Aging Studies of Sr-doped LaCrO3/YSZ/Pt Cells for an Electrochemical NOx Sensor

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Abstract

The stability and NO_x sensing performance of electrochemical cells of the structure Sr-doped $LaCrO_{3-\delta}$ (LSC)/yttria-stabilized zirconia (YSZ)/Pt are being investigated for use in NO_x aftertreatment systems in diesel vehicles.   Among the requirements for NO_x sensor materials in these systems are stability and long lifetime (up to ten years) in the exhaust environment. In this study, cell aging effects were explored following extended exposure to a test environment of 10% O_2 at operating temperatures of $600\sim700^oC$. The data show that aging results in changes in particle morphology, chemical composition and interfacial structure, Impedance spectroscopy indicated an initial increase in the cell resistance during the early stages of aging, which is correlated to densification of the Pt electrode. Also, x-ray photoelectron spectroscopy indicated formation of $SrZrO_2$ solid state reaction product in the LSC, a process which is of finite duration. Subsequently, the overall cell resistance decreases with aging time due, in part, to roughening of YSZ-LSC interface, which improves interface adherence and enhances charge transfer kinetics at the O_2/YSZ/LSC triple phase boundary. This study constitutes a first step in the development of a basic understanding of aging phenomena in solid state electrochemical systems with application not only to sensors, but also to fuel cells, membranes, and electrolyzers.

1

Introduction

Increasingly stringent emissions regulations will require the development of comprehensive on-board diagnostic systems for exhaust gas monitoring and feedback control of emission aftertreatment systems. Compact, inexpensive sensors will be needed for detection of regulated pollutants including hydrocarbons, carbon monoxide, and oxides of nitrogen (NO_x). For example, an on-board NO_x sensor will be needed to monitor the regeneration of the NO_x reduction catalyst in the next generation of diesel or lean burn gasoline engines. NO_x sensors for exhaust gas monitoring have been proposed based on ionically-conducting solid-state electrochemical devices operated in the mixed-potential or amperometric modes.[1,2] Typical operating conditions for these sensors can include O_2 concentrations of 5-15%, temperatures in the range of 600-700°C, and NO_x concentrations in the range of 10-1000ppm.[3-5] It is expected *a priori* that the NO_x sensing response for these sensors will be strongly dependent on the electrode microstructure, the sensor operating conditions (i.e., temperature and cell configuration), and the concentrations of the various gas species present. However, these dependencies, particularly the effects of electrode microstructure, are often difficult to quantify and may change significantly with extended operation.

Sr-doped $LaCrO_{3-\delta}$ (LSC) perovskite has been identified as a potential NO_x sensor electrode material when coupled with a yttria-stabilized zirconia (YSZ) electrolyte.[6-8] LSC has previously been investigated for SOFC anode and interconnect applications because of excellent high temperature (800-1000°C) electronic conductivity.[9,10] This conductivity results from the partial substitution of La with Sr, which induces the formation of aliovalent chromium (Cr^{3+}/Cr^{4+}).[11] Other perovskite metal oxides such as $LaFeO_3$ and Sr-doped $LaCoO_3$ have also been investigated as NO_x sensor electrodes in both amperometric and potentiometric

configurations.[12,11] The high temperature performance and stability of these materials tend to be strongly dependent on characteristics such as particle morphology, chemical and structural stability, and electrode-electrolyte interfacial structure. In addition, there may be a significant influence from surface effects at the gas/electrode interface. Although the electrochemical performance of various perovskite electrodes on YSZ has been actively studied,[1,2,7,11] we are not aware of any reports regarding the long-term behavior (i.e. aging) with respect to the performance of these materials as sensor electrodes. This is important because it has been noted that most high temperature sensor and SOFC electrode materials exhibit long-term performance changes due to aging.[12] For example, there is a substantial body of literature describing aging effects in related perovskites used for SOFC cathodes, most notably Sr-doped $LaMnO_3$ (LSM).[13-15] Those reports describe significant cathodic polarization and aging effects, suggesting a need for similar systematic analyses of the aging processes in perovskite materials used as sensor electrodes.

In this work, time-dependent changes in structure, composition and electrochemical behavior for LSC/YSZ/Pt cells following extended operation in 10% O_2 at 600-700°C have been evaluated. Detailed materials characterization has been performed using scanning electron microscopy (SEM), X-ray photoelecton spectroscopy (XPS) and X-ray diffraction (XRD), and these results have been correlated with electrochemical impedance spectroscopy (EIS). The effects of the observed aging processes are evaluated with respect to the NO_x sensing performance of the cell.

3

Experimental

A three electrode cell configuration was obtained by depositing the LSC working electrode (WE), and Pt counter electrode (CE) and reference (RE) electrodes on an YSZ electrolyte substrate. The cell design is shown in Figure 1. YSZ substrates were prepared from 8 mol% YSZ powder (TZ8Y, Tosoh) by uniaxial pressing at 34.5 MPa, and isothermal sintering at $1500^{o}C$ for 2 hr. Prior to pressing, the powder was milled in ethanol with 0.75% poly(vinyl butyral) (Butvar S-98) binder for 48 hours, dried and reground. After sintering, both sides were polished with 600-grit SiC sandpaper and ultrasonically cleaned in ethanol. Typical final dimensions of the YSZ substrates were 16.5 mm in diameter and 0.7 mm in thickness.

LSC working electrodes were prepared from $La_{0.85}Sr_{0.15}Cr_{1.01}O_3$ powder (Praxair) mixed with screen printing paste (Heraeus V-006). Prior to use, the LSC powder was milled in ethanol for 48 hr, dried and reground. Working electrodes were deposited at the center of one face of the YSZ substrates by casting the ink using a circular (7.5 mm) mask. Subsequently, the LSC was sintered in air at $1200^{o}C$ for 2 hr. The resultant electrode thickness was approximately 10μm. Reference and counter electrodes were fabricated by hand-painting Pt paste (Heraeus CL-11-5349) on the opposing side of the YSZ substrate, followed by sintering at $1000^{o}C$ for 1 hr. The counter electrode was symmetrically opposed to the working electrode. Pt wires were used to make electrical connection to the electrodes by pressure contact. The LSC/YSZ/Pt cells were thermally and electrochemically aged in a quartz tube heated in a tube furnace at $600-700^{o}C$. The gas composition was controlled to 10% O_2 and 0-500 ppm NO_x using a standard gas handling system equipped with thermal mass flow controllers. Typically, the cells were aged under anodic polarization by applying a positive bias of 250 mV to the LSC WE using a potentiostat/galvanostat (Radiometer PGZ-301). The resultant current flow between the WE and

4

CE was recorded. At selected time intervals impedance spectra were collected at the imposed potential. Subsequently, the cell was placed at open circuit and the impedance spectrum was collected following a 20 min relaxation time. For the aged samples, the total time under anodic polarization was 121 hrs; the total time under thermal aging only which occurred during the periodic 20 min. relaxation times amounted to 24 hr.   Impedance measurements were made over the frequency range 0.05 Hz - 100 KHz using an ac sine wave amplitude of 25 mV. To facilitate a quantitative comparison, an equivalent circuit was fit to the impedance data (Zview, Scribner Associates). After aging, cell components were examined to evaluate changes in morphology, composition and structure. Microstructural features were evaluated with field emission scanning electron microscopy (FESEM) at 6 kV (Hitachi, 4500). Surface morphology of the YSZ underlying the electrodes (i.e., the electrode/electrolyte interface) was examined by removing the LSC and Pt electrodes from selected cells using 4 M HCl solution. The crystal structure of the LSC film was identified by X-ray diffraction (XRD) using Cu Kα radiation and an analyzing graphite crystal at 40 kV (Philips, APD3720). Elemental analysis was performed using energy dispersive X-ray analysis (EDX) with a spot size of approximately 2 μm at 15 kV. X-ray photoelectron spectroscopy (XPS) was conducted for quantitative compositional analysis of selected LSC electrodes before and after aging. XPS depth profiling was performed using Ar ion sputtering at 2 kV (Physical Electronics, Inc., Quantum 2000). The spectra were recorded under a pressure of $<10^{-7}$ Pa using Al Kα excitation operated at the accelerating voltage of 23.50 eV and output power of 40.3 W.   The irradiated spot size was 200 μm.   Sputtering rate was estimated to be 40 Å/min, calibrated to the sputter rate of 1000 Å Ta_2O_5 film. The Cr $2p$ spectra were fitted using XPSpeak after correcting the baseline using the Shirley method.[18] The fitted peaks contained a mixture of 91% Gaussian and 9% Lorentzian components. The goodness of fit

5

was determined by the value of χ^2 down to about 2. The binding energy was calibrated based on C $1s$ level at 284.6-284.8 eV.

Sensitivity to NO_x as a function of aging time with anodic polarization at +250 mV at $600^{\circ}C$ in 10% O_2 was also evaluated. In this test, the cells were periodically exposed to varying NO_x levels of 100 and 500 ppm of NO, and 100 and 500 ppm of NO_2. During NO_x testing, the current resulting from the electrochemical biasing was monitored and recorded as a measure of the NO_x sensitivity. Test durations ranged up to two weeks of continuous operation.

Results and Discussion

Particle morphology of LSC, Pt and YSZ. — It is well known that electrode microstructure and the associated particle morphologies strongly affect the diffusion and transport kinetics of oxygen to the gas/electrode/electrolyte triple phase boundary (TPB). Surface transport of ionic species generated from gas phase or catalyzed on the electrode surface can also be affected. In order to characterize the morphology and porosity of the un-aged electrodes, and to monitor any changes due to aging, FESEM was used to examine both the un-aged and aged LSC and Pt electrodes, and the underlying YSZ interface. Fig. 2(a) shows the surface of a typical un-aged LSC electrode. The LSC is porous, and consists of particles ranging from approximately 100-500 nm. After aging at $600^{\circ}C$ at +250 mV anodic polarization, numerous crack appear on the surface and the average particle size increased slightly, as shown in Fig. 2(b). The cause of the surface cracking is not currently understood.

Fig. 3 shows cross-sectional views of Pt electrodes before and after aging under the same conditions as described above for LSC. The un-aged Pt electrode (Fig. 3(a)) exhibits high porosity, which is desirable for efficient gas diffusion and transport. After aging (see Fig. 3(b),

6

the Pt is significantly more dense with a concomitant reduction in porosity and surface area. It is probable that the Pt densification process is one of the major origins of cell aging to be discussed subsequently. Note that aging-effects for the WE and CE have both an electrochemical as well as a thermal component, whereas the RE will only be affected predominately by thermal effects. Comparison of the aging effects at the RE and CE can provide some insight as to the relative magnitude of the electrochemical-aging effect. FESEM images of the aged RE (not shown) revealed only slight coarsening relative to the aged CE shown in Fig. 3(b). Additionally, in contrast to the electrochemically-thermally-aged cell, thermally (only)-aged LSC electrodes (no applied bias) did not develop the cracks on the electrode surface seen in Fig. 2(b); however, particle size increase noted above was the same in both cases. A general conclusion is that current flow through the cell had a significant effect on the aging process by enhancing the densification of the Pt CE and by inducing surface cracking (spallation) of the LSC WE.

The surface morphologies of the YSZ at the Pt/YSZ and LSC/YSZ interfaces were examined following removal of the Pt and LSC electrodes. A LSC/YSZ/Pt cell was aged at 600°C at +250 mV applied potential (121 hr total, with an additional total 24 hr thermal aging only at interspersed OCV intervals), following which the electrodes were removed by ultrasonication in a HCl solution. Qualitative elemental analysis using XPS showed no residual La, Sr or Cr, indicating complete removal of the LSC from the YSZ substrate. Fig. 4(a) shows an FESEM image of the YSZ surface at a point away from where the electrodes had been placed. The surface appears smooth with residual features resulting from the polishing procedure. The YSZ surface under the Pt CE exhibited no apparent difference from the bare YSZ area, as shown in Fig. 4(b). In contrast, however, the unaged LSC/YSZ interface shows significant surface roughening when compared to the bare YSZ or the Pt/YSZ interface,. This is shown in Fig. 4(c),

where it is clear that the YSZ/LSC interface has become significantly rougher, with the formation of cracks. Upon close inspection of the YSZ surface, small features can be seen to have developed which are comparable in size to the LSC particles (100-500 nm). This evolution of the YSZ morphology strongly indicates that these features correspond to the contact points between the LSC particles and the YSZ surface. These interfacial contacts form the TPB, which is consistent with prior observation made in the related LSM-YSZ system.[19,20] Such interfacial contact will improve the adherence between the LSC and YSZ, since the 100-500 nm sized LSC particles can be closely packed on the deep YSZ cracks as well as on rough surfaces.

Structural Characterization.— Fig. 5 shows XRD patterns for LSC electrodes, sintered onto YSZ, both before and after aging at 700°C for a week. Both traces show the pattern for orthorhombic LSC (*Pbnm*) overlapped with the pattern for YSZ. An impurity phase, believed to be $SrCrO_4$, appears at approximately 23-30°. This is consistent with prior reports indicating that $ACrO_4$ (A=Ca, Sr) is often present in the doped lanthanum chromites, probably due to the limited solubility of the Sr in LSC.[21, 23] No excess Cr_2O_3 is discernable in the XRD patterns. No change in the diffraction pattern was found after aging at 600 °C at +250 mV anodic polarization. However, after aging at 700°C under the same conditions as for the 600 °C sample a small new peak appears near 31° and is attributed to the formation of $SrZrO_3$ (orthorhombic, *Pnma*). The $SrZrO_3$ forms as a result of a reaction between $SrCrO_4$ and Zr at the YSZ-LSC interface. The formation of $SrZrO_3$ reaction product is limited by the availability of the $SrCrO_4$ impurity at or near the interface. There is no evidence for formation of $La_2Zr_2O_7$, a common secondary phase often formed in composite LSM/YSZ SOFC cathode materials.[24-26] This is not surprising since the formation of $La_2Zr_2O_7$ has been shown to result from Mn

8

dissolution out of the LSM, resulting in excess La to react with YSZ. No corresponding reaction is expected in the more stable LaCrO$_3$ system. Also apparent in the pattern for the aged electrode is a splitting and sharpening of the peaks at high 2θ for both YSZ and LSC. This indicates grain coarsening consistent with the particle growth observed in the SEM images.

Conclusive evidence of the formation of SrZrO$_3$ was obtained by EDX analysis on the aged LSC. Fig. 6(a) presents an FESEM image of a cross-section from an LSC electrode after aging at 700°C. The image shows the LSC to be 8.6 μm thick and composed of particles approximately 100-500 nm in size. EDX was used to evaluate the relative elemental distributions both near the nearer the LSC/YSZ interface and in the bulk of the LSC. The analysis was conducted by focusing on two spots in the cross-section at 25 and 75% of the distance between the top surface of the LSC and the YSZ interface; these are marked as [S] and [B] in Fig. 6(b), respectively. Near the surface [S], only Sr, La, Cr and O were observed to be present. In contrast, closer to the YSZ interface [B], a tiny Zr peak is also apparent. These data support the XRD result that SrZrO$_3$ is present in the LSC electrode. Also, they indicate that the formation of SrZrO$_3$ must be localized in proximity to the LSC-YSZ interface. EDX examination at several other spots near the LSC/YSZ interface yielded similar results. It is also interesting to note the large peak intensity of the Sr signal relative to La and Cr at [S], compared to the smaller relative signal at [B]. This further indicates that the chemical composition of the electrode seems to be significantly different at these two points in the sample.

Surface composition.— More detailed analyses of surface composition were conducted using XPS depth profiling on LSC electrodes before and after aging at 600-700°C. For the un-aged LSC, Fig. 7(a) shows the compositional profile as a function of depth from the top surface. The

9

depth from the top surface was calculated based on the calibrated sputter rate of Ta_2O_3 thin film. These data indicate that the surface of the un-aged LSC is O- and Sr-rich, which is consistent with the EDX data discussed above. The relative atomic ratios at the surface are listed in Table 1. At the surface of the un-aged electrode, the particle surfaces exhibit relative atomic ratios that are quite different from the theoretical values obtained based on the chemical formula $La_{0.85}Sr_{0.15}Cr_{1.01}O_{3-\delta}$. Similar observations have been made in Ca-doped $LaCrO_3$, where Sakai, et al., used Auger spectroscopy to show that within a few nanometers of the surface there exists a calcium-rich region.[23] In contrast, in the bulk (of the surface particles) the relative atomic ratios approach the theoretical values. From Fig. 7(a), this point is seen to be reached at approximately a depth of 28 nm from the surface. Note that, in the context of the present XPS data, "bulk" does not refer to the cross-section of the entire electrode, but rather to the bulk (as opposed to surface) part of the depth-profiled particles at the surface of the electrode.

Depth profile data for the aged cells indicate that the surface composition remains non-stoichiometric after aging the cell at 600°C at +250 mV, as shown in Fig. 7(b). However, upon depth profiling the Cr and La atomic concentrations in the anodically-aged LSC approach the theoretical values more quickly with depth than the un-aged samples reaching the "bulk" values at approximately12-16 nm from the surface). While this surface non-stoichiometric layer appears to become thinner during anodic aging, it is still O- and Sr-rich. Of particular interest in the aged sample is a remarkable increase in the oxygen content. The relative atomic ratios of O/La and O/Cr increased 43% and 23%, respectively, compared to those for the un-aged LSC. Table 1 shows a comparison of surface composition before and after aging by anodic (+250 mV) and cathodic (-250 mV) polarization. In contrast to the anodically-polarized LSC, under cathodic polarization there is a decrease in the O and Sr contents compared to the un-aged LSC.

10

Thus, the chemical composition of the LSC surface, and in particular the O content, is dependent upon the polarization direction. In order to maintain charge neutrality, the changes in oxygen content are likely to be associated with concurrent changes in valency of the Cr atoms at the surface.

In order to identify the oxidation state of Cr on the non-stoichiometric surface, curve fitting was carried out on the Cr $2p_{3/2}$ peak for both the un-aged and aged LSC. The experimental peak shape was modeled by employing multiple-splitting patterns derived for Cr^{3+}, Cr^{4+} and Cr^{6+}. Fig. 7(c) compares the original spectrum of the un-aged LSC with the fitted one. The best fit to the experimental Cr $2p$ spectrum is obtained by assigning the peaks at 575.4, 577.0 and 580.0 eV to Cr^{+3}, Cr^{+4} and Cr^{+6}, respectively. It should be noted that the lack of reported XPS data on Cr-containing perovskites makes assigning peaks somewhat tenuous, and our resultant binding energy values are slightly different from those of simple chromium oxides such as Cr_2O_3 and CrO_2.[27,28] The fitting process indicates that the relative concentrations of the valence states for chromium are 68.6% Cr^{3+}, 26.2% Cr^{4+} and 5.22% Cr^{6+} at the surface of the un-aged LSC. The content of Cr^{4+} exceeds the theoretical Cr^{4+} content of 15% induced by the strontium substitution for lanthanum. We speculate that this must be associated with the excess O and Sr at the top surface. We postulate that the Cr^{+6} can result from the impurity $SrCrO_4$. A non-stoichiometric surface composition may influence the initial electrochemical behavior for the cell by altering the surface catalytic properties of the electrode.

A comparison of curve fitting results for the Cr $2p_{3/2}$ peak for the un-aged and aged LSC is also shown in Table 1. We emphasize that in these studies the oxidations states and the compositions of the aged LSC are "frozen" upon cooling to room temperature from testing conditions. The fitting results show that Cr^{4+} content increases from 26.2% to 28.7% during

aging under anodic polarization, which is consistent with the increased oxygen content in the surface XPS data. The production of abundant O_2 gas at the TPB could result in partial oxidation of Cr^{3+} to Cr^{4+} at the surface. In contrast, aging under cathodic polarization results in a decrease of Cr^{4+} content from 26.2% to 22.9%, which is also consistent with the decreased surface-oxygen content shown by the XPS data. These data seem to indicate that the redox reactions can occur not only at the TPB, but also at the gas-electrode surface away from the TPB. This results in a distribution of Cr oxidation states at the surface that depends on bias direction. Previous studies sustain the conclusion that in porous, non-stoichiometric, and electron conducting metal oxide electrodes, oxygen exchange is not limited to only the TPB but can occur throughout the electrode structure..[29,30]

Impedance spectroscopy.—Impedance spectroscopy was employed to evaluate the effect of aging on the electrochemical behavior of the LSC/YSZ/Pt cells. Data obtained at open circuit following anodic biasing for various time periods at 600°C and 700°C is shown in Figures 8(a) and 8(b), respectively. As a point of reference, the uppermost curve in each figure was obtained following biasing for 1.5 hr; the bottom curve was obtained following 52.5 hr of polarization. In most cases, a small arc in the frequency region of 20-300 Hz is observed along with a dominant arc at lower frequency (0.7-10 Hz). Because of instrumental limitations, the arc attributed to YSZ electrolyte bulk resistance in the few tens of kHz range, is not shown.

From the data shown in Figure 8, it is noted that a very large initial ohmic resistance (greater than 20 Kohm) is observable at both 600°C and 700°C. Following anodic biasing the resistance decreases rapidly, especially at the higher temperature. Reduced cell resistance at

higher temperature is attributed to both higher oxygen conductivity of YSZ and higher electronic conductivity of LSC

Impedance spectroscopy experiments performed on a Pt/YSZ/Pt cell following aging indicate a significant increase in the cell resistance as a result of Pt coarsening, as discussed previously. Electrode coarsening would be expected to result in cell resistance increase because of reduced TPB length and decreased diffusivity of O_2 gas through the electrode that occurs with densification. Nevertheless, the overall impedance of the LSC/YSZ/Pt cell is dominated by the LSC electrode.

An approximate equivalent circuit can be used to interpret the impedance spectra shown in Figure 8. The circuit shown in Fig. 9 consists of two parallel resistance (R/constant phase element(CPE) sub-circuits in series. In Fig. 9, R_s represents the series resistance corresponding to the lead wire resistance and the bulk impedance of the YSZ electrolyte at high frequencies. R_1 corresponds to the first small semicircular arc in the intermediate frequency regime, which can be associated with O_2 gas diffusion and transport[31] and/or bulk resistance of the LSC and Pt electrodes.[32] The second contributing element of the low frequency arc, R_2, is attributed to the charge transfer reaction, related to the LSC/YSZ interface resistance. Monitoring changes in the values of these circuit elements as a function of aging time provides insight into the operative aging mechanisms..

Figure 10 shows the measured values of the R_1 and R_2 elements as a function of time during aging at temperatures of 600°C and 700°C. From Figure 10(a) it is seen that R_1 increases slowly with time at 600°C, with attainment of apparent equilibrium occurring after approximately 32 hr aging time. At higher temperature, the increase is much more rapid with apparent equilibrium being obtained after approximately 15 hr of aging. The magnitude of R_1 is

also higher at the higher temperature. The increase in the value of R_1 may be associated with reduced surface area and decreased efficiency of gas transport in the electrodes due to the particle coarsening effects noted above. Also the formation of $SrZrO_3$ near the LSC-YSZ interface may contribute to the increase in R_1. In contrast, the value of R_2 decreases with time and at higher temperature (see Fig. 10(b)). Improved interfacial contact at the TPB resulting in improved charge transfer kinetics is believed to be responsible for the large reduction in R_2. R_s was also observed to decrease with aging time and at higher temperature (not shown).

The formation of $LaZr_2O_7$ or $SrZrO_3$ in SOFC anodes has been associated with increased resistance.[24-26] However, the effect of $SrZrO_3$ formation in the LSC/YSZ system differs from that for LSM/YSZ SOFC anodes.[26,27] In a previous report on the interface reactions of LSM/YSZ SOFC anodes, Leng et. al. found that the formation of impurity secondary phases at the interface resulted in blocking of the transfer of oxygen anions and hence increased cell resistance.[33] McIntosh et al showed that this effect could be reversed and the cell impedance reduced after cathodic polarization.[34] In our case, it appears that the small amount of $SrZrO_3$ that forms at the interface does not affect charge transfer kinetics.

Following applications of anodic bias for various time periods the cell was allowed to relax at for 20 minutes at open circuit while the OCV was recorded. Fig. 11 shows characteristic behavior at 600 and 700°C. At 700°C the final OCV (recorded after 20 min relaxation) attains an apparent equilibrium value of approximately 130 mV following 10h of applied bias. In contrast, at 600°C the OCV is still asymptotically approaching an equilibrium value which is higher than that obtained at 700 °C even after 52 hr of anodic bias. The relaxation behavior is related to the kinetics of O^{2-} exchange at the TPB, which are faster at the higher temperature. This exchange rate is affected by the surface chemistry of the LSC electrode, including the distribution of Cr

14

oxidation states. The increased amount of Cr^{4+} after aging causes the LSC to "trap" O^{2-} in order to maintain charge neutrality, resulting in decreased kinetics for O^{2-} transport out of the cell during relaxation. In any case, the kinetics of relaxation processes will be slower at lower temperature, resulting in a slower attainment of the equilibrium OCV.

NO_x sensing performance upon a long term aging.—In an attempt to gain additional insight into the practical effects of long term aging on NO_x sensing performance, a LSC/YSZ/Pt cell was evaluated for its response to varying NO_x concentrations during extended aging in 10% O_2. Fig. 12(a) compares the NO_x response of the cell before and after anodic polarization at 600^oC for 15 days. The initial response data taken prior to aging show an unstable baseline, and the NO_x response, particularly to NO, is poor. After aging, the baseline is considerably more stable and the sensitivity to both NO and NO_2, particularly NO, improved as indicated in both Figure 12 (a) and 12(b). In addition, following aging more rapid response and recovery times are evident (τ_{90} approximately 1s). The improvement in sensing response is likely attributable to decreased cell resistance, which is consistent with the impedance changes discussed above. These results underscore the fact that aging of the NO_x sensing electrodes is crucial for obtaining stable and reproducible behavior. Similar remarks may also pertain to sensors for other gases, although different aging characteristics will not doubt be evident.

Conclusions

A solid-state electrochemical cell comprised of LSC/YSZ/Pt was evaluated for the effects of aging and for NO_x sensor performance. The Pt electrode was found to densify considerably

15

during initial aging. Aging results in minimal coarsening of the LSC but significant changes in surface chemical composition depending on the bias direction. While these data were obtained at the surface of particles at the gas phase/LSC boundary, the inference is that oxidation and reduction reactions occur not only at TPB but also at the LSC electrode-gas interface. During cell fabrication and aging the LSC-YSZ interface (TPB) coarsens considerably. This coarsening results in enhanced interfacial adherence and improved charge transfer. XPS surface analysis indicated that both the unaged and anodically-aged LSC surface showed oxygen and strontium elemental enrichment, with the aged surface showing greater relative oxygen enrichment. In contrast, a cathodically-aged electrode showed surface depletion in oxygen and strontium. Curve fitting of the Cr $2p_{3/2}$ showed that distribution of chromium oxidation states changes as a function of polarization. The Cr^{+4} increases in concentration relative to Cr^{+3} in the anodically-aged electrode while it decreases in a cathodically-aged electrode. Aging improves NO_x sensing response, showing long-term improvements in baseline stability and sensing response after 10-15 days of anodic aging in 10% O_2, which is consistent with other experimental findings associated with aging phenomena. Since Pt electrodes show considerable aging effects, either a pre-aging protocol of the Pt electrode or choice of an alternative material is recommended. Aging studies with new cells including a new counter electrode alternative to Pt is underway and will be reported in the forthcoming paper.

Acknowledgment

16

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Figure Captions

Fig. 1. Schematic showing the geometric relationships for the three-electrode configuration used in this work.

Fig. 2. FESEM images of the surface of the LSC working electrode (a) before and (b) after anodic aging at +250 mV at 600°C in 10% O_2 for 121 hours (note that periodic 20 min. OCV measurement cycles were interspersed, resulting in an additional 24 hr total thermal-only aging).

Fig. 3. FESEM images showing the cross-section of Pt counter electrodes (a) before and (b) after anodic aging at +250 mV (right?) at 600°C in 10% O_2 for 121 hours (note that periodic 20 min. OCV measurement cycles were interspersed, resulting in an additional 24 hr total thermal-only aging).

Fig. 4. FESEM images showing the surface of (a) as-fabricated YSZ and (b) YSZ interface following deposition, sintering, then removal of LSC and (c) YSZ interface after LSC anodic aging at +250 mV at 600°C in 10% O_2 for 121 hours (note that periodic 20 min. OCV measurement cycles were interspersed, resulting in an additional 24 hr total thermal-only aging).

Fig. 5. X-ray diffraction pattern for the LSC WE before (a) and after (b) anodic aging at +250 mV at 700°C in 10% O_2 for 121 hours (note that periodic 20 min. OCV measurement cycles were interspersed, resulting in an additional 24 hr total thermal-only aging).

Fig. 6. (a). FESEM image showing the cross-section of the LSC electrode anodically-aged at +250 mV at 700°C in 10% O_2 for 121 hours (note that periodic 20 min. OCV measurement cycles were interspersed, resulting in an additional 24 hr total thermal only aging), and, (b) EDX elemental analyses at two locations from the LSC/YSZ interface corresponding to point S and B in Fig. 6(a).

Fig. 7. XPS depth profile showing relative atomic concentration (%) versus depth from the top surface (nm) before (a) and after (b) after anodic aging at +250 mV at 600°C in 10%O_2 for 121 hours (note that periodic 20 min. OCV measurement cycles were interspersed, resulting in an additional 24 hr total thermal only aging). and (c) curve fitting to the Cr 2p spectrum for the un-aged LSC.

Fig. 8. Impedance spectra obtained at OCV as a function of aging time for the LSC/YSZ/Pt cells aged at (a) 600°C and (b) 700°C.

Fig. 9. Circuit representation used to evaluate the impedance measurements shown in Fig. 8.

Fig. 10. Values for R_1 and R_2 circuit elements (shown in Fig. 9) obtained by fitting to the impedance spectra shown in Fig. 8 at 600 and 700°C.

Fig.11. Values for the OCV obtained at the conclusion of a 20 min. relaxation time following anodic aging at +250 mV in 10%O_2 at 600 and 700°C.

Fig. 12. NO$_x$ sensing performance for a LSC/YSZ/Pt cell during extended anodic at +250 mV in 10% O$_2$. Fig. 12(a) compares the NO$_x$ response of the cell before and after anodic polarization at 600°C for 13 days. Fig. 12(b) shows baseline stability and stability of response to 100 and 500 ppm NO as a function of aging time.

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