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Effect of Sr Surface Segregation of $\text{La}_{0.6}\text{Sr}_{0.4}\text{Co}_{0.2}\text{Fe}_{0.8}\text{O}_{3-\delta}$ Electrode on Its Electrochemical Performance in SOC

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The degradation mechanism of $\text{La}_{0.6}\text{Sr}_{0.4}\text{Co}_{0.2}\text{Fe}_{0.8}\text{O}_{3-\delta}$ (LSCF) electrode is investigated by examining its electrochemical behavior under equilibrium potential at elevated temperature and corresponding surface compositional changes. Diluted nitric acid etching treatment is conducted to confirm the correlation between the surface changes and the variation of electrochemical performance. It has been shown that the increase of polarization resistance of LSCF electrode has a linear dependence on the square root of time and arises from degradation of mass transfer process taking place at the gas-solid interface of electrode, such as oxygen adsorption/desorption and surface diffusion. Comparison of the behavior of the electrode before and after nitric acid treatment shows that the presence of surface inhibited species can account for the above observations. This inhibited species is confirmed by X-ray photoelectron spectroscopy to be a surface segregated Sr-based material, which supports the claim that surface Sr segregation is detrimental. A further lifespan study of LSCF electrode up to 158 h under 1 A/cm² electrolysis current demonstrates that the current can improve and stabilize the performance, which could be ascribed to the removal of surface Sr species due to the incorporation of surface Sr back into the lattice of LSCF.

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Solid oxide electrolyzer cells (SOECs) have attracted tremendous attention as a promising device to produce hydrogen or syngas through high temperature electrolysis (HTE) process.¹⁻⁶ However, the biggest barrier for SOEC to become commercially viable is its high degradation rate. For instance, aging studies of Ni-YSZ|YSZ|LSM-YSZ cells made at Risø showed degradation rates within the range of 2%/kh to 5%/kh, comparing with less than 2%/kh of similar cells tested under fuel cell mode.^{2,7} One of the sources of degradation is the delamination of anode of SOEC, especially at high current density, which is identified as a result of the accumulation of oxygen generated, when LSM ($\text{La}_{1-x}\text{Sr}_x\text{MnO}_{3-\delta}$) based anode is employed.⁸⁻¹² Thus, materials to replace LSM are desperately needed.

Currently, $\text{La}_x\text{Sr}_{1-x}\text{Co}_y\text{Fe}_{1-y}\text{O}_{3-\delta}$ (LSCF) is under intensive research as a potential anode, or air electrode, material for SOEC to replace traditional LSM electrode.¹³⁻¹⁵ As a mixed ionic and electronic conductor (MIEC) with high catalytic activity, LSCF performs much better than LSM as cathode in SOFC.¹⁶⁻¹⁹ Besides, the ionic conductivity of LSCF is believed to be able to mitigate the above-mentioned delamination phenomenon.² However, the stability of LSCF as air-electrode has yet to be thoroughly verified experimentally. One of the major concerns for LSCF is the surface segregation of Sr.²⁰⁻²⁶ This has been confirmed to be caused by the mismatch of the ionic radius of Sr and La, and the trend to minimize surface stress/strain and surface charge.^{20,23} Oh et al.²¹ has shown the appearance of Sr-O based precipitation by Auger electron spectroscopy on the surface of LSCF annealed at elevated temperature, 600–900°C, for 100 h. Druce et al.²⁵ also observed an increase of Sr concentration on the surface of LSCF after annealing the sample at 400, 600, and 800°C for 8 h by means of Low energy ion scattering.

In the meantime, although above groups have detected Sr surface segregation, the role of surface Sr enrichment and segregation on the electrochemical performance of electrode is still unclear. Simner et al.²⁶ attributed the aging of LSCF electrode operated in fuel cell mode to the Sr surface segregation as SrO. Apart from studies on porous LSCF electrode, investigations on model thin film $\text{La}_{0.6}\text{Sr}_{0.4}\text{Co}_{0.2}\text{Fe}_{0.8}\text{O}_{3-\delta}$ (LSC) and $\text{SrTi}_{1-x}\text{Fe}_x\text{O}_{3-\delta}$ (STF) electrode tested at low temperature range (up to 600°C) reported by several groups have indicated that the removal of surface Sr-based second phase can improve the electrochemical performance of thin film electrode.^{22,27-29} In contrast to above proposed detrimental effect of surface Sr-based

species, a previous work on the activation effect of cathodic current on the performance of LSCF electrode done by Baumann et al.³⁰ showed that the improvement of performance was benefitted from the enrichment of surface SrO. Thus, a clear relationship between the emergence of surface Sr-based species and its effect on the performance of a porous LSCF electrode under a typical SOC operating temperature has not yet been well established.

Consequently, it is necessary to fully understand the relationship between the degradation of the performance of a porous LSCF electrode and its surface compositional change at a typical SOC operating temperature in the first place, to serve as a basis for the lifespan study under anodic current later. In the work presented herein, variation of electrochemical performance of LSCF electrode in half-cell at high temperature, 750°C, under equilibrium potential was studied by electrochemical impedance spectroscopy (EIS) and the corresponding surface chemical compositional changes were investigated by X-ray photoelectron spectroscopy (XPS). Samples with nitric acid etching treatment were also examined to clearly verify the effect of surface compositional change. In addition, scanning electron microscopy (SEM) and X-ray diffractometry (XRD) studies were performed to inspect if there is any synergistic effect of microstructure change and interfacial reaction. At the end, lifespan analysis on LSCF air electrode was conducted under high electrolysis current (1 A/cm²) for 158 h to study its stability in the electrolyzer mode.

Experimental

In this work, half-cells with three-electrode configuration were used to study the electrochemical performance degradation of LSCF electrode. YSZ electrolyte substrates were prepared by die pressing YSZ powder (8 mol % Y_2O_3 – ZrO_2 , Tosoh, Japan) and firing at 1450°C for 4 h in air. The electrolyte substrates are about 19 mm in diameter and about 1 mm in thickness. Cathode slurry was prepared by fully grinding the mixture of $\text{La}_{0.6}\text{Sr}_{0.4}\text{Co}_{0.2}\text{Fe}_{0.8}\text{O}_{3-\delta}$ (LSCF, Fuelcellmaterials, US) and VEH 500 binder (Fuelcellmaterials, US) with a weight ratio of 1:1. LSCF working electrode of about 15 μm thickness with a geometric area of 0.5 cm² was coated onto the center of electrolyte by slurry coating and subsequently sintered at 900°C for 2 h. Pt counter electrode, also by slurry coating, was applied onto the electrolyte symmetrically opposite to working electrode and the Pt reference electrode was painted as a ring at the edge of the electrolyte on the same side of counter electrode. The gap between the counter

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Table I. Summary of testing procedures for sample 1–10.

Samples	Description	Testing condition	Nitric acid etching treatment	Testing condition	EDS	XPS	SEM
Sample 1	As-prepared half cell	24 h 750°C OCV					✓
Sample 2	As-prepared half cell	24 h 700°C OCV					
Sample 3	As-prepared half cell	24 h 650°C OCV					
Sample 4	As-prepared half cell	0.1 h 750°C OCV	✓	24 h 750°C OCV			
Sample 5	As-prepared half cell	24 h 750°C OCV	✓	48 h 750°C OCV			
Sample 6	Raw powder				✓	✓	
Sample 7	As-prepared half cell					✓	✓
Sample 8	As-prepared half cell	24 h 750°C annealing				✓	
Sample 9	As-prepared half cell	24 h 750°C annealing	✓			✓	
Sample 10	As-prepared half cell	158 h 800°C 1 A/cm ² electrolysis				✓	

and reference electrodes is about 4 mm. For those half-cells under electrochemical characterization, another layer of Pt was applied onto the cathode layer serving as current collector. In this work, 10 samples were fabricated and tested under various conditions as summarized in Table I. Details will be illustrated later in the section of Results and discussion.

During the electrochemical characterization, half-cells were placed in an in-house built SOFC test station, held by alumina housing. LSCF electrode was exposed to lab air. After the furnace reached the desired temperature, the sample was left to equilibrate for half an hour before conducting electrochemical test. The electrochemical impedance spectra were recorded by a Solartron 1255B frequency response analyzer (FRA) over a frequency range from 100 kHz to 0.1 Hz with an AC amplitude of 10 mV under open circuit voltage (OCV) condition during the testing at different temperatures (650, 700 and 750°C) under OCV or anodic current.

Nitric acid etching treatment was done by soaking samples into diluted nitric acid (pH $\approx$ 3) for 20 min followed by washing with distilled water for three times. The aim of this step is to remove the possible surface components of LSCF particles in electrode, as the possible metal oxide formed on the surface is reactive with nitric acid. Thus, by comparing the performance of electrode with and without, before and after nitric acid treatment, the relation of surface precipitation and the electrochemical performance degradation can be clearly revealed.

X-ray diffractometer (PW1820, Philips) was adopted to check the possible reaction products between YSZ and LSCF powder mixture, with a weight ratio of 1:1, sintered at 750°C for 100 h. Scanning electron microscope (JSM-7600F, JEOL, Japan) coupled with Energy Dispersive X-ray Detector was used to examine the morphology of electrode before and after annealing, and check the composition of raw LSCF material. X-ray photoelectron spectroscope (Axis-ULTRA, Kratos) was employed to study the surface chemical compositional change of electrode.

Results and Discussion

Electrochemical response evolution of half-cells.— Figure 1 shows the Nyquist plot evolution of sample 1–3 tested at different temperatures, 750, 700 and 650°C, under OCV for 24 h. In the figure, $t = 0$ h is defined as the time when the first electrochemical test was conducted. In the Nyquist plot, the high-frequency intercept of the impedance arc with real axis represents the ohmic resistance, R_s , while the difference between high- and low-frequency intercepts denotes the polarization resistance, R_p , which characterizes the electrode. As shown in Figure 1a, it can be observed that R_s remains the same value during the testing, while R_p increases gradually, which implies that the degradation mainly comes from the electrode. The same phenomena have been observed when the testing temperature was lowered down (Figure 1b and 1c).

To further locate the origin of this increase in R_p , analysis of the difference in impedance spectra (ADIS) was performed.³¹ The real part of the spectra, $Z'(f)$, is differentiated with respect to $\ln(f)$, where f is the frequency. The difference between this value obtained after

testing the cell for a certain time, t , and the initial value at $t = 0$ h is calculated and named $\Delta Z'_t(f)$, according to Equation 1. The plots of $\Delta Z'_t(f)$, against f , in which fast Fourier transform (FFT) filter was used to reduce the noise, for the three samples are shown in Figure 2. From Figure 2a, it can be observed that the increase of R_p comes from the change of a process happening at around 100 Hz. According to previous reports, this process is referred as mass transfer process, or so-called “surface” process, including oxygen adsorption/desorption, dissociation/association and diffusion, which happens at the gas-solid interface in electrode.^{32–34} Samples under lowered testing temperatures also show similar change in the plots (Figures 2b and 2c). Thus, the gradual slower “surface” process during the testing would mean that the degradation of LSCF electrode is caused by a change of surface property regardless of the testing temperature.

$$\Delta Z'_t(f) = \frac{\partial (Z'_t(f))}{\partial \ln(f)} - \frac{\partial (Z'_{t=0}(f))}{\partial \ln(f)} \quad [1]$$

Figure 3 displays the dependence of R_p increases with time and square root of time. For convenience sake, the relative change of R_p , i.e. R_p/R_{p0} , was used, instead of its absolute change. From Figure 3b, the increase of R_p presents a linear dependence on the square root of time. This dependence was also observed previously by Constantin et al.³⁵ on LSCF electrode with YSZ as electrolyte, implying that a diffusion process is involved in the degradation of LSCF electrode, which is highly possible to be the Sr diffusion to the surface of LSCF particles.²³ The slope of this linear dependence can be obtained from the linear fitting and can be regarded as an indicator of the degradation rate of LSCF electrode. As indicated in the plot, the slope increases from 0.0139 to 0.1360 with the increase of testing temperature from 650 to 750°C, meaning a faster degradation at higher testing temperature. Previous report²¹ on the formation of surface Sr-O based second phase also presented a trend that at higher temperature more second phase emerges on the surface of LSCF pellet.

Effect of nitric acid etching treatment.— In this part, nitric acid etching treatment was employed to provide evidence for the effect of surface compositional changes on the degradation of LSCF electrode. Two cells, sample 4 and 5, were treated with nitric acid following certain procedures as summarized in Table I. Sample 4 was tested for a few minutes at the beginning to obtain its initial performance. Then the sample was unloaded from the test station for nitric acid etching treatment followed by testing for another 24 h at 750°C. For sample 5, it was tested at 750°C for 24 h first, followed by nitric acid etching treatment and then testing for another 48 h.

Figure 4 shows the dependence of R_p relative increases with the square root of time for sample 4 and 5. For the first 24 h, R_p of sample 4 decreased at first and then increased with a slope of 0.1276 by linear fitting, which is only slightly smaller than the value for sample 5, 0.1360, indicating a rather similar surface property of LSCF particles in freshly prepared electrodes with or without nitric acid treatment. However, for the last 48 h testing of sample 5, R_p at first decreased to a value smaller than that before acid treatment, but larger than initial measurement before 24 h testing, and then increased with a

Figure 1. Electrochemical impedance spectroscopy evolutions of half-cells tested at (a) 750°C (sample 1), (b) 700°C (sample 2), and (c) 650°C (sample 3) under OCV for 24 h ($t = 0$ h is defined as the time when the first electrochemical test was conducted).

slope which is drastically reduced from the initial value of 0.1360 to 0.0706, meaning that the surface property of LSCF particles has changed during the first 24 h testing for sample 5. Note that R_p after the nitric acid etching treatment was slightly larger than that before treatment, and R_p decreased at first and then increased again for both samples. This could be explained by that the acidity would attack the surface of LSCF³⁶ and cause morphological change, leading to a slight higher R_p direct after acid treatment. Then the morphology would be modified by the heat-treatment during the initial period of testing after acid treatment, resulting in an decreased R_p during this period. Nevertheless, exact reasons accounting for this phenomenon need to be further investigated.

The changes on the R_p and degradation rate for sample 5 before and after the nitric acid treatment evidently reflect that the degradation of LSCF electrode is caused by the change of surface composition. For sample 4 with freshly prepared LSCF electrode, only limited surface substance emerged, thus, the effect of nitric acid etching treatment was limited. While for sample 5 which has been tested for 24 h, substantial surface substance presented, leading to a compromised performance. After the removal of surface substance by nitric acid, the performance improved and the degradation rate decreased. Similar effect of the etching treatment on the electrochemical performance has also been observed previously on model thin film electrode.^{22,27,28} Jung et al.²⁸ used 10% diluted buffered hydrofluoric acid to remove the surface layer on thin film STF and observed reduced polarization

resistance after the etching tested at 485–560°C. Kubicek et al.²² and Cai et al.²⁷ used diluted hydrochloric acid to conduct chemical etching after testing at 600°C under OCV for 72 h and obtained a reduced resistance which was lower than initial value before 72 h testing but an accelerated degradation rate after etching treatment. However, in this work, the smallest R_p for sample 5 after acid treatment is still larger than initial measurement before 24 h testing, which could be ascribed to the low pH value ($\text{pH} \approx 3$) of the acid used, which can only dissolve segregated second phase but cannot remove the whole surface layer. Besides, another discrepancy is that the degradation rate after acid treatment is lower than that before treatment in this work as opposed to an accelerated degradation rate observed by Cai et al.,²⁷ which needs further investigation.

XPS studies.— To further confirm the above conjecture, the composition of raw LSCF powder (sample 6) was checked by EDX and the surface compositions of LSCF particles in raw LSCF powder, freshly prepared LSCF electrode (sample 7), LSCF electrode after 24 h annealing (sample 8) and nitric acid treated LSCF electrode after annealing (sample 9) were checked by XPS. The results are listed in Table II. The EDX result has confirmed that the bulk composition of LSCF raw material is 30 cation % for La, 20 cation % for Sr, 9 cation % for Co and 41 cation % for Fe, which is close to its stoichiometric ratio of 6:4:2:8. However, the XPS result of raw LSCF material shows that in the surface area of LSCF particles, the Sr concentration is 35 cation %

Figure 2. ADIS plots for half-cells during testing at (a) 750°C (sample 1), (b) 700°C (sample 2), and (c) 650°C (sample 3) under OCV for 24 h.

(Sample 6). This is in consistence with previous observation³⁷ that Sr tends to enrich at the surface area of LSCF particle. For freshly prepared LSCF electrode, Sr concentration detected by XPS increases to 45 cation % (Sample 7). After 24 h annealing, this value further rises to 54 cation % (Sample 8). Afterwards, nitric acid etching treatment

reduces the Sr concentration to 37 cation % (Sample 9), close to the value of raw material. Moreover, above increase and decrease of Sr concentration is accompanied with decrease and increase of La and Fe concentration as can be observed in Table II, while Co concentration remains almost constant.

Figure 3. Dependence of polarization resistance increase with (a) time and (b) square root of time for half-cells tested at 750°C (sample 1), 700°C (sample 2), and 650°C (sample 3) under OCV for 24 h.

Figure 4. Effect of nitric acid treatment on square root of time dependence of polarization resistance increases annealed at 750°C for sample 4 and 5 (Sample 4 was tested to obtain its initial performance at the beginning, and then it was unloaded from the test station for nitric acid etching treatment followed by another 24 h testing at 750°C; Sample 5 was tested at 750°C for 24 h first, followed by nitric acid etching treatment and testing for another 48 h).

Table II. Results of EDX and XPS for raw LSCF powder (Sample 6), freshly prepared LSCF electrode (Sample 7), LSCF electrode after 24 h annealing (Sample 8) and nitric acid treated LSCF electrode after annealing (Sample 9).

Element	EDX (cation %)		XPS (cation %)			
	Sample 6	Sample 6	Sample 7	Sample 8	Sample 9	
La	30	29	21	21	24	
Sr	20	35	45	54	37	
Sr _S * 3d	3d _{3/2}	-	5	10	13	6
	3d _{5/2}	-	6	10	14	7
Sr _B * 3d	3d _{3/2}	-	12	12	13	12
	3d _{5/2}	-	12	13	14	12
Sr _S / Sr _B	-	0.46	0.82	1.00	0.54	
Co	9	10	11	10	13	
Fe	41	26	23	15	26	

*: Sr_B denotes Sr in LSCF perovskite lattice; Sr_S denotes the surface Sr-containing component including Sr²⁺ in the perovskite surface termination layer, and/or Sr-based second phase.

To further confirm if there is any surface segregated Sr-based second phase other than LSCF perovskite, peak fitting was conducted on the XPS spectra of Sr as shown in Figure 5. The Sr 3d spectrum showed a doublet state due to spin orbit, coupling of 3d_{3/2} and 3d_{5/2}, as shown in the figure. Two pairs of Sr 3d_{3/2} and 3d_{5/2} couple can be

Figure 5. Peak fitting results of Sr spectra for (a) raw LSCF powder (sample 6), (b) freshly prepared LSCF electrode (sample 7), (c) LSCF electrode after 24 h annealing (sample 8), and (d) nitric acid treated LSCF electrode after annealing (sample 9).

Figure 6. Concentration variations of total Sr, Sr_S and Sr_B along sample 6–9 (sample 6, raw LSCF powder; sample 7, freshly prepared LSCF electrode; sample 8, LSCF electrode after 24 h annealing; sample 9, nitric acid treated LSCF electrode after annealing).

extracted by peak fitting of the Sr 3d spectrum. The pair with lower binding energy, ≈ 133.5 eV for $3d_{3/2}$ and ≈ 132 eV for $3d_{5/2}$, is identified as bulk-bound state Sr, denoted as Sr_B, in the lattice of LSCF perovskite oxide.³⁷ While the pair with higher binding energy, ≈ 135.5 eV for $3d_{3/2}$ and ≈ 133.9 eV for $3d_{5/2}$, is recognized as the surface Sr-containing component in this study, denoted as Sr_S, on the surface of LSCF particles in electrode.^{30,38} This “surface” component may include Sr²⁺ in the perovskite surface termination layer, and/or Sr-based second phase segregated. Concentrations of these two Sr states in LSCF electrode for the four samples, sample 6–9, are also summarized in Table II. For LSCF raw material, the ratio of Sr_S to Sr_B is 0.46 (Sample 6). Electrode sintering process increases this value to 0.80 (Sample 7). After 24 h annealing, this value reaches 1.00 (Sample 8). At last, nitric acid treatment reduces this value to 0.54 (Sample 9). Concentration variations of total Sr, Sr_S and Sr_B along the four samples are plotted in Figure 6. From the figure, one can see that the increase of total Sr concentration originates from the increase of Sr_S, while the concentration of Sr_B almost remains constant.

Combining the XPS results with above electrochemical characterization, one can see that the evolution of the polarization resistance is accompanied with the change of “surface” Sr-containing component. That is, the polarization resistance increases along with the increase of Sr_S, and the polarization resistance and degradation rate decrease as the decrease of Sr_S. According to previous reports,^{13,39} increasing

Figure 8. XRD pattern of YSZ and LSCF 1:1 powder mixture sintered for 100 h at 750.

Sr in $\text{La}_{1-x}\text{Sr}_x\text{CoO}_{3-\delta}$ and LSCF perovskite phase will lead to higher oxygen reduction reaction activity. Thus, it is reasonable to say that the increase of Sr-based second phase dominates the increase of Sr_S over the enrichment of Sr in the termination layer in this work. Otherwise, the performance would be improved by the Sr enrichment in the termination layer of perovskite phase other than degrade during the testing.

SEM and XRD studies.— SEM images of the top views of LSCF electrode were taken before and after 24 h testing at 750°C as presented in Figure 7. There is no observable change on the microstructure and particle size. Besides, XRD spectrum of LSCF and YSZ powder mixture sintered at 750°C for 100 h was taken and shown in Figure 8. From the spectrum, one can see that there is no second phase like SrZrO₃ detected. These results eliminate possible synergistic effects of microstructure change and interfacial reaction on the degradation of LSCF electrode.

Consequently, from the results obtained, it can be concluded that the degradation of LSCF electrode under OCV at elevated temperature arises from the out-diffusion of lattice Sr to the surface and segregated as second phase on the LSCF electrode. Schematic illustrations of the surface compositional change of the LSCF particles in electrode for sample 5 are shown in Figure 9. For raw LSCF materials, the surface area is enriched with Sr, as well as little Sr-based second phase (Figure 9a). During the fabrication process, surface second phase increases slightly (Figure 9b). However, the 24 h testing will further out-diffuse the Sr from the bulk to the surface of LSCF particle and

Figure 7. SEM top views of LSCF electrode (a) before (sample 7, freshly prepared LSCF electrode) and (b) after (sample 1, half-cell tested at 750°C) 24 h testing.

Figure 9. Schematic illustrations of the surface compositional change of the LSCF particles for sample 5 during fabrication and testing: (a) for raw LSCF materials, surface is enriched with Sr as well as little Sr-based second phase; (b) for freshly prepared electrode, surface Sr-based second phase increases a bit; (c) for electrode after testing for 24 h, surface Sr-based second phase increases again, while the bulk LSCF become Sr-deficient due to the Sr out-diffusion; (d) for nitric acid treated electrode, surface Sr-based second phase reduces to the level comparable to raw material.

segregated as second phase (Figure 9c), degrading the performance. In the course of fabrication and testing, bulk LSCF has become Sr-deficient due to out-diffusion of Sr (Figure 9c). At last, nitric acid washes the surface Sr-based second phase off (Figure 9d), which improves the performance of electrode. Besides, the degradation is also slowed down since the Sr out-diffusion is decelerated as a result of the reduction of Sr content in the bulk of LSCF, which makes LSCF more tolerable to Sr doping. This surface second phase can be inferred as SrO and/or as reaction products formed with chemi-absorbed gases (SrCO_3 or $\text{Sr}(\text{OH})_2 \cdot x\text{H}_2\text{O}$), since the concentrations of all the elements detected by XPS decrease except for Sr during the annealing. The above results support the conclusion^{22,26} that surface Sr-based species is detrimental to the electrochemical performance of a porous LSCF electrode.

Electrochemical response evolution under SOEC operation.—

Figure 10 shows the polarization and ohmic resistance variation of half-cell with LSCF air electrode under electrolysis current of 1 A/cm^2 at 800°C (Sample 10) for 158 h. From the figure, it can be seen that the polarization resistance evolution of LSCF electrode under electrolyzer mode is quite different from that under OCV condition. Initially, the performance was improved by the anodic current. After about 8 h, the performance was gradually stabilized at a certain level until the end of the testing. As discussed above, the degradation under OCV is caused by the segregation of Sr-based inhibited species on the surface of LSCF particles, thus, the improvement and stabilization of the performance under electrolysis current could be possibly ascribed to the removal of surface Sr-based species due to the incorporation

of surface Sr back into the lattice of LSCF. Besides, a continuous increase of ohmic resistance can be also observed, which may be the result of interfacial reaction at 800°C or a degradation of electrolyte. Nevertheless, the exact reasons accounting for the above behaviors need to be further clarified.

Conclusions

The degradation mechanism of LSCF air electrode was inspected under OCV at 750°C . It has been found that the increase of polarization resistance of LSCF under OCV condition shows a linear dependence on the square root of time. ADIS analysis demonstrated that this increase mainly comes from the change of process happening at around 100 Hz, which was previously identified as mass transfer process. A comparison of the behavior of the sample before and after nitric acid etching treatment showed that the degradation rate after nitric acid etching treatment has been dramatically reduced compared to the one before the treatment, indicating that the degradation is most likely due to the emergence of surface inhibited species on LSCF electrode, which can be removed by nitric acid treatment. XPS examination showed that the “surface” Sr, including Sr^{2+} in the perovskite termination layer and Sr-based second phase like SrO, and/or the reaction products formed with chemi-absorbed gases ($\text{Sr}(\text{OH})_2 \cdot x\text{H}_2\text{O}$ and SrCO_3), increases upon the annealing and decreases upon the nitric acid etching treatment. Furthermore, SEM and XRD studies eliminate the possible synergistic effects of microstructure change and interfacial reaction between LSCF and YSZ on the degradation. Based on these results, the degradation of LSCF electrode under OCV can be concluded to be the surface segregation of Sr-based species, which retards the mass transfer process, including oxygen surface adsorption/desorption, surface dissociation/association and surface diffusion. This confirms the detrimental role of surface Sr-based second phase on the electrochemical performance of LSCF electrode. At last, lifespan test under anodic current of 1 A/cm^2 demonstrated that the anodic current can improve and stabilize the performance of LSCF electrode. This could be ascribed to the removal of surface Sr species due to incorporation of surface Sr back into LSCF lattice, which will be further investigated in the future.

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Figure 10. Polarization (R_p) and ohmic (R_s) resistance variation of half-cell with LSCF air electrode tested under SOEC operation (sample 10) with an anodic current of 1 A/cm^2 at 800°C for 158 h.

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