time the oxygen surface exchange coefficient of LSC films can be increased by the water addition. On the other hand, the degradation rate is also accelerated under wet conditions due to increased cation composition changes at the surface. Obviously, the effect of water on such electrochemical reactions at mixed conducting perovskites should generally be paid attention to.

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