Activating Oxygen Chemistry on Metal and Metal Oxides: Design Principles of Electrochemical Catalysts

By

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Submitted to the Department of Materials Science and Engineering in partial fulfillment of the requirements for the degree of

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Abstract

Electrochemical energy storage and conversion devices are important for the application of sustainable clean energies in the next decades. However, the slow kinetics of oxygen evolution reaction (OER) and oxygen reduction reaction (ORR) lead to great energy loss in many electrochemical energy devices, including polymer electrolyte membrane fuel cells (PEMFCs), water splitting electrolyzers, and rechargeable metal-air batteries, which hampers the development of new-energy applications such as electric vehicles. To increase the energy efficiency of ORR and OER processes, various catalysts have been studied for oxygen electrocatalysis, but they are still not active enough or not stable enough in developing commercial friendly electrochemical devices.

In this work, systematic studies have been applied on two catalyst systems: Pt-metal (Pt-M) alloys for ORR and perovskite oxides for OER. The combination of electrochemical characterizations with transmission electron microscopy (TEM) techniques provides deeper insights on how the basic physical and chemical properties could influence the stability and activity of the catalysts. For Pt-M ORR catalysts, it is found that using transition metal with more positive dissolution potential or forming protective Pt-rich shell by mild acid treatment can improve their stability in acid electrolyte. While for perovskite oxide OER catalysts, it is found that a closer distance between O 2p-band and Fermi level leads to higher activity but lower stability at pH 7, due to the activation of lattice oxygen sites. Moreover, with the help of environmental TEM techniques, structural oscillations are observed on perovskite oxides in the presence of water and electron radiation, caused by the oxygen evolution after water uptake into the oxide lattice. Such structural oscillation is greatly suppressed if the formation and mobility of lattice oxygen vacancy is hampered. The various new activity and stability descriptors for oxygen electrocatalysis found in this work not only provided practical guidelines for designing new ORR or OER catalysts, but also improved our fundamental understandings of the interactions between catalysts and electrolyte.

Thesis Supervisor:Yang Shao-HornGail E. Kendall Professor of Mechanical Engineering,Professor of Materials Science and Engineering

Dedicated to My Beloved Parents & My Dear Brother: Zhaohong & My Girlfriend: Wendy

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Chapter 1. Introduction

1.1. Motivation

Environmental friendly energy storage and conversion technique is one of the major challenges for the next decades,^{1,2} which is critical to bridge the sustainable new energy sources to the final user demands. This is because many clean energy sources, such as solar power and wind power, are usually generated not at the places where we need them, and not at the time when we need them. Therefore, we have to first store the clean energies, usually in chemicals, and then convert them back to electricity when we need energies in power grids or electric vehicles, as shown in Figure 1-1. Electrochemical methods provides many potential solutions to store and convert renewable energy sources at the room temperature, such as polymer electrolyte membrane fuel cells (PEMFCs),³⁻⁵ water splitting electrolyzers^{1,2,6,7} and rechargeable metal-air batteries.⁸⁻¹¹



Figure 1-1. The role of energy storage and conversion is to bridge the gap between the renewable energy sources and user demands, including power grids and electric vehicles.

However, the sluggish kinetics of oxygen reduction reaction (ORR) and oxygen evolution reaction (OER) limit the efficiency of these electrochemical technologies.^{1-7,9-12}

As shown in Figure 1-2, if we use electrochemical water splitting to store energy in H₂ and O₂ and use PEMFC to convert the chemical energy back into electricity, very high overpotential will be required to drive OER and ORR, which lead to extra energy input during the energy storage and less energy output during the energy conversion. To make the electrochemical devices more efficient and more commercial friendly, people need to develop cost-effective, highly active and highly stable catalysts for ORR and OER. So far, researchers have tried many different kinds of materials for oxygen electrocatalysis, including Pt-metal (Pt-M) alloys for ORR¹³⁻²⁵ and transition metal oxides for OER.^{10,11,26-33} These new catalysts showed promising ORR or OER catalytic activities, but were still not active enough or not stable enough to make practical and commercial friendly electrochemical devices.^{6,28,34-42} There is still a great need to further activating the oxygen chemistry on metal and metal oxides catalysts.



Figure 1-2. The voltage vs. the power density during the water splitting (blue) and fuel cell working (red) processes, respectively. The slow kinetics in the OER and ORR caused major energy loss in many energy storage and conversion processes.

1.2. Previous Activity and Stability Descriptors for ORR and OER Catalysts

In the road of pursuing higher activity and higher stability, finding descriptors is of great significance in saving time and budget, which could connect the basic properties of materials with its catalytic performance and guide the direction of designing new catalysts.^{20,28,29,43} So far, many ORR or OER activity descriptors have been discovered, as partially shown in Figure 1-3. Most of these activity descriptors are related with the Sabatier Principle: either too strong or too weak surface adsorption would lead to less activity. Therefore, if to plot the ORR or OER activity versus the adsorption strength of oxygen on the catalysts surface, we will get a volcano-shape slot.⁴⁴ However, the adsorption strength of a new material can hardly be predicted, which makes Sabatier Principle a less practical guide for developing new catalysts. Therefore, researchers started to look for other descripting properties, especially the bulk properties, which are related to the surface adsorption strength and can be more easily estimated and/or controlled. One example is the d-band theory for oxygen adsorption on transition metals: when the d-band center of the transition metal is lower, the anti-bonding state of surface oxygen adsorption will become higher relative to the Fermi level, leading to stronger surface bonding.^{45,46} This allows us to tune the electronic status of Pt-M alloys to adjust the surface adsorption strength of oxygen, and therefore to further improve the ORR activity.^{13-14,17,27-30,47} Similarly, for OER activity of perovskite oxides, we found that when the eg occupancy of the transition meal site is closer to unity²⁹ or if the O 2p-band center is closer to Fermi level,²⁸ the perovskite oxides will exhibit higher specific OER activity in alkaline electrolyte. These descriptors have helped us find out several highlyactive OER catalysts, including Ba_{0.5}Sr_{0.5}Co_{0.8}Fe_{0.2}O_{3-δ} (BSCF) and PrBaCo₂O_{5+δ} (PBCO).



Figure 1-3. Some activity descriptors for ORR and OER discovered previously. With the sequence from left to right, the ORR descriptor plots are adapted from Ref. 45, 46, 47 and 43; while the OER descriptors are adapted from Ref. 44, 48, 29 and 28.

Despite various activity descriptors that have been discovered, so far we still have less stability descriptors for both OER and ORR catalysts. In the development of electrochemical energy devices, the stability of catalysts is as important as the activity. However, many of the state-of-art high-activity Pt-alloy ORR catalysts and oxides OER catalysts suffer from the fast degradation, especially in neutral or low pH electrolyte, which is related to the interaction between catalysts and the species in the electrolyte (e.g. H^+ , OH⁻, H₂O, O₂, etc.). Therefore, it is of great importance to look into the interaction between water/electrolyte and catalysts, investigate the mechanism of oxygen electrocatalysis and catalysts degradation, and find new guidelines that could help us to optimize activity and stability of the catalysts simultaneously.

1.3. Thesis Overview

In order to study the electrocatalytic mechanisms and degradation mechanisms during the OER and ORR as well as to find new activity and stability descriptors for oxygen electrocatalysis, in this thesis, systematic *in situ* and *ex situ* characterizations were applied on both Pt-M alloy system for ORR and perovskite oxides system for OER. We combined electrochemical characterizations with transmission electron microscope (TEM) techniques to investigate the interactions between catalysts and electrolyte, which lies behind the new descriptors discovered in this work.

In **Chapter 2**, we tested the evolutions of ORR activities, CO stripping voltages and chemical compositions of various $Pt_{0.5}M_{0.5}$ nanoparticles during cyclic stability test in acid electrolytes.⁴⁹ We found that alloying with transition metals that have more positive dissolution potential could prevent transition metal leaching and improve both the bulk and surface stabilities during voltage cycling tests. This implies that in the competition between alloying formation and metal dissolution, the metal dissolution driving force is more influential. Meanwhile, transition metals with more positive dissolution potential have less beneficial adjustments of Pt electronic structure and therefore lead to lower ORR activities. The competing between activity and stability leads to a volcano-like relationship between the ORR activity after 1200 voltage cycles and the dissolution voltage of the transition metal. Among all the tested Pt-M catalysts, Pt-Ni showed the highest activity at the end of stability test.

To further investigate the degradation process and optimize the ORR activity of Pt-Ni system, in **Chapter 3** we used pre-acid-leaching protocol to control the formation of Pt-rich shell on the surface of Pt-Ni particles.⁵⁰ It is found that both the smaller particle size and the formation of dense surface Pt shell after mild acid treatment and post annealing can improve the stability of the Pt-Ni nanoparticles during the ORR in acid electrolyte. With the help of these guidelines, a H_2SO_4 -treated and annealed Pt-Ni catalyst was successfully fabricated, which for the first time demonstrates both the initial and 30k-cycled ORR activity higher than the PEMFC cathode catalyst target made by U.S. Department of Energy (DOE). Systematic study of the activity and stability descriptors was also applied onto the perovskite oxides for OER, which is the reverse reaction to ORR. In **Chapter 4**, we extended our previous understandings of OER catalysts at high pH to that in neutral-pH electrolyte, which is important for reversible metal-air batteries and water splitting.⁵¹ We found that both eg-filling and O 2p-band, which are activity descriptors discovered in alkali electrolyte, are still effective at neutral-pH. Oxides with eg closer to 1 or O 2p-band closer to Fermi level will have higher OER activity at both high and neutral pH. In addition, two different degradation mechanisms were discovered at pH 7. When the Fermi level of perovskites is closer to its O 2p-band center, the oxides become unstable, accompanied with A-site atom leaching. When the distance between O 2p-band center and Fermi level is larger, the oxides become stable under low OER overpotential, but are still unstable under high OER overpotential accompanied with B-site atom leaching. Therefore, O 2p-band is also a stability descriptor at neutral pH.

The stability studies in the above chapters were done using *ex situ* characterizations, meaning we have to stop the electrochemical process and take the materials out for the measurements. To study the interaction of water and perovskite oxides in situ, in Chapter 5, we applied environmental transmission electron microscopy (ETEM) techniques to run electrochemical reactions directly in the TEM chamber,⁵² which allows direct observation of the oxygen evolution and the degradation of catalysts. It is found that when we introduce water vapor into the TEM chamber, BSCF can first uptake water into the lattice, and then O₂ gas can be evolved inside BSCF, causing the breathing-like lattice oscillation. Since the O₂ gas was trapped inside of the bubble structures, we were able to confirm the oxygen evolution during oscillations using electron energy loss spectra (EELS). We were also able to use a bubble model to simulate the bubble growing and shrinking processes with first-order approximations. On the contrary, for other perovskites with the Fermi level farther away from the O 2p-band, the greater energy penalty of oxygen vacancy formation and smaller oxygen ion mobility can hamper the water uptake and therefore the structural oscillations are weaker or absent. These atomic scale observations further demonstrate that the critical influence from bulk electronic structures as well as the electrolyte(water)-catalyst interactions to the oxygen catalysis mechanism and the stability of the catalysts.

Finally, conclusions and perspective of fundamental approaches/strategies toward better understanding of oxygen electrocatalysis and new design principles of OER and ORR catalysts will be discussed in **Chapter 6**.

Chapter 2. ORR Activity and Stability Trends of Pt_{0.5}M_{0.5} Nanoparticle in Acid Electrolyte

2.1. Introduction

The slow kinetics of ORR is the major energy loss of many low-temperature energy conversion devices, including PEMFCs and rechargeable metal-air batteries.³⁻⁵ The traditional ORR catalyst is pure Pt, which has high ORR activity but low abundance in the earth. To make more commercial friendly energy conversion devices, significant efforts have been made to improve the stability and activity of Pt-based materials, in order to reduce the Pt loading in these devices. Recently, Pt-M alloy catalysts are widely studied as the ORR catalysts for PEMFCs with up to two-order higher ORR activity than pure Pt.^{13-25,53-57} The improved ORR activity in Pt-M alloys is benefited from the strain^{14,18,19,58-60} and the ligand^{13-14, 17, 27-30} effects, which could tune the electron d-band to adjust the surface adsorption of oxygen species (e.g. OH, OOH, etc.) and therefore to optimize the heights of energy barriers between catalytic intermediates.^{4, 31-33} However, alloying with transition metals also brings severe degradation issues involving M loss through leaching^{15,16,36,61-66} or dealloying,^{67,68} which lead to the decreasing of ORR activity caused by the reduction in the beneficial electronic structure modification associated with alloying.^{10,13,44-45} In order to stabilize Pt-M catalysts in acid electrolyte, it is essential to understand the effect of transition metal leaching and the accompanied activity change of Pt-M catalysts under cyclic voltage operations.

Although there are many studies on the stability and activity of Pt-M during ORR, different experimental conditions and sample preparation methods were applied in these studies, $^{36,58,61-63}$ which prevented us from learning the influence of transition metal chemistry to the leaching process by directly comparing the results in these different works. In this chapter, a systematical activity and stability study on a series of Pt-M nanoparticles is reported in order to develop rational selection criteria of transition metal for long-lived Pt-M ORR catalysts.⁴⁹ In Pt-M alloy, the alloy formation energy (E_{alloy}) represents the driving force to prevent dealloying, which is a measure of the Pt-M bond

energy with respect to Pt-Pt and M-M; and the dissolution potential ($V_{dissolve}$) on the contrary, represents the driving force of metal leaching. To make the alloy more stable, higher E_{alloy} and more positive $V_{dissolve}$ are preferred. However, in Pt-M, E_{alloy} is found to scale with $V_{dissolve}$, as shown in Figure 2-1. The dependency between E_{alloy} and $V_{dissolve}$ could be originated from d-electron filling. If the d-band center of M is close to Fermi level, on one hand it leads to more filling in bonding states and less filling in anti-bonding states when alloying with Pt and thus have stronger E_{alloy} ,⁴ while on the other hand M is also easier to be reduced by protons in acid and therefore have more negative $V_{dissolve}$.⁴⁵



Figure 2-1. E_{alloy} vs. $V_{dissolve}$ of various Pt-M alloys. The values of $V_{dissolve}$ (M \Leftrightarrow Mn⁺ + n e⁻) were taken from the CRC handbook.⁶⁹ The values of E_{alloy} shown as black solid circles were taken from Ref.47, while the values for E_{alloy} shown as blue open circles were evaluated from studies of Pt alloy phase diagrams.⁷⁰⁻⁷⁸

To study how the competition between these two thermodynamic properties will influence the ORR activity and stability of Pt-M alloys, accelerated cyclic stability tests were applied on a series of Pt-M nanoparticles from Premetek Co. (20 wt% on Vulcan XC-72 carbon), where M = Fe, Co, Ni, Cu, Ru, Pd, and Ir. All of these nanoparticles have a nominal Pt:M ratio of 1:1 and similar particle sizes ~3.5 nm. Pt nanoparticles (46 wt% supported by Vulcan carbon) from Tanaka Kikinzoku (TKK) was used as a reference. Then chemical composition, particle size, surface area, CO oxidation onset voltage and

ORR activity of these Pt-M catalysts were characterized as a function of voltage cycling in acid. It is found that the loss of ORR and CO oxidation activities was governed by the extent of transition metal leaching. In addition, the Pt-M nanoparticles were found to lose more M and became less stable when $V_{dissolve}$ of M is negative in standard condition. Meanwhile, the activity increased when $V_{dissolve}$ was more negative. The results provide insights into the rational design of Pt-M nanoparticle catalysts with enhanced stability and activity.

2.2. Experimental Methods

Rotating disk electrode configuration

Rotating disk electrode (RDE) configuration was employed for the electrochemical measurements in this chapter, with a rotatable working electrode (PINE Instrument), a Pt wire as the counter electrode, and a saturated calomel electrode (SCE, Analytical Sensor, Inc.) as the reference electrode. The working electrode was prepared by drop-casting the ink of pure Pt or Pt-M nanoparticles onto the glassy carbon electrode (GCE, 5 mm in diameter, Pine Instrument) after polishing. The loading is 10 μ gPt/cm²disk. The measured potentials vs. SCE were calibrated to the reversible hydrogen electrode (RHE) using H₂/H⁺ redox in this chapter. Accelerated cyclic voltage tests between 0.6 and 1.0 V vs. RHE at 20 mV/s and room temperature without any rotation were applied in Ar-saturated 0.1 M HClO₄, which is diluted from 70% HClO₄ (GFS Chemicals) using deionized water (DI water, 18 MΩ). The electrochemical surface area (ESA) of Pt was measured using the hydrogen adsorption and desorption (HAD) methods in Ar-saturated 0.1 M HClO₄ electrolyte at 10 mV/s between 0.05 and 0.35 V vs. RHE after a double-layer correction with the conversion factor of 210 μ C/cm²_{Pt}, which was also used in previous works.⁷⁹

ORR activity measurements

ORR activities were measured using cyclic voltammetry (CV) between 0.05 and 1.1 V vs. RHE at 10 mV/s and at rotation speeds of 100, 400, 900, 1600 and 2500 rpm in 0.1 M HClO₄ O_2 -saturated electrolyte with O_2 bubbling (99.999%, Airgas) inside the electrolyte. Then double-layer current were corrected by subtracting the background CV

curve measured in Ar-saturated electrolyte. Ohmic loss were corrected by $E_{\text{correct}} = E - iR$, where *i* is the measured current, and *R* is the electrolyte resistances determined by high-frequency alternating current impedance. The kinetic current i_k , was calculated from the Koutecky-Levich equation⁵³: $1/i = 1/i_k + 1/i_D$, where i_D is the mass-transport limited current obtained from CV curves.⁵³ The specific and the mass ORR activities were obtained by normalizing i_k with the ESA and the weight of Pt in Pt-M nanoparticles, respectively. The ORR activity at 0.9 V vs. RHE was compared among different Pt-M samples.

CO stripping measurements

CO stripping method was employed in this work to probe the evolution of surface chemistry of Pt-M nanoparticles. First, CO gas was bubbled and adsorbed onto the Pt-M surface at 0.1 V vs. RHE in O_2 -free 0.1 M HClO₄ electrolyte. Then CO in the solution was removed by bubbling Ar for at least 30 min, while the working electrode was kept at 0.1 V vs. RHE to catch a mono layer of CO on the surface. After that, CV scanning was performed between 0.05 and 1.1 V vs. RHE at 5 mV/s under Ar bubbling, and then the CO oxidation peak could be obtained by subtracting the background CV from the CO stripping curve. The potential at which the current attained 5% of the peak current prior to reaching the peak in the positive-going sweep was defined as the CO stripping onset voltage in this study.

TEM characterizations

TEM was used to determine the particle size distributions of Pt-M samples using a JEOL 2010F high-resolution transmission electron microscope (HRTEM) operated at 200 kV with a resolution of 0.19 nm. TEM samples were prepared by either drop-casting as-received particles onto lacey carbon coated Cu or Ni TEM grids (Electron Microscopy Science) or gently scratching the cycled particles from disk-electrode surface with TEM grids. The diameters (*d*) of over 100 nanoparticles for each Pt-M catalysts were measured from HRTEM images using ImageJ v1.44p (National Institute of Health, USA). Parallel-beam energy dispersive spectroscopy (EDS) data were collected and the atomic compositions were determined using INCA (Oxford Instruments) software. For each Pt-M sample, three different spots with a diameter of ~ 200 nm with a total of over 100 nervec.

particles were used to collect the average Pt:M ratios before and after stability tests. The TEM-based surface area (TSA) was computed as $6/(\rho_{PtM}d_{\nu/a})$,⁸⁰ where $d_{\nu/a} = \sum_{i=1}^{n} d_i^2 / \sum_{i=1}^{n} d_i^3$, and ρ_{PtM} is the mass density of bulk Pt-M alloy.

2.3. Bulk and Surface Evolutions Caused by Transition Metal Leaching

The evolution of particle size, metal composition and surface area of Pt-M nanoparticles after 100 and 1200 stability cycles were shown in Figure 2-2. First, before any stability cycling, the pristine Pt-M samples showed similar sizes (~3.5 nm), Pt-M ratios (~1:1), and surface areas (both ECA/TSA). In addition, CV measurements showed that the as-received particles have similar specific ESA to TSA (Figure 2-2c and Figure 2-2d). They also have similar particle size distributions and morphologies, as shown in Figure 2-3 and Figure 2-4. The similar initial chemistry and morphology of the particles provided the platform for the systematic comparison of activity and stability of Pt-M catalysts in the acid electrolyte. After 1200 CV cycles, significant M loss can be observed in metals with $V_{dissolve} < 0$ (i.e. Fe, Co, and Ni). In contrast, for M = Cu, Ru, Pd with $V_{dissolve} > 0$ V, there is very little or no transition metal loss during voltage cycling (Figure 2-2b). This suggests that $V_{dissolve}$ can be treated as a descriptor for the stability of M in Pt-M catalysts with potential cycling (Figure 2-5). The more negative the $V_{dissolve}$, the severer the dissolution of M. In fact, Figure 2-1 has implied that the dissolution driving force from $V_{dissolve}$ (e.g. -0.45 eV/electron for Ni in the dissolution reaction $Pt_zNi \rightarrow zPt + Ni^{x+1}$ +xe⁻, from Figure 2-1) is stronger than the stabilizing force from E_{allov} (e.g. -0.2 eV/electron for Pt-Ni from Figure 2-1, calculated as $(z+1)E_{alloy}/x$). So it is understandable that $V_{dissolve}$ dominated the dissolution process in Pt_{0.5}M_{0.5} particles. It worth noticing that this statement may be specific to the Pt-M nanoparticles with initial Pt:M ratio of 1:1 and particle size range from 2 to 5 nm. With higher Pt:M ratios or larger particles, the Pt protective layer may form on the surface before or after acid leaching,^{17,24,57,58} which has big influence to the activity and stability of the Pt-M catalysts. While in our case, Pt content might not be high enough to form the surface condensed layer during dealloying, and instead a Pt skeleton may form on the particle surface after severe leaching on transition metals with $V_{dissolve} < 0$ V, which has been reported before.^{35,37} The formation

of surface Pt skeleton could also be the reason that the trend in M dissolution among $Pt_{0.5}M_{0.5}$ particles was not captured by the evolution of particle size, ESA or TSA considering experimental uncertainties of these measurements (Figure 2-2c and Figure 2-2d).



Figure 2-2. (a) The average particle diameter change of Pt-M particles during cyclic tests (black: as-received; grey: after 100 cycles; light grey: after 1200 cycles. This is the same as in (b), (c) and (d)). The error bars represent the standard deviation of the mean of particle size distribution (more than 100 particles for each sample were measured). (b) The transmission metal (M) composition of the Pt-M nanoparticles before and after voltage cycling in atomic percent, as evaluated by EDS using spectra of three different areas (with diameters ~ 200 nm) contacting over 100 particles. The error bars represent the standard deviation of chemical composition measurements at different EDS areas. The horizontal black line marked 50% atomic composition of M. (c) The surface area calculated using TEM images (TSA). The error bars comes from

the standard deviation of EDS results. (d) The ESA calculated from hydrogen adsorption/desorption peaks of CV curves. The error bars represent the standard deviation of the ESA measurements.



Figure 2-3. TEM images of Pt-M nanoparticles, including as-received samples and samples after 100 and 1200 cycles in acid electrolyte.



Figure 2-4. Histograms of particle size distributions for as-received and after-cycled Pt-M nanoparticles. The particle sizes were evaluated by HRTEM images. More than 100 particles were measured in each of the panel above.



Figure 2-5. Transition metal loss after 1200 cycles (green) and the specific ORR activity of as-received Pt-M catalysts (red). Here the transition metal loss was defined as the metal composition change from Figure 2-2b.

In addition to the evolution of bulk metal concentration detected by EDS, the evolution of surface metal concentration was also studied using CO stripping method, which is to oxidize the surface monolayer of CO on Pt-M nanoparticles at certain voltage.

The onset voltage of CO stripping is sensitive to surface Pt:M ratio since pure Pt surface is usually easier to be strongly poisoned by CO molecules and lead to a higher onset voltage.^{16,81,82} Figure 2-6 showed that for M with $V_{dissolve} < 0$ V, the onset voltage of CO stripping on Pt-M rapidly increased to the value of pure Pt after 1000 cycles (Figure 2-6c), reflecting the totally dissolving of M from the nanoparticle surface and the formation of Pt skeleton surface structure. While for those with $V_{dissolve} > 0$ V, the onset voltages after 1000 cycles stayed nearly unchanged from their initial values that are very different from the pure Pt particles (Figure 2-6c), implying these transition metals are stable on the surface over cycles. The less onset voltage shift after 1000 cycles at higher $V_{dissolve}$ (Figure 2-6d) is in consistent with the less bulk M dissolution after 1200 cycles at higher $V_{dissolve}$ (Figure 2-2b), implying that Pt-M particles with more positive $V_{dissolve}$ have better stability both on the surface and in the bulk.



Figure 2-6. (a)(b) Representative CO stripping curves of Pt-Co and Pt-Pd, with large and small change in onset voltage after 1000 cycles, respectively (black: as-prepared, dark grey: cycled 100 times, and light grey: cycled 1000 times). (c) The CO stripping onset voltage change of Pt-M particles during cyclic tests (black: as-received; grey: after 100 cycles; light grey: after 1000 cycles). Here the standard deviation of three

different measurements for each alloy is used to represent the uncertainty of the onset voltage. (d) Onset voltage shift for CO stripping after 1000 cycles (green) and the specific ORR activity of as-received Pt-M catalysts (red). Here the onset voltage shift was defined as $V_{1000-cycled}-V_{as-received}$ in (c).

2.4. Optimization of Both Activity and Stability

The $V_{dissolve}$ also showed close relationship with the ORR activity, as shown in Figure 2-7. The Pt-M nanoparticles with more negative $V_{dissolve}$ tend to have higher specific and mass ORR activities before CV cycles (Figure 2-7c and Figure 2-7d). This trend can be explained using d-band center theory: M with more negative $V_{dissolve}$ usually has a smaller atom size and more negative electronegativity, causing a larger compressive strain and a greater ligand effect, which can shift down the Pt d-band center and therefore yield a higher ORR activity.^{15,18,47,53,54,83} At the same time, no noticeable enhancement was observed in the ORR activity for those M with positive $V_{dissolve}$ before voltage cycling. This implies that for Pt-M catalysts, the stability and activity cannot be optimized at the same time by varying the chemistry. After 1200 CV cycles, all Pt-M with negative $V_{dissolve}$ values (Fe, Co and Ni) showed slight decrease in the mass and specific ORR activities, which still remained twice higher than the pure Pt. The activity descending of these negative- $V_{dissolve}$ alloys is in consistent to their severe M leaching during voltage cycling, which can cause the loss of beneficial alloying effects.^{11, 14, 45-46} In the contrast, Pt-M catalysts with positive $V_{dissolve}$ showed less changes in ORR activities after 1200 cycles, corresponding to their higher chemical stability against transition metal leaching.



Figure 2-7. (a) and (b) Representative ORR curves of as-received Pt-Fe and Pt-Pd nanoparticles under different rotation speeds, respectively. (c) Specific and (d) mass oxygen reduction activities of the Pt-M nanoparticles at 0.9 V vs. RHE and room temperature in 0.1 M HClO₄ (black: as-prepared, dark grey: cycled 100 times, and light grey: cycled 1200 times). Here the standard deviation of three different measurements for each alloy is used to represent the uncertainty of the mean of activity. The activity of pure Pt nanoparticles of comparable particle sizes before voltage cycling is marked as black horizontal lines in (c) and (d).

In practical applications, the mass ORR activity per gram of Pt is directly related to the performance and cost of the devices such as PEMFCs. And from Figure 2-7d, it is found that after 1200 cycles, there is a volcano trend between the mass ORR activity and the dissolution potential of M. When Pt was alloyed with Fe or Co who has very negative $V_{dissolve}$, the ORR activity dropped too fast; while when Pt was alloyed with Ru or Pd who has positive $V_{dissolve}$, the ORR activity was always low before and after CV cycles.
Therefore, the highest mass ORR activity after 1200 cycles was found on Pt-Ni, as a result of the balancing between stability and activity.

2.5. Chapter 2 Conclusions

In this chapter, combined the electrochemical and TEM characterizations were applied on a series of Pt-M nanoparticles to investigate the influence of alloy chemistry to the catalytic performance during the ORR in acid electrolyte. It was found that when Pt was alloyed with more negative- $V_{dissolve}$ transition metals, despite the stronger alloyformation energy, the Pt-M nanoparticles demonstrated greater M dissolutions both in the bulk and on the surface after voltage cycling in acid electrolyte, accompanied by bigger shifts in onset voltages of CO stripping and ORR activities. The fact that the Pt-M nanoparticles become less stable with the $V_{dissolve}$ of M is more negative implying that during the competition between $V_{dissolve}$ and E_{alloy} , $V_{dissolve}$ is more dominating. In addition, alloying Pt with negative- $V_{dissolve}$ transition metals could lead to more beneficial electronic structure adjustment. This implies that in Pt-M alloy catalysts, the stability and activity are competing with each other. As a result, a volcano trend was observed between cycled mass ORR activity and V_{dissolve}, and Pt-Ni showed the highest mass ORR activity after 1200 cycles. This work highlights the critical role of the dissolution thermodynamics of transition metal solute in Pt-M catalysts on the extent of transition metal leaching in acid, ORR activity and CO oxidation activity. The new design principles discovered in this work is important to the development of new Pt-based ORR catalysts with higher activity and longer durability in acid electrolyte.

Chapter 3. Acid-treatment and Annealing Effects on Pt-Ni Nanoparticles for ORR Electrocatalysis

3.1. Introduction

In **Chapter 2**, it is found that the stability and ORR activity of Pt-M alloy catalysts in acid electrolyte is closely related to the transition metal dissolution from both the bulk and the surface. In addition, it is found that $Pt_{0.5}Ni_{0.5}$ nanoparticles have the highest mass ORR activity after 1200 CV cycles among all Pt_{0.5}M_{0.5} samples tested in Chapter 2, showing a balanced catalytic performance between stability and activity. However, the stability and activity of the tested commercial Pt_{0.5}Ni_{0.5} nanoparticles were still far from the official 2017 performance targets for initial fuel cell catalyst activity and fuel cell durability made by DOE.^{84,85} One way to improve the catalytic performance of Pt-Ni catalysts is to dealloy Ni-rich Pt-Ni precursor particles with controlled acid leaching protocols, in order to form a Pt-rich protective shell and a Ni-rich core. Previous work has shown that having Ni or Co compositions greater than 50 at.% in PtNix or PtCox nanoparticles could lead to the formation of spongy particles with nano-scale porosity due to severe metal leaching,^{37,86} while small particles below certain critical size could avoid such porosity formation.^{24,87,88} However, the effects of material preparation methods, such as acid-leaching protocol and post-acid-leaching heat treatment, on metal leaching and surface porosity formation are still poorly understood. In addition, many of the previous stability and activity characterizations were done using RDE setups, rather than in real fuel setups,^{89,90} which is critical to the development of efficient, durable and practical ORR catalysts for PEMFCs.

To further improve the ORR stability and activity of Pt-M, particularly the Pt-Ni catalysts, in this chapter we systematically studies how the particle morphology, dealloying process and heat treatments could influence the formation of Pt-rich protective layer on the surface of Pt-Ni nanoparticles and prevent the Ni leaching in acid electrolyte.⁵⁰ Scanning transmission electron microscopy (STEM) data revealed that smaller particle sizes, less-oxidative acid treatments and post-dealloying heat treatments

could significantly reduce Ni leaching and nanoporosity formation while encouraged surface passivation, all resulting in improved stability and higher catalytic ORR activity in acid electrolyte. The new design principles of more active and more stable ORR Pt-alloy catalysts enabled the swift translation of fundamental atomic-scale understanding on catalyst synthesis, electrochemical catalysis and degradation into industrial catalytic material scale-up coupled to unprecedented device performance. As a result, new fuel cell catalysts that exceeded the official 2017 DOE cathode catalyst targets were successfully synthesized, which were important for the reduction of the costly Pt usage in PEMFCs and the commercialization of fuel cell vehicles.

3.2. Experimental Methods

Sample preparation

In this study, two different Pt_{0.25}Ni_{0.75} nanoparticles (P1 and P2) supported on highsurface-area carbon were synthesized by Johnson Matthey Fuel Cells Ltd (UK). P1 and P2 have similar shapes and initial Pt:Ni ratios, but different particle size distributions (PSDs):⁹¹ P2 has a smaller average particle diameter of ~ 5 nm with a narrower PSD, while P1 has a larger average particle diameter of ~8 nm with a broader PSD, as shown in Figure 3-1. Here we start with much higher Ni concentration (75%) so that after controlled dealloying process, we can get the high surface area core-shell nanoparticle catalysts with compact Pt-rich protective shell and still high-Ni-concentration core for beneficial electronic structure adjustment. In this work, various acid-leaching conditions and post-dealloying treatments were applied to either P1 or P2, as shown in Figure 3-2, which includes: (1) 1 M nitric acid at 70 °C for 24 h in air (marked as P1-NA and P2-NA) or (2) 0.5 M sulfuric acid at 80 °C for 24 h in nitrogen (P2-SA). The acid-treated catalysts were then rinsed with DI water and dried in N2 at room temperature. Some P2-SA catalysts were then further annealed annealed at 400 °C for 4 h in 5 % H₂ and 95% N₂, marked as P2-SA-AN. In addition, Pt nanoparticles (46 wt% supported by Vulcan carbon) from TKK was used as the reference ORR catalyst. The catalytic performance of the above ORR catalysts was measured by fuel cell testing using 50 cm² catalyst-coated membranes (CCMs) made by the decal transfer method, with a loading of $0.1 \text{ mg}_{Pt}/\text{cm}^2$ in

the cathode and 0.05 mg_{Pt}/cm^2 in the anode. In CCMS, Nafion[®] D2020 ionomer was utilized with an ionomer to carbon weight ratio of 0.95 and 0.6 in the cathode and anode, respectively. 20 wt.% Pt/C was used as the anode catalyst for hydrogen oxidation reaction (HOR). Nafion[®] NRE211 (25 µm thick) was used as the separator membrane. The carbon fiber paper backing (~200 µm) coated with a microporous layer (MPL, ~30 µm) was used as the gas diffusion medium. Detailed procedure for the fuel cell test and membrane electrode assembly (MEA) can be found in previous work.⁹²



Figure 3-1. Particle size distribution of (a) pristine P1 and (b) pristine P2 particles. More than 100 particles of each sample were measured to calculated the average of particle diameter (d_{avg}) and the standard deviation of particle size distribution (σ).



Figure 3-2. Schematic of the Pt-Ni nanoparticles treated in different conditions. The precursors were either treated in (1) 1 M nitric acid at 70 °C for 24 h in air (P1-NA and P2-NA) or (2) 0.5 M sulfuric acid at 80 °C for 24 h in nitrogen (P2-SA). After the dealloying, some P2-SA catalysts were thermally annealed at 400 °C for 4 h in 5 % H_2 and 95% N_2 , marked as P2-SA-AN.

Electrochemical measurements

Before electrochemical measurements, MEAs were first conditioned in fuel cells for 7 h, and then were conditioned by a series of initial electrochemical measurements for a total run time of 17 h. Voltage cycling tests were applied on some of the MEAs in 200/50 standard cubic cm per min of H_2/N_2 at 80 °C, 100 % RH and 101 kPa_{abs} for up to 30,000 (30k) cycles, at a scan rate of 50 mV/s between 0.6 and 1.0 V vs. RHE (30k-cycled). For each electrochemical measurement, averages were calculated from at least 4 MEAs, and the standard deviations were used as the error bars in the figures. The ORR activities were measured from the H_2/O_2 polarization curves obtained at 80°C, 100 % relative humidity (RH) and 150 kPa_{abs} after high frequency resistance-correction.⁹² Pt ESA were measured following the similar method in **Chapter 2**.

Electron probe micro-analysis

The evolution of bulk chemical compositions were characterized by electron probe micro-analysis (EPMA) using an SX100 electron probe micro-analyzer from CAMECA Instruments, Inc. Small pieces of MEAs ($\sim 4 \times 10$ mm) were cut from the center of the samples and mounted in brominated epoxy under vacuum. Then the samples were polished to mirror finish using first the polishing papers and then the 1-micron diamond

suspension. A thin layer (~3 nm) of Au-Pd alloy was then sputter coated immediately after final lapping to provide surface electron conductivity needed for EMPA. The cross-sectioned MEAs were analyzed with an electron probe of 15 KV and 10 nA. Specific experimental parameters can be found in previous publication.⁵⁰

TEM characterizations

TEM samples were prepared by using a razor to remove the carbon paper diffusion layer, carefully cleaning the MPL off the membrane and scraping the membrane directly into a scintillation vial. The cathode scrapings were then ultra-sonicated briefly in ethanol (Sigma-Aldrich), and then drop-casted onto lacey carbon coated Cu TEM grids (Electron Microscopy Science). TEM and STEM characterizations were performed using a JEOL 2010F HRTEM operated at 200 kV with a point resolution of 0.19 nm. For each sample, over 100 catalyst nanoparticles were measured using HRTEM images to determine the PSDs. The bright field diffraction contrast images were formed by aligning a 20 µm aperture with the transmitted beam, and captured by a CCD camera. The HRTEM images were analyzed using Gatan Digital Micrograph v2.01 (Gatan Inc.) and ImageJ v1.44p (National Institute of Health, USA). High angle annular dark field (HAADF) STEM images were formed by aligning the Ronchigram with optic axis and a 50 µm condenser aperture with the center of the Ronchigram. The electron beam with a probe size of 0.5 nm and a camera length of 40 cm was used to minimize the effect of diffraction contrast on the HAADF images. Parallel-beam and STEM EDS data were collected from individual catalyst particles and analyzed using the INCA (Oxford Instruments) software. The Ni and Pt atomic compositions were determined from the Ni-K series and the Pt-L series using the INCA software as described in previous work.⁶⁶ For parallel-beam EDS measurements on each sample, three different spots with a diameter of ~ 200 nm (totally containing over 100 particles) were used to collect the average atomic percentage of Ni.

3.3. Activity and Stability Trends

Different from the RDE setup used in **Chapter 2**, in this chapter the ORR activity and stability of Pt-Ni nanoparticles were measured using the real fuel-cell setup (Figure

3-3). Although the RDE setup is simpler and faster for electrochemical characterizations, the fuel cell setup could provide more practical information of the catalytic performance of the catalysts, which is closer to the commercial applications. Figure 3-3a showed that before any cycling, the P1-NA and P2-NA cathodes with the Pt loading of 0.1 mg_{Pt}/cm ²_{geo} had a comparable voltage curve to the pure-Pt cathode with four times higher Pt loading $(0.4 \text{ mg}_{Pt}/\text{cm}_{geo}^2)$. This implies both P1 and P2 have roughly four times higher ORR activity than Pt at the beginning. However, after 30k cycles, both of them had an obvious voltage drop, indicating the loss of ORR mass activity. This can be further demonstrated in Figure 3-3b and Figure 3-3c, where we compared the specific and mass ORR activity of different Pt-Ni catalysts at 0.9 V vs. RHE. It is found the mass activity of P1-NA was reduced by $\sim 2/3$ after 30k cycles, which is much higher than the activity loss on P2-NA and the other P2-derived catalysts. Moreover, if to normalize the activity by their ESA, Figure 3-3b showed that the specific activity of P1-NA dropped more than 1/3 after 30k cycles, while on the contrary, the specific activities of P2-NA and the other P2derived catalysts actually increased after cycling. The mass activity loss in P2-derived catalysts was mainly caused by the loss of ESA. These activity profiles provided us a general stability and catalytic performance ranking, where P2-SA-AN > P2-SA > P2-NA > P1-NA. In fact, all those P2-derived catalysts became the first ones to exceed the US DOE 2017 PEMFC cathode catalyst target (initial activity >0.44 A/mg_{Pt} and activity loss <40 % after 30k voltage cycling,⁸⁴ see Figure 3-3d).



Figure 3-3. (a) Fuel cell polarization curves of P1-NA and P2-NA cathodes at different aging stages (conditioned and 30k-cycled), and of conditioned Pt as a reference. The catalyst loadings were 0.1 and 0.4 mg_{Pt}/cm² for the dealloyed PtNi and commercial Pt catalysts, respectively. (b) Specific activity and (c) mass activity of the Pt-Ni catalysts. The activities were measured at 0.9 V vs. RHE, where dark grey, light grey and white represent conditioned, 10k-cycled and 30k-cycled MEA, respectively. From (a) to (c) the error bars represent the standard deviations of activity measurements among at least 4 MEAs for each sample. (d) The end-of-life (EOL, 30k-cycled MEA) vs. beginning-of-life (BOL, conditioned MEA) mass activity for catalysts from this work and from previous work on MEAs: 3M NSTF PtCoMn, NSTF Pt₃Ni₇,⁹³ Pt₃Co/CNC and Pt₂Ni/CNC,⁹⁴ Supplier Pt Alloy and pure Pt.^{85,95} The solid and dash horizontal lines in (b) and the red star and the green square regions represent the DOE 2017 PEMFC cathode catalyst targets for BOL mass activity (0.26 A/mg_{Pt}),⁸⁴ respectively.

As we discussed in **Chapter 2**, the activity loss in Pt-M catalysts could be resulted from metal leaching or particle coarsening. To examine the potential origins of activity

loss in these Pt-Ni catalysts, we measured their Ni contents over cycles using EPMA. Figure 3-4a exhibited that P1-NA had less Ni than P2-derived catalysts before cycling. Additionally, sulfuric-acid treated P2 (P2-SA and P2-SA) had more Ni than the nitric-acid treated P2-NA before cycling. Since the two precursor nanoparticles P1 and P2 have the same stoichiometry of Pt_{0.25}Ni_{0.75}, the difference in Ni content before cycling was mainly caused by different acid treatment conditions and different initial particle sizes. After 30k cycles, P1-NA showed the most Ni leaching with the least Ni content left (~5 at.%), while P2-SA-AN showed the highest Ni content left (~15 at.%). The trend of Ni loss is in consistent to the previous stability trend we observed in ORR mass activity, as shown in Figure 3-4b. In general, higher Ni content corresponds to higher mass activity after 30k cycles. On the other hand, the specific activities were found to be independent of Ni content, see Figure 3-4c. In fact, the specific activity represents the intrinsic activity per surface active site, and therefore is more related to the near surface compositions and structures than to the total Ni loss.⁸⁶ Therefore, we need the help of TEM to detect the evolution of surface chemistry and surface structure before and after cycling.



Figure 3-4. (a) EPMA-determined Ni concentrations, where black, dark grey, and white represent pristine CCM, conditioned and 30k-cycled MEA, respectively. (b) and (c) The average Ni concentrations determined by EPMA plotted against the mass and specific activities of the MEAs, respectively. (Dark grey: conditioned; white: 30k-cycled.) From (a) to (c), the activity error bars represent the standard deviation of activity measurements among at least 4 MEA samples, while the Ni-content error bars represent the standard deviation of EMPA measurements among at least 3 different locations. (d) TEM-determined mean particle size from different MEAs, where black, dark grey and white represent pristine CCM, conditioned MEA and 30k-cycled MEA, respectively. For each sample over 100 particles were measured to get the average size, while the error bars represent the standard deviation.

3.4. Atomic-scale Dealloying Study

With the help of TEM, we first examined the particles before CV cycling, as shown in Figure 3-5. First we found P1-NA had a larger average diameter and a broader size distribution (\sim 7 nm ± 3 nm) than P2-derived catalysts (\sim 5 nm ± 1 nm), as shown in Figure 3-4d. In addition, EDS data demonstrated that P2-NA had higher Ni content

 $(25\pm3 \text{ at.}\%)$ than P1-NA $(19\pm6.9 \text{ at.}\%)$, in agreement with previous EPMA results in Figure 3-4a. TEM images showed that the particle porosity of P1-NA is higher than P2-NA. The observed porosity is similar to that of other Pt-M nanoparticles in previous studies after acid-leaching.^{24,37,66,96} The size difference could be the origin of the large stability and activity differences between P1-NA and P2-derived catalysts. Because the Ni leaching and the formation of the "spongy particles" usually corresponds to the dealloying above a certain critical size (Rayleigh critical length).^{66,67,97} This is also true in P1-NA, where the size of the porous particles was as large as 20 nm and as small as 6 nm (Figure 3-5a), implying the critical size is ~ 6 nm. This critical size is smaller than the average particle size of P2-NA, which would lead to less porosity and less Ni leaching in P2-NA. Moreover, this critical size of ~6 nm is smaller than that in previous studies, which are usually 10-30 nm.^{24,87,88} One potential reason could be that we used more oxidative hot HNO₃ to treat P1-NA and P2-NA, which lead to a higher Ni dissolution rate than those non-oxidative acid (HClO₄ or H₂SO₄) treatment at room temperature in previous studies.^{24,87,88} This is in consistent with our observation that when P2 is alternatively treated by H₂SO₄ (P2-SA), it exhibited less porosity and higher Ni content compared with HNO₃-treated P2-NA (Figure 3-5c and Figure 3-5e). Moreover, a Pt-rich surface layer can be found in the HAADF STEM imaging and EDS mapping of all observed P2-SA nanoparticles (Figure 3-5f). Similar Pt-rich skin can also be observed in P2-SA-AN but not in P2-NA (Figure 3-5f), indicating the formation of Pt protective surface layer might be the reason of the better stability in H₂SO₄-treated P2-SA and P2-SA-AN.



Figure 3-5. Bright-Field diffraction contrast TEM images with PSDs, Ni atomic percentages determined from parallel-beam EDS (left) and HAADF STEM images with point-mode EDS (right) from catalyst particles taken from pristine CCMs. (a) and (b) P1-NA, (c) and (d) P2-NA, (e) and (f) P2-SA, (g) and (h) P2-SA-AN. Here σ represents the standard deviation of PSD from at least 100 measurements and the standard deviation of EDS results among 3 different locations. The insert on the top

right corner is the HRTEM image of a nanoparticle with a diameter of \sim 5 nm that clearly shows porosity from CCM.

The average particle sizes of both P1-NA and P2-derived catalysts had a slightly increase (~1 nm) after conditioning (Figure 3-6) and 30k cycles (Figure 3-7), but this change was still within the experimental uncertainty. Meanwhile, large Ni loss was found in P1-NA by EDS after conditioning and cycling (only $\sim 1\%$ left after 30k cycles, Figure 3-7a), which is in agreement with previous EPMA results. In contrast, P2-NA retained more Ni (4.3%, Figure 3-7c), and remarkably P2-SA and P2-SA-AN kept considerable Ni (24% and 31% respectively) even after 30k cycles (Figure 3-7e and Figure 3-7g). Moreover, the big spongy particles in P1-NA before cycling disappeared and were replaced by donut-like particles after conditioning (Figure 3-6b), which might be resulted from the severe dissolution of highly porous particles and redeposition of Pt to form Ptenriched-shell particles.^{24,37,66,96} In fact, considering the intensity in HAADF images is proportional to the product of the thickness and Z^2 (Z being the atomic number), and the EDS data in Figure 3-6b revealed that the core and surface of the particle have similar Pt:Ni ratios, the low brightness near the particle core in Figure 3-6b can only be interpreted as the donut-shape morphology. To support the above hypothesis, here we calculated the relative thickness of different positions on the Pt-Ni particles using the relationship that the intensity in the HAADF images is proportional to the product of the thickness and Z². Here the relative thickness is defined as $t = I / (c_{Ni}Z_{Ni}^{2} + c_{Pt}Z_{Pt}^{2})$, where I is the HAADF image intensity, c_{Ni} and c_{Pt} are the atomic composition of Na and Pt determined by the point EDS data, Z_{Ni} and Z_{Pt} are the atomic number of Ni and Pt. The ratios of the relative thickness between centers and edges of particles in Figure 3-5, Figure 3-6and Figure 3-7 are shown in Table 3-1. From Table 3-1 we can find that for P1-NA, the thickness ratios between centers and edges are always below 1, implying severe porosity. This is different from P2-NA after conditioning (Figure 3-6d) and 30k cycles (Figure 3-7d), where the low brightness in the center could be attributed to the high Pt concentration on the shells rather than the donut shape.



Figure 3-6. Bright Field diffraction contrast TEM images with PSDs, Ni atomic percentages determined from parallel-beam EDS (left) and HAADF STEM images with point mode EDS (right) for catalysts taken from conditioned MEA. (a)(b) P1-NA, (c)(d) P2-NA, (e)(f) P2-SA, (g)(h) P2-SA-AN. Here σ represents the standard deviation of PSD from at least 100 measurements and the standard deviation of EDS results among 3 different locations.



Figure 3-7. Bright-Field diffraction contrast TEM images with PSDs, Ni atomic percentages determined from parallel-beam EDS (left) and HAADF STEM images with point-mode EDS (right) for catalyst particles taken from 30k-cycled MEAs. (a) and (b) P1-NA, (c) and (d) P2-NA, (e) and (f) P2-SA, (g) and (h) P2-SA-AN. Here σ

represents the standard deviation of PSD from at least 100 measurements and the standard deviation of EDS results among 3 different locations.

| Conditions | | P1-NA | P2-NA | P2-SA | P2-SA-AN |
|---------------|---------------------------------|-------|-------|-------|----------|
| tcenter:tedge | Pristine CCM (Figure 3-5) | 0.49 | 0.86 | 1.43 | 1.18 |
| | Conditioned MEA (Figure 3-6) | 0.67 | 1.21 | 1.05 | 1.39 |
| | 30k-cycled MEA (Figure 3-7) | 0.72 | 0.92 | 1.09 | 1.02 |

Table 3-1. The ratio of relative thickness between centers and edges of particles in Figure 3-5, Figure 3-6 and Figure 3-7. The ratio below 1 implies the porosity.

P1-NA exhibited much worse durability not only in the high Ni loss and the high porosity, but also in the big ORR activity drop. After 30k cycles, P1-NA showed only $\sim 1/3$ of its original mass activity and $\sim 1/2$ of its original specific activity, while P2-NA showed almost no change in mass and specific activity considering the measurement uncertainty (Figures 2b and 2c). The much reduced activity of P1-NA in PEMFCs could be attributed to a greater Ni loss near surface regions, which reduced the surface electronic structure modifications of Pt atoms brought by transition metal alloying.¹⁴⁻ ^{16,18,19,59,60,98-100} The development of a Pt-rich passivation layer is expected to improve the resistance to base metal leaching and activity dropping, which might be another reason for the higher durability of P2-NA than P1-NA. Meanwhile, the point EDS analysis revealed that P2-SA-AN nanoparticles retained considerably more Ni near surface regions than P2-SA after conditioning and 30k cycling (Figure 3-6e, Figure 3-6g, Figure 3-7e and Figure 3-7g), where no noticeable Ni loss in near surface regions was observed after conditioning and 30k cycles. The increase in stability with the thermal annealing observed in MEA in our study is in good agreement with previous RDE work by Wang et al.¹⁰¹ It is proposed that the exceptional stability and high mass and specific activities of P2-SA-AN in PEMFCs can be attributed to the ability of surface regions to retain Ni, which might be critical to maintain modified electronic structures of surface Pt atoms associated with Ni necessary to provide enhanced mass and specific activities relative to pure Pt nanoparticle catalysts. This again proves the importance of surface shell to the activity and stability of dealloyed Pt-alloy nano-catalysts, and indicates that annealing could be a future standard process to improve the stability of Pt-metal co-shell catalysts.

3.5. Chapter 3 Conclusions

In this chapter, the evolutions of morphology, chemistry and ORR activity of various dealloyed Pt-Ni nanoparticles were investigated before and after the voltage cycling tests in real fuel cell setups, which provided deeper understandings to the porosity formation and metal leaching mechanism of Pt-Ni catalysts in acid electrolyte. Several new design principles were discovered to facilitate the formation of the Pt-rich protective layer on the particle surface and therefore to improve the stability of Pt-Ni particles. First, reducing the particle size below the critical value can suppress the porosity generation and promote the formation of a Pt-rich passivation shells. Second, using less oxidative acid to dealloy the Pt-Ni particles can further promote the formation of core-shell structures and prevent the loss of Ni contents during ORR. Third, post-acid-treatment annealing can lead to the formation of comparatively dense Pt shells, providing much better resistance to Ni leaching and helping to improve both specific and mass activities during electrochemical cycling. These observations emphasized the critical role of particle size, acid-leaching and annealing treatment in forming Pt-rich passivation layers and preventing transition metal loss during ORR in acid electrolyte. With the above new design principles, new Pt-alloy catalysts that meets and exceeds the official 2017 DOE targets of PEMFC cathode catalysts were synthesized for the first time.

Chapter 4. Activity and Stability Trends of Perovskite OER Catalysts at Neutral pH

4.1. Introduction

In the precious chapters, several design principles were discovered from systematic activity and stability studies on Pt-alloy ORR catalysts, which are widely used in PEMFCs.¹³⁻²⁵ These design principles can be used to improve the catalytic performance of Pt-based ORR catalysts to reduce the overpotential from the slow kinetics of ORR near room temperature, which is the main source of energy loss in PEMFCs.^{92,102} On the other hand, the OER, which is the reverse reaction of ORR, also suffers from the slow kinetics near room temperature. The overpotential loss from OER is the major source of energy loss in water splitting electrolyzers^{1,2,6} and rechargeable metal-air batteries.^{8,9} Therefore, the development of new OER catalysts with higher activity and longer durability is critical to improve the efficiency of these electrochemical technologies in pursuit of sustainable energy.

Following the same philosophy we used to improve the catalytic performance of Ptbased catalysts for ORR, for OER we are also looking for the stability and activity trends by varying the chemistry to adjust the electronic and atomic structures of the catalysts. Among many different kinds of OER catalysts, perovskite transition-metal oxides (ABO₃) have raised great interests, not only because they have comparable activities to preciousmetal-oxides catalysts in high-pH alkaline solution, but also because the great freedom in changing their chemistry, which makes them a good modeling system to systematically study the relationship between OER catalytic performance and various basic material properties.^{26-31,103} Previous studies of perovskite OER catalysts mainly focused on the high-pH applications (e.g. pH 13 or 14), where people found that the perovskites with an eg occupancy close to unity²⁹ or an O 2p-band center close to the Fermi level²⁸ exhibited higher specific OER activity in alkaline electrolyte. However, if the O 2p-band of the perovskite is too close to the Fermi level, like in BSCF, surface oxygen redox during the OER may lead to surface amorphization and A-site loss (Ba or Sr in BSCF) at pH 13.^{28,39,40} The stable (double)perovskite oxides with the highest specific OER activity found so far was PBCO.²⁸ Meanwhile, OER is not only critical for high-pH applications, but also important for many electrochemical devices operated at neutral or slightly acidic operation conditions to avoid carbonate formation, including cocatalysts for photoanodes,^{6,41,42} water-oxidation-coupled CO₂ reduction¹⁰⁴ and rechargeable Zn-air batteries.¹⁰⁵ However, so far, the stability and activity of perovskite oxides at neutral pH are still poorly understood, and the design principles of neutral-pH OER catalysts are highly needed.

In this chapter, the evolutions of OER activity, particle morphology and chemical contents during the OER at pH 7 and pH 13 were studied on various perovskite catalysts, including LaCoO₃ (LCO), LaNiO₃ (LNO), LaMnO₃ (LMO), LaFeO₃ (LFO), BSCF, PBCO, and SrCoO₃₋₆ (SCO).⁵¹ It is observed that the OER activity descriptors discovered previously at high pH, such as e_g filling numbers and O 2p-band positions, are still effective at neutral pH. However, the OER activities of all perovskite oxides dropped dramatically at neural pH. Meanwhile, the stability trend of perovskite oxides at pH 7 is different from that at pH 13. By combining electrochemical characterization and TEM results, two different corrosion mechanisms at pH 7 were identified. For perovskites with the oxygen 2p-band center closer to the Fermi level, the chemical degradation with A-site atom leaching was observed, which is consistent to the prediction from the thermodynamic stability (Pourbaix diagram). While for perovskites with the oxygen 2p-band center farther away from the Fermi level, the oxidative degradation mechanism with B-site leaching only under high current/overpotential was observed, which is consistent to the results of density function theory (DFT) calculation using local leaching model.

4.2. Experimental Methods

Materials preparation

Perovskite catalysts were synthesized using a conventional solid-state route.²⁸ IrO₂ (99.99%) were bought from Alfa Aesar Premion as the precious-metal oxides reference. The specific surface area of each oxide sample was determined using Brunauer–Emmett–

Teller (BET) analysis on a Quantachrome ChemBET Pulsar from a single-point BET analysis performed after 12 h outgassing at 150 °C.

Electrochemical measurements

The RDE configuration was used for electrochemical measurements in this chapter, with a rotatable working electrode at the rotation speed of 1600 rpm, a Pt wire as the counter electrode, and a SCE (Pine Instrument Co.) as the reference electrode. All potentials were calibrated to the RHE scale using H_2/H^+ redox. The ink of the oxides were prepared by dissolving 20 mg of oxides, 4 mg of acetylene black carbon and 4 mg of Nafion® in 4 ml of THF, following by 1 h of ultra-sonication. Working electrodes were prepared by drop-casting 10 μ L of oxide ink on a polished 0.196 cm² glassy carbon electrode, as described previously.²⁸ The oxide loading is $0.25 \text{ mg}_{ox}/\text{cm}^2_{disk}$. 0.1 M KOH (Sigma-Aldrich, 99.99%) solution prepared with DI water (18 M Ω) is used as the pH 13 electrolyte, while the pH 7 electrolyte was prepared with 0.4 M NaH₂PO₄ (Sigma-Aldrich), 0.6 M Na₂SO₄ (Sigma-Aldrich), proper amount of NaOH (Mallinckrodt) and proper amount of DI water. A scan rate of 10 mV/s and a scan range between 1.1 and 1.8 V vs. RHE were used for all CV measurements. All CV, galvanostatic and potentiostatic OER measurements were done in O₂ (99.999%, Airgas) saturated and bubbled electrolyte. Error bars in all activity data represent the standard deviation of multiple independent measurements. Ohmic losses were corrected by subtracting the ohmic voltage drop from the measured potential, using an electrolyte resistance determined by high-frequency alternating current impedance. The system resistance measured in pH 7 electrolyte (~15 Ω) is smaller than that in pH 13 electrolyte (~40 Ω), and therefore the Ohmic drop within the narrow $pores^{106}$ might not be a reason for the activity reduction observed at pH 7.

TEM characterizations

TEM samples of pristine oxides were prepared by dropping the catalyst ink onto lacey carbon coated Cu TEM grids (Electron Microscopy Science). TEM samples of post-OER oxides were prepared by directly scratch the working electrode with Cu TEM grids after OER measurements. TEM images in this work were taken on JEOL 2010F operated at 200 kV with a point resolution of 0.19 nm. Bright field diffraction contrast imaging was used to determine particle size distributions and general morphology of the catalyst nanoparticles. The digital images were analyzed using Gatan Digital Micrograph v2.01 (Gatan Inc.) and ImageJ v1.44p (National Institute of Health, USA). HRTEM images were recorded without an objective aperture and were analyzed using Gatan Digital Micrograph. Parallel-beam EDS data were collected and the atomic compositions were determined using INCA (Oxford Instruments). For each oxides sample, three different spots with a diameter of ~ 200 nm were used to collect the bulk chemical composition, while three different spots with a diameter of ~ 5 nm at the particle edges were used to collect the surface chemical composition. Error bars in all EDS data represent the standard deviation of the results on multiple spots.

DFT studies

Spin polarized DFT calculations of the O 2p-band center were performed with the Vienna Ab-initio Simulation Package (VASP)¹⁰⁷ using a plane wave basis set, the GGA-Perdew-Wang-91¹⁰⁸ exchange correlation function, and the Projector Augmented Wave (PAW) method.¹⁰⁹ An effective O 2p-band center of each perovskite systems was determined by taking the centroid of the projected density of states of O 2p states relative to the Fermi level. In addition, the leaching reaction energies of perovskites were calculated with the same DFT approach described above. The detailed parameters and DFT method can be found in the previous work.⁵¹

4.3. Activity and Stability Descriptors at Neutral pH

Micron-sized LCO was firstly used to investigate the stability window of perovskites in pH 7 electrolyte (0.4 M NaH₂PO₄ and 0.6 M Na₂SO₄ balanced by proper amount of NaOH). At high pH, LCO was known to be stable,^{29,30,44} which was verified here in CV measurement from 1.1 to 1.8 V vs. RHE (Figure 4-1a), in galvanostatic measurement up to 50 μ A/cm²_{ox} (Figure 4-1b), and in potentiostatic measurements up to 1.78 V vs. RHE (Figure 4-1c) at pH 13. However, in the pH 7 electrolyte, LCO not only showed obvious decrease in OER activity (Figure 4-1d), but also became unstable at high current (Figure 4-1e) or high voltage (Figure 4-1f) accompanied with further considerable

OER activity decrease. A similar instability under high OER current/potential at pH 7 can also be found in LNO (Figure 4-2), LMO (Figure 4-3) and LFO (Figure 4-4). In general, the perovskite oxides become less stable at pH 7, especially under high OER current or overpotential, implying the stability becomes a more critical issue at neutral pH compared to that at high pH. The degradation mechanism of these perovskite oxides under more oxidative conditions at neutral pH will be discussed in a later session. To avoid the influence of catalyst degradation, in the following studies of OER activity descriptors, a much smaller OER current of 5 μ A/cm²_{ox} will be employed.



Figure 4-1. Electrochemical measurements of the LCO OER activity. (a)(d) CV experiments, where numbers indicate cycles. (b)(e) Galvanostatic experiments at various current densities. (c)(f) Potentiostatic experiments at various voltages. (a)-(c) was measured at pH 13, while (d)-(f) was measured at pH 7.



Figure 4-2. Electrochemical measurements of the LNO OER activity. (a)(d) CV experiments, where numbers indicate cycles. (b)(e) Galvanostatic experiments at various current densities. (c)(f) Potentiostatic experiments at various voltages. (a)-(c) was measured at pH 13, while (d)-(f) was measured at pH 7.



Figure 4-3. Electrochemical measurements of the LMO OER activity. (a)(d) CV experiments, where numbers indicate cycles. (b)(e) Galvanostatic experiments at various current densities. (c)(f) Potentiostatic experiments at various voltages. (a)-(c) was measured at pH 13, while (d)-(f) was measured at pH 7.



Figure 4-4. Electrochemical measurements of the LFO OER activity. (a)(d) CV experiments, where numbers indicate cycles. (b)(e) Galvanostatic experiments at various current densities. (c)(f) Potentiostatic experiments at various voltages. (a)-(c) was measured at pH 13, while (d)-(f) was measured at pH 7.

After examining more samples, we found that all the perovskite OER catalysts in our study showed reduced OER activities at pH 7 compared with those at pH 13 (Figure 4-5). The increase of overpotential at 5 μ A/cm²_{ox} varied from 150 to 300 mV on different perovskites when to change the pH from 13 to 7. A potential reason for the activity reduction at pH 7 could be the surface poisoning by phosphate buffer. Meanwhile, commercial IrO₂ had less than 30 mV increase of OER overpotential from pH 13 to pH 7 (Figure 4-5), implying IrO₂ had a high resistance to surface poisoning and a good chemical stability across a wide pH range compared with perovskites.^{7,48,110,111} We also found that at low overpotentials, perovskites showed comparable Tafel slopes at pH 7 (~100 mV/dec) compared to pH 13 (~70 mV/dec). While at high current (i.e. high overpotential), these oxides showed much larger Tafel slopes (~300 mV/dec), see Figure 4-5a, which might be related to the instability of the structure at high current/voltage discussed in the previous session.



Figure 4-5. (a) Tafel plots of LNO, LCO, BSCF and PBCO at pH 7 and 13, obtained from galvanostatic measurements. (b) The O 2p-band center trend at pH 7 of selected oxides at 5 μ A/cm²_{ox}. (c) The O 2p-band center trend at pH 13 at 5 μ A/cm²_{ox}. The horizontal lines in (b) and (c) represent the activity of IrO₂ at 5 μ A/cm²_{ox}. Here O 2p-band positions were calculated using DTF. All activities were obtained from galvanostatic measurements after 2 h. The error bars in above figures represent the standard deviation of multiple measurements.

Next step, we checked whether the OER activity descriptors for perovskites established at pH $13^{28,29}$ are still valid at pH 7. As mentioned before, to avoid the unstable region at high current/voltage for many of these perovskites at pH 7, we compared the overpotential at a low specific current of 5 μ A/cm²_{ox} at pH 7 (Figure 4-5b) and pH 13 (Figure 4-5c). It demonstrated that perovskites have higher OER activity when their O 2p-band is closer to their Fermi level at both pH 7 and pH 13. In addition, an e_g

occupancy close to unity is also found to be related to high OER activity at both pH 7 and 13 (Figure 4-6). Therefore, we can conclude that the OER activity descriptors for perovskites previously found at pH 13 can be extended to pH 7, which means we can use similar approaches at high pH to develop OER catalysts at neutral pH.



Figure 4-6. OER activity vs. e_g electron filling at 5 μ A/cm²_{ox} under pH 7 and 13. Two "volcano plots" can be found, with much lower activities at pH 7. Those materials with quota marks in the names are the catalysts that are not stable at 5 μ A/cm²_{ox} at pH 7. The horizontal lines represent the activity of IrO₂ at 5 μ A/cm²_{ox}. The black lines are only for eye guidance.

4.4. Two Degradation Mechanisms of Perovskite Oxides at Neutral pH

The stability of these perovskites before and after OER at pH 7 was analyzed by TEM. It is worth noting that although the same activity descriptor from pH 13 can be used at pH 7, the stability trends at pH 7 are very different from that at pH 13. Firstly, the amorphization region of perovskites (shaded region in Figure 4-5b and Figure 4-5c) extended at pH 7, where the oxides show amorphized surface after OER. As an example, PBCO remained stable after OER at pH 13, but became amorphous after OER at pH 7 (Figure 4-11). Secondly, the perovskites in the stable region (unshaded region in Figure 4-5b and Figure 4-5c), like LCO, could be stable up to 50 μ A/cm²_{ox} at pH 13,²⁸ but showed surface amorphization at pH 7 under such high current (Figure 4-7a), accompanied by the loss of B-site elements (i.e. Co in LCO, shown in Figure 4-7b). This was also observed in other perovskites with O 2p-band away from the Fermi level

including LNO (Figure 4-8), LMO (Figure 4-9) and LFO (Figure 4-10), which are all stable under 5 μ A/cm²_{ox}, but become unstable under 50 μ A/cm²_{ox} at neutral pH with Bsite elements leaching. Thirdly, the perovskites with the O 2p-band closer to the Fermi level like PBCO became surface amorphized (Figure 4-11a), which was associated with loss of A-site elements, (i.e. Pr and Ba in PBCO, shown in Figure 4-11b) at current densities as low as 1 μ A/cm²_{ox} and even after soaking at pH 7 for 2 h without applying any current/potential. This is also true for BSCF (Figure 4-12) and SCO (Figure 4-13), whose surfaces become amorphized after OER or just soaking at pH 7 with A-site elements leaching. The above observations demonstrated that the O 2p-band is an important stability descriptor for perovskite OER catalysts at neutral pH, which determines two different degradation mechanisms, and requires different optimization methods in the future. For oxides with an O 2p-band far away from the Fermi level (e.g. LCO), it is critical for the development of more stable electrocatalysts to stabilize the electroactive B-site against the degradation, especially at higher current densities. While for oxides with an O 2p-band close to the Fermi level (e.g. PBCO), A-site leaching should be prevented under all current and voltage ranges by adding A-site element salts into the electrolyte or adding protective layer on the surface of the oxides.



Figure 4-7. (a) TEM images and (b) EDS-determined chemical compositions of LCO in pristine state and operated at 0 (soaking), 5 and 50 μ A/cm²_{ox} for 2 h at pH 7. The error bars in (b) represent the standard deviation of multiple spots.



Figure 4-8. (a) TEM images and (b) EDS-determined chemical compositions of LNO in pristine state and operated at 0 (soaking), 5 and 50 μ A/cm²_{ox} for 2 h at pH 7. The error bars in (b) represent the standard deviation of multiple spots.



Figure 4-9. (a) TEM images and (b) EDS-determined chemical compositions of LMO in pristine state and operated at 0 (soaking), 5 and 50 μ A/cm²_{ox} for 2 h at pH 7. The error bars in (b) represent the standard deviation of multiple spots.



Figure 4-10. (a) TEM images and (b) EDS-determined chemical compositions of LFO in pristine state and operated at 0 (soaking), 5 and 50 μ A/cm²_{ox} for 2 h at pH 7. The error bars in (b) represent the standard deviation of multiple spots.



Figure 4-11. (a) TEM images and (b) EDS-determined chemical compositions of PBCO in pristine state and operated at 0 (soaking), 1 and 5 μ A/cm²_{ox} for 2 h at pH 7. The error bars in (b) represent the standard deviation of multiple spots.



Figure 4-12. (a) TEM images and (b) EDS-determined chemical compositions of BSCF in pristine state and operated at 0 (soaking), 1, 5 and 50 μ A/cm²_{ox} for 2 h at pH 7. The error bars in (b) represent the standard deviation of multiple spots.



Figure 4-13. (a) TEM images and (b) EDS-determined chemical compositions of SCO in pristine state and operated at 0 (soaking), 1 and 5 μ A/cm²_{ox} for 2 h at pH 7. The error bars in (b) represent the standard deviation of multiple spots.

Traditionally, people use Pourbaix diagrams to predict the thermodynamic stability of species under various pH and voltages. For the perovskites studied in this chapter, the

Pourbaix diagrams predict the instability of A-site atoms at pH 7 in the OER region for oxides from both the stable region (Figure 4-14) and the amorphized region (Figure 4-15), which is not fully consistent with the experimental observation that A-site leaching was only observed for oxides in the amorphized region. A potential explanation is that the kinetics of A-site leaching was sluggish for those oxides with O 2p-bands far from the Fermi level; in contrast, these oxides tended to leach more B-site cations under high current/potential at pH 7. To explain the B-site leaching in those perovskites with O 2pbands far from the Fermi level under high potential/current conditions at pH 7, we performed DFT calculations on LCO to estimate the thermodynamic driving force of La (A-site, see Figure 4-16a) and Co (B-site, see Figure 4-16b) as a function of the degrees of elements leaching. It can be found that at 1.23 V vs. RHE, the free energy increased as a function of the leaching degree for both A-site and B-site leaching (blue bars in Figure 4-16), indicating that at 1.23 V vs. RHE, the pristine structure is thermodynamically stable. When the voltage is increased to 1.75 V vs. RHE, which is the voltage needed to apply an OER current of 5 μ A/cm²_{ox} on LCO, the free energy of both A-site and B-site leaching cases reached the lowest values at x or y = 0.25. This means under low current/overpotential, thermodynamically LCO tends to be stablized at limited surface leaching stages. After limited A or B site elements loss from the surface, the leaching will stop, leading to the stability of LCO under low current/overpotential at pH 7. On the contrary, when the voltage is 2.33 V vs. RHE, which corresponds to the OER current of 50 μ A/cm²_{ox} on LCO, DFT calculation shows the free energy decrease with the leaching degrees. This implies that thermodynamically, LCO will tend to continuously lose the Asite and B-site elements at pH 7 under high current/overporential conditions, which is consistent to the surface amorphization observed under TEM. The DFT calculation also shows that under the high current/overpotential conditions, the thermodynamic driving force of the oxidation of B-site ions that is associated with amorphization and phase separation (such as a CoO_z phase) is much higher than the leaching of La^{3+} , suggesting the loss of B-site elements could be faster than that of A-site elements, which is also consistent to the TEM and EDS observations. More details of the DTF calculation could be found in Ref. ⁵¹. These DFT results demonstrate that the surface degradation process kinetically determined the stability of perovskite oxides at neutral pH. Even the bulk

calculation (Pourbaix diagram) predicts the instability of LCO at pH 7, the DFT calculation on the surface allows LCO to be stable under lower current/overpotential.



Figure 4-14. Pourbaix diagram of the Co-La-O(H) system predicted by DFT (data from materialsproject.org). Dashed lines indicate H_2/H^+ and H_2O/O_2 . Co and La cation concentrations were assumed to be 10⁻⁶ M in the electrolytes.



Figure 4-15. Pourbaix diagram of the Pr-Ba-Co-O(H) system predicted by DFT (data from materialsproject.org). Dashed lines indicate H_2/H^+ and H_2O/O_2 . Pr, Co and Ba cation concentrations were assumed to be 10^{-6} M in the electrolytes.



Figure 4-16. The computed DFT leaching reaction energies of (a) La leaching and (b) Co leaching in LCO at various La vacancy concentration (x) and Co vacancy concentration (y), at applied potential of 1.23 V (blue), 1.75 V (red), and 2.33 V (green) vs. RHE at pH 7.

4.5. Chapter 4 Conclusions

In summary, by systematically studying the activity and stability of OER perovskite catalysts at pH 7, we found that both an e_g occupancy close to unity and an O 2p-band close to the Fermi level lead to higher OER activity at pH 7, which are activity descriptors previously discovered at high pH. Meanwhile, two different dissolution mechanisms were discovered at pH 7, which are closely related to the O 2p-band position of the perovskites. Perovskites with O 2p-band close to the Fermi level showed leaching of A-site cations and surface amorphization at any condition in pH 7 electrolyte, while the perovskites with O 2p-band far from the Fermi level were stable under low

current/potential but suffered from phase separation of B-site cations at high current/potential. Cation leaching plays a more important role for instability at pH 7 as compared to pH 13 because of the much higher OER overpotential under the same current at neutral pH. Therefore, it is necessary to identify the key material challenges faced in the design of efficient and stable non-precious-metal oxides catalysts for electrochemical devices at neutral pH, such as the A-site vs. B-site instability in different perovskites. Optimized design strategies need to be devised to address both challenges separately.

Chapter 5. Environmental TEM Study of Structural Oscillations and Oxygen Evolution in Perovskite Oxides

5.1. Introduction

Previous discussions in Chapter 4 demonstrate that the electronic structures of perovskite oxides have great influence to the activity and stability during the OER. Having O 2p-band closer to the Fermi level brings faster OER kinetics but also surface amorphization to the oxides. In fact, the interaction between water and oxides is not only critical to the stability and activity during the OER, but also important to the surface wetting,¹¹²⁻¹¹⁵ photocatalysis,^{114,116-118} sensors,¹¹⁴ and proton conducting ceramic membranes.¹¹⁹⁻¹²² Recent studies have shown that decreasing coverage of hydroxyl groups on perovskite oxide surface at the water/oxide interface not only reduces wetting and but also enhance oxygen reduction kinetics in basic solution.¹¹³ Moreover, the formation and transportation of oxygen vacancies $(V_0^{\bullet\bullet})$ can affect the interaction between water and perovskite oxides by allowing the water to intercalate into the perovskites via water incorporation reaction: $H_2O + V_0^{\bullet} + O_0^{\times} \rightarrow 2OH_0^{\bullet}$ (here O_0^{\times} and OH_0^{\bullet} represent the oxygen atom and hydroxyl group in the lattice oxygen site, respectively).^{119,120,122} On one hand, this water intercalation process makes it possible to use perovskites as the solid electrolyte (i.e. proton conductors) in fuel cells,^{119,120,122} hydrogen pumps^{119,120} and hydrogen sensors.¹²⁰ On the other hand, the insertion of water molecules into the oxygen lattice with the help of oxygen vacancy maybe related to the surface amorphization of the OER-active perovskites whose O 2p-band is closer to the Fermi level and therefore the oxygen vacancy formation energy is low. It is of great significance to examine the interaction between water and oxides such as BSCF, which contains high concentrations of oxygen vacancies and shows high water uptake,¹²³ high OER activity,^{28,29,124,125} fast oxygen surface exchange,^{43,126,127} fast oxygen ion transportation¹²⁸ and low energy penalty of oxygen vacancy formation.¹²⁶ However, most of the previous studies on the interaction between water and perovskite are *ex situ*, meaning the interaction results rather than the kinetic interaction processes were observed after taking the perovskites out of the water. To study the complicated interactions between water and oxides that are far away from the equilibrium conditions, we need the help of *in situ* characterization techniques.

Traditional in situ oxides characterizations in water environment include wetting angle measurements,¹¹³ ambient pressure X-ray photoelectron spectroscopy (APXPS)¹²⁹⁻ ¹³¹ and environmental electron microscopes.^{132,133} In this chapter, we focused on the *in* situ ETEM technique, which allows atomic-scale observation of the interaction between gas(vapor)/liquid and the surface/subsurface layers of materials.132-135 As an example, previous ETEM studies showed that the electron beam in TEM chamber is able to split water on Pr_{1-x}Ca_xMnO₃, observed by the formation of SiO₂ from SiH₄ placed within the chamber to react with the generated O₂ gas.^{132,133} However, the interpretation of these observations could be ambiguous, since the amorphous SiO₂ formed on the oxides surface might come from the side reactions of SiH₄ with H₂O rather than with O_2 .¹³⁶ The direct experimental evidence of the oxygen evolution in ETEM is still missing. Meanwhile, spectroscopic information can be obtained through EELS using electron microscopes. For example, a recent environmental scanning electron microscope (ESEM) study provided direct evidence of water trapping in the multilayer graphene oxide membrane using EELS.¹³⁵ Therefore, combining *in situ* ETEM with EELS is a powerful approach to study the interactions between water vapor and oxides, especially those oxides prone to bulk uptake of water.

Inspired by the *in situ* observation proposed above, in this chapter, we applied ETEM observations on BSCF and other perovskite oxides in water environment. Dramatic "breathing-like" structural oscillations of BSCF were observed with the formation and collapse of gaseous bubbles in this material. In contrast, no structural oscillation is observed when exposing BSCF in high vacuum (HV) or in presence of O_2 under electron beam (e-beam). Increasing the e-beam dose rate or the water content increased the oscillation frequency but decreased the oscillation amplitude. The formation of O_2 was observed by EELS during the structural oscillations, suggesting the bubble formation is related to the oxygen evolution in the bulk of BSCF under electron beam irradiation. On the contrary, the structural oscillations were weakened or absent for
SCO, LSC, and LCO with less oxygen vacancy and lower oxygen ion mobility, which is likely caused by their O 2p-band farther away from Fermi level. This work provides direct experimental proof of the oxygen evolution under ETEM and the first observation of structural oscillation caused by the water splitting inside of oxides, which provided nano-scale observations of the interaction between water and perovskites.

5.2. Experimental Methods

Material preparation

BSCF, LCO, SCO, and LSC were synthesized using a conventional solid-state route.²⁸ The specific surface area of each oxide sample was determined using BET analysis on a Quantachrome ChemBET Pulsar from a single-point BET analysis performed after 12 h outgassing at 150 °C. LCO, SCO and $La_{0.5}Sr_{0.5}CoO_{3-\delta}$ (LSC) were synthesized by conventional solid-state routes.²⁸ The synthesized oxides were ground and then annealed a second time in air at 1100 °C for LCO and LSC, following by slowly cooling down to room temperature. The SCO was prepared by sintering at 1300 °C for 24 hours and quenched to room temperature. All oxides reported in this chapter are single-phase, as analyzed by X-ray diffraction using a PANalytical X'Pert Pro powder diffractometer. The structural information can be found in Table 5-1. The TEM samples were prepared by milling and directly dropping dry powders onto the lacey carbon or SiN TEM grid without dispersing in any solutions, to prevent the contamination of water or other solvent.

Table 5-1. Crystal structures and lattice parameters of oxides perovskites used for ETEM characterization in Chapter 5.

| Compound | Space Group | a (Å) | b (Å) | c (Å) |
|----------|-------------|----------|-----------|-----------|
| BSCF | Pm-3m | 3.981(2) | 3.981(2) | 3.981(2) |
| LCO | R-3c | 5.440(2) | 5.440(2) | 13.090(4) |
| LSC | P4/mmm | 3.833(7) | 3.833(7) | 3.804(5) |
| SCO | Imma | 5.480(2) | 15.768(5) | 5.543(4) |

ETEM characterizations

TEM and HRTEM images, as well as the electron diffraction patterns (EDP) shown in this chapter were taken using an aberration corrected field emission gun transmission electron microscope, FEI Titan S/TEM, operated at 80 kV. The phase field was tuned to ~20 mRad. The pressure of the HV condition was 10^{-6} Torr. During the ETEM experiments, up to 100 mTorr of H₂O vapor was introduced into the TEM chamber. The *in situ* videos containing TEM images and EDP were recorded using the video capture mode in the FEI TEM Imaging & Analysis software. All videos are presented at the realtime frame rates at which they were acquired. In each movie, the diameter of the most obvious hollow structure (bubble) was measured frame-by-frame to monitor the oscillation amplitude and frequency. EELS with the energy resolution was ~ 1 eV was collected in the diffraction mode using a Gatan Tridiem post-column energy filter, and the energy axis was calibrated using the zero loss peak. The e-beam spot for EELS measurement is ~ 50 nm in diameter, and the acquisition time is ~ 5 min for each spectrum. The electron beam intensities were as reported by the FEI Titan software, based on calibrated readings of the electron beam current on the larger phosphor screen.

5.3. Structure Oscillations of BSCF in H₂O Vapor under e-beam

BSCF was found stable in HV under 80 kV e-beam in TEM chamber (Figure 5-1a) and its electron diffraction patterns (EDP) showed a stable cubic structure with the Pm3m space group (Figure 5-2a), consistent with previous studies.³⁹ This means e-beam accelerated up to 80 keV does not have obvious influence to the atomic structure of BSCF.



Figure 5-1. (a) TEM images of BSCF in BSCF (chamber pressure $< 10^{-6}$ Torr, e-beam dose rate of 1450 e/A²s) (b) TEM images of BSCF in O₂ gas (80 mTorr O₂, e-beam dose rate of 500 e/A²s).

Upon introduction of 30 mTorr of H₂O vapor under the e-beam dose rate of 1 e/Å²s, several dynamic bubble-like hollow structures formed on the BSCF particle, seen at the edge of the particle in Figure 5-2c with continuous breathing-like inflation and shrinking oscillations. When increased the H₂O pressure to 10 mTorr and the e-beam dose rate to 10 e/Å²s, a faster and larger scale breathing motion can be observed (Figure 5-2d). To evaluate the amplitude and frequency of the breathing motion, we measured the diameter change of the largest bubble in the view over time during both slow and fast oscillations, as shown in Figure 5-2e and Figure 5-2f, which demonstrated that higher H₂O pressure and higher e-beam dose rate could fasten the oscillation. Such breathing-like oscillation was continuously observed for more than 10 minutes, and stopped immediately upon removal of H₂O from the microscope, as indicated by the return of the HV base pressure $(\sim 10^{-6} \text{ Torr})$. In contrast, no structural oscillation was observed on BSCF under up to 80 mTorr of O_2 and 500 e/Å²s of electron dose rate (Figure 5-1b), implying the structural oscillation is closely related to the interaction between oxides and water, rather than the high pressure of other gases in the ETEM chamber. Remarkably, our *in situ* EDP showed that the core of BSCF kept its original $Pm\bar{3}m$ crystalline structure during the oscillations, with the appearance and disappearance of diffraction reflections resulting from real space rotations of the crystalline lattice (Figure 5-2g and Figure 5-2h). More images of the structural oscillations that occur in BSCF can be found in Figure 5-3.



Figure 5-2. (a) TEM images and EDP from a pristine BSCF particle (Particle A). (b) TEM images and EDP from BSCF in the HV, following the structural oscillations. EDP were collected from the entire particle. (c) Images extracted from a video of the structural oscillations, in mild conditions (30 mTorr H₂O, e-beam dose rate of $1 \text{ e/A}^2\text{s}$). (d) Images extracted from a video of the structural oscillations obtained in a harsher condition (50 mTorr H₂O, e-beam dose rate of $10 \text{ e/A}^2\text{s}$). The blue dashed lines in (c) and (d) are guides to help in the comparison of the motion of the particle edges. (e) and (f) present quantitative measurements of the changes in bubble size vs. time under the mild and harsher conditions, respectively. (g) and (h) present EDP from BSCF under the mild and harder conditions, respectively. The number of seconds shown in panels (c)-(h) represents the passage of time after the initiation of the environmental stimulus. The faint white-dotted lines superimposed upon the EDP in panels (a), (b), (g) and (h) show the expected location of the standard reflections for BSCF.



Figure 5-3. TEM images of another BSCF particle (Particle C) (a) before, (b) during slow, (c) during fast and (d) after breathing motion. Slow breathing condition: 10 mTorr H₂O and 20 e/Å²s e-beam dosing. Fast breathing condition: 10 mTorr H₂O and 100 e/Å²s e-beam dosing. The right image in panels (a) and (d) are the fast fourier transform of the corresponding HRTEM image in the middle of each panel, patterned by standard BSCF perovskite structure. The orange circle in the left image of penal (a) represents the EELS collecting region of the results in Figure 5-5.

To study the influence of H_2O and e-beam on the oscillatory motions, the bubble size evolution were measured under lower vs. higher water pressure on Particle B (Figure 5-4a) and under lower vs. higher e-beam dosing on Particle C (Figure 5-4b). By counting the number of peaks in unit time and measuring the spanning of size evolution during each oscillation, we calculated the frequencies and amplitudes of the oscillation of hollow structures on multiple particles under a range of e-beam dose rates and H_2O vapor conditions, as shown in Figure 5-4c and Figure 5-4d. Figure 5-4 showed that having both

e-beam and H₂O vapor are critical to trigger the breathing. Neither high e-beam with too low H₂O pressure (e.g., Particle D in 0.11 mTorr H₂O under 500 e/Å²s in Figure 5-4c) nor too low e-beam with high H₂O pressure (e.g., Particle C in 1 mTorr H₂O under 20 e/Å²s in Figure 5-4c) can trigger the breathing motion. Moreover, both higher e-beam and higher H₂O partial pressure could increase the frequency of motion at a slight or none cost to the displacement of particle breathing (Figure 5-4c and Figure 5-4d). For example, for Particle B under e-beam dosing of 40 $e/Å^2s$ (Figure 5-4a), when the H₂O pressure increased from 0.4 mTorr to 11 mTorr, the breathing frequency increased from 0.29 to 1.25 Hz, while the maximum displacement decreased from 20.5 to 13.5 nm. Similarly for Particle C in Figure 5-4b, in 10 mTorr H₂O, when the e-beam increased from 20 to 100 e/Å²s. the breathing frequency increased from 0.03 to 0.55 Hz, while the maximum displacement decreased from 14 to 8 nm. Such water and e-beam dependence indicates that the breathing motion should originate from a reaction that involves both electrons and H_2O_1 , which may lead to the generation of a gas not only on the surface, but also under sub-surface layers of BSCF to cause the expansion/ contraction of the oxide lattice. This sub-surface gas creation causes the observed expansion/contraction of the oxide lattice. The increased rate of gas generation may also cause the hollow structure to collapse more quickly, which can explain the slightly decreased maximum displacement of the structural oscillations observed in harsher reaction conditions.



Figure 5-4. (a) Bubble size (average diameter) evolution of Particle B over time in the presence of an e-beam dose rate of 40 e/Å²s and a H₂O pressure of 0.4 and 11 mTorr. (b) Bubble size evolution of Particle C over time in the presence of 10 mTorr H₂O pressure and an electron dose rate of 20 and 100 e/Å²s. (c) and (d) are the frequency and displacement of the structural oscillations as a function of different e-beam dose rate and H₂O pressure, as indicated, respectively. Particle A, B, C and D represent different BSCF particles, differentiated by color. The numbers under columns represent the H₂O pressure in the unit of mTorr. The numbers above columns represent the e-beam dose rate in units of e/Å²s.

After back to HV conditions, the HRTEM image showed an amorphization layer (~2 nm) on the surface of Particle A, with the particle core remain perovskite with the space group of $Pm\bar{3}m$ (Figure 5-2b). A similar amorphized layer was also observed in other

particles (Figure 5-3d) after the structural oscillation. We speculate that the amorphous layer forms from the residue of the bubble structures that are created during the e-beam induced BSCF oscillation. We note that the core of the BSCF particles remained unchanged, which is consistent with the *in situ* EDP observations.

5.4. EELS Evidence of Oxygen Evolution from BSCF

To further reveal the chemical change of BSCF during breathing and the potential reaction causing such oscillation, EELS was collected before and during the breathing motion (i.e. before and during the introducing of H_2O vapor into TEM chamber). The EELS data in Figure 5-5 showed no appreciable change in characteristic peaks in O Kedge spectra of BSCF¹³⁷ before and during the structural oscillation, indicating the bulk of BSCF particle is chemically stable during the breathing process, consistent with the previous observations in HRTEM images and in situ EDP. The increase of molecular O₂ characteristic peak ~531 eV suggests the generation of O_2 gas,¹³⁸ as shown in Figure 5-5a. In order to further confirm whether O_2 was generated during the oscillations, the low energy region of EELS from 15 to 40 eV was investigated (Figure 5-5b). In addition to the H:1s-O:2p peak from H₂O vapor, which could also be assigned to the H-H peak from H_2 , we also observed a notable O_2 low loss peaks that can be compared to the reference peaks of H₂O, H₂ and O₂ in this low energy region in Figure 5-6. The distinction of the spectra for BSCF in water from a superposition of the dry oxide low loss and reference H₂O vapor (Figure 5-6) suggests the evolution of molecular oxygen rather than the background signal from H₂O environment.



Figure 5-5. EELS of BSCF before ("BSCF in HV") and during ("BSCF in H₂O") the structural oscillations, in the energy ranges associated with the (a) O K-edge and (b) H K-edge / O_2 low loss region, respectively. The "BSCF in HV" spectra were collected in 10^{-3} mTorr HV under an electron dose rate of ~ 200 e/Å²s, while the "BSCF in H₂O" spectra were collected in 10 mTorr H₂O under an electron dose rate of ~200 e/Å²s. The sample region from which this EELS data was collected is shown in Figure 5-3a. The reference spectra of the O₂ gas ("O₂") and H₂O vapor ("H₂O") are also collected in 10 mTorr O₂ and 30 mTorr H₂O, respectively. The characteristic peaks of BSCF, O₂, H₂O and carbonate were labeled in black, red, blue and green, respectively.



Figure 5-6. Reference EELS for H K and low loss region of water (green), pure H_2 gas and pure O_2 gas, provided by Dr. Eric Stach from previous study.¹³⁹

At the same time, several characteristic peaks of carbonate including O:2p-CO₃:2sp peak in the O K-edge¹³⁷ (Figure 5-5a) and C: $1s/\pi^*$ -O:2p and C: $1s/\sigma^*$ -O:2p peaks in the C K-edge¹⁴⁰ (Figure 5-7a) were found to increase in the breathing condition, indicating the formation of carbonates (BaCO₃, SrCO₃, etc.) during breathing, which might be caused by a reaction between BSCF and the supporting lacey carbon from the TEM grid. This first *in situ* observation by TEM is of great consequence to the performance of catalysts and battery materials, which may similarly react with their carbon supports to cause the degradation of electrode structure and performance. However, structural oscillation was also observed on the carbon-free SiN grid (Figure 5-7b), indicating that the observed carbonate formation is not the physical origin of the breathing motions.



Figure 5-7. EELS of BSCF before (black, "BSCF in HV") and during (red, "BSCF in H₂O") breathing motion, in the regions of C K-edge. The "BSCF in HV" spectra were collected in 10^{-3} mTorr HV under the e-beam dosing of ~ 200 e/Å²s, while the "In H₂O" spectra were collected in 10 mTorr H₂O under the e-beam dosing of ~200 e/Å²s. The TEM grid in (a) is amorphous Carbon, while the TEM grid in (b) is SiN. The reference peak positions from carbonate and amorphous carbon were labeled in blue and black, respectively.

5.5. Mechanistic Discussion of Oxygen Evolution and Bubble Formation in BSCF

With the observation of O_2 formation from EELS results, here we propose that the structural oscillations observed in BSCF in presence of H₂O vapor under the electron beam is caused by the OER within BSCF particles, as shown in Figure 5-8, which is supported by the following considerations. First, previous work has shown that BSCF particles have high oxygen nonstoichiometry in the perovskite structure and thus demonstrate significant H₂O uptake¹²³ by a process well known for oxide proton conductors: $H_2O + V_0^{\bullet\bullet} + O_0^{\times} \rightarrow 20H_0^{\bullet}^{119,120,122}$. As H_2O reacts with BSCF to form hydroxyl ions (OH_o^{\bullet}) on the surface, hydroxyl ions can diffuse from surface to the bulk lattice, with counter flow of O^{2-} ions (O_0^{\times}) from bulk to the surface. Second, the e-beam reaching the BSCF particle surface could give rise to a positive electric potential due to the secondary electron emission effect, as suggested by previous in situ ETEM study.¹³³ The hydroxyl group on lattice oxygen site can then evolve molecular O2 under the ebeam induced oxidative potential $(20H_0^{\bullet} \rightarrow 2V_0^{\bullet\bullet} + O_2 + H_2 + 2e^-)$. The oxidative potential may also lead to the evolution of molecular O2 from the perovskite lattice $(20_0^{\times} \rightarrow 2V_0^{\bullet \bullet} + 0_2 + 4e^-)$ at low oxygen pressure.¹⁴¹ Any lattice oxygen vacancies generated during oxygen release from BSCF lattice can be refilled as OH₀ through the capture of H₂O, which allows continuous O₂ generation within the lattice of BSCF. The O₂ trapped and accumulating within BSCF particles caused the formation and inflation of gas bubbles in near-surface regions, which finally resulted in the breaking and shrinking of bubbles. The oscillatory motion suggested the breaking bubbles can recover after shrinking, which may be due to the high mobility of oxygen ions of BSCF,¹²⁸ allowing the O₂ to accumulate again to re-inflate the bubbles..



Figure 5-8. A scheme of water intercalation accompanied by water splitting within BSCF particles, which leads to structural oscillations observed on BSCF in H_2O vapor under electron beam.

The above oscillation process can be described using a simple model with the following first-order approximations. First, the oxygen gas in the bubbles can be treated as an ideal gas. Second, oxygen evolution and oxygen release are the rate-determine steps that control the bubble growth and shrinking, respectively. Third, the rates of oxygen evolution and release can be treated as constants. With the above approximations, we find derive the evolution of bubble size as a function of time, which is shown below.

If we treated the oxygen gas in the bubbles as ideal gas, we will have:

$$p_{bubble}V_{bubble} \approx n_{O_2}RT \tag{1}$$

where p_{bubble} is the pressure inside the bubble, V_{bubble} is the volume of the bubble, n_{O_2} is the mole number of oxygen gas in the bubble, R is the gas constant, and T is the temperature. In classic bubbles:

$$p_{bubble} - p_{TEM} = \frac{4S_{BSCF}}{d} \tag{2}$$

Where p_{TEM} is the pressure in TEM, S_{BSCF} is the surface energy of BSCF, and *d* is the bubble size (bubble diameter). Here $p_{bubble} \gg p_{TEM}$ due to the low pressure in TEM and high pressure in bubble to cause BSCF deformation. Therefore:

$$p_{bubble} \approx \frac{4S_{BSCF}}{d}$$
 (3)

Combine (1) and (3), notice that $V_{bubble} = \frac{\pi}{6} d^3$, we have:

$$n_{O_2} \approx \frac{2\pi S_{BSCF}}{3RT} d^2 \tag{4}$$

This gives us:

$$n_{O_2} \propto d^2 \tag{5}$$

During bubble growing and shrinking process, since we assume oxygen evolution and oxygen leaking are the rate-determine steps, respectively, then:

$$\Delta(n_{O_2}) = \alpha_{OER}\Delta(t)$$
(6) in bubble growing process;
$$\Delta(n_{O_2}) = \beta_{leak}\Delta(t)$$
(7) in bubble shrinking process.

where *t* is the time, α_{OER} is the oxygen evolution rate, and β_{leak} is the oxygen leaking rate. For the first-order approximation, if we treat the rates of oxygen evolution and leaking as constants, from (6) and (7) we can get:

$$\Delta(n_{O_2}) \propto \Delta(t) \tag{8}$$

Combining (5) with (8), we can then get:

$$\Delta(d^2) \propto \Delta(t) \tag{9}$$

This means no matter in growing or shrinking process, the square of the bubble diameter always changed proportional to the growing or shrinking time. This relationship can be tested by plotting the square of bubble size (d^2) against the time (*t*) using the data in Figure 5-2e, which is shown in Figure 5-9. The good matching between the measured bubble size evolution and the modeling results implies our bubble oscillation mechanism with inside oxygen evolution explains the observations well.



Figure 5-9. The square of the bubble size (d^2) versus the time (*t*) during the first growing process (solid) and the first shrinking process (open) of Particle A (data points from Figure 5-2e). The red lines are the linear fitting of the growing and shrinking processes with R² values of 0.98 and 0.99, respectively.

5.6. Influence of Electronic Structures to Structural Oscillations

As discussed in previous chapters, the electronic structures have great influence to the lattice oxygen vacancies and the OER stabilities in perovskite oxides. Basically when the O 2p-band is closer to the Fermi level, the lattice oxygen vacancies will be generated and activated during the OER between the interaction of water and oxides. In this chapter we further studied the influence of electronic structures and oxygen vacancies to the structural oscillations in water vapor and under e-beam. Among all the oxides tested in this chapter, BSCF is known to have its O 2p-band center closest to the Fermi level,¹²⁶ which lead to the lowest vacancy formation energies $(E_{vac})^{126}$ and the highest oxygen ion mobility,^{126,128} as shown in the Figure 5-10. In comparison, brownmillerite SCO has larger gap between O 2p-band center and Fermi level,^{126,142} higher E_{vac}¹²⁶ and lower mobility of oxygen ions.¹⁴³ As a result, the observed lattice oscillation in SCO were confined to thin surface layers of ~1 nm, even under a harsh H₂O and e-beam irradiation condition (in 30 mTorr H₂O under 1250 e/Å²s). For LSC and LCO with O 2p-band center farther away from the Fermi level and much higher E_{vac}, no structural oscillation was observed in >10 mTorr H₂O and under >100 e/Å²s. The absence of structural oscillation in these oxides can be attributed to the fact that the O 2p-band centers are far from the

Fermi level, which correlates with increased energy penalty for oxygen vacancy formation and reduces oxygen ion mobility. Therefore, it is difficult for these oxides to uptake H_2O to form OH_0^{\bullet} , and the transport of oxygen or hydroxyl ions is sluggish, confining oxygen evolution to the surface of oxides with an inactive lattice. Moreover, if changing the transition metal ions from Co to Mn, the O 2p-band center further moves away from the Fermi level,¹²⁶ therefore the structural oscillation was also absent for Pr₁₋ _xCa_xMnO₃ (previously reported and studied on the same instrument in 112 mTorr H₂O under 5000 e/Å 2 s¹³³). The above observations provided direct evidence that tuning the O 2p-band center closer to the Fermi level and reducing the energy penalty for oxygen vacancy formation can facilitate water uptake and ion transport in oxides, which can activate the oxygen evolution not only on the surface but also inside the oxides under ebeam irradiation. These observations not only provide deeper insight into the activity and stability of highly active perovskite OER catalysts, but also open new possibilities in the design and development of many new materials. In the future, we may be able to activate water splitting or hydrogen/oxygen transportation through the water-oxide interaction using high-energy electrons, high-energy photons or strong fields. This would be helpful in developing new energy storage devices, hydrogen/oxygen pumps or gas sensors.^{119,120,122}



Figure 5-10. Comparison of structural oscillations in BSCF to the lack thereof for other oxides in H₂O and under e-beam. The axis indicates the location of the O 2p-band centers (relative to Fermi level), E_{vac} , and oxygen tracer diffusion coefficient (D, measured at 900 °C under 0.2-1 atm of O₂), taken or estimated from previous studies.^{126,128,142-144} The water vapor pressures and electron dose rates for each oxide samples were listed above the corresponding TEM images. The number of seconds shown on each TEM image represents the passage of time after the initiation of the environmental stimulus.

5.7. Chapter 5 Conclusions

In summary, we demonstrated that in the H_2O environment, BSCF exhibited significant breathing-like oscillatory motion under e-beam irradiation in ETEM. During this oscillation, the frequency increased and the amplitude decreased under higher H_2O content or higher e-beam dose rate. EELS showed O_2 formation during breathing, attributed to oxygen evolution in H_2O vapor catalyzed by the BSCF. The structural oscillation can be explained by the intercalation of H_2O into the bulk of BSCF and the ebeam-induced, BSCF-catalyzed oxygen evolution that leads to the generation of O_2 throughout near-surface layers of BSCF. In contrast, the structural oscillation is weak or absent in other Co- or Mn-based oxides, because the water uptake is hindered by their lower oxygen ion mobility and greater energy penalty for oxygen vacancy formation, which is due to the larger gap between O 2p-band center and Fermi level. These *in situ* observations provide a thorough understanding of the interaction between water and oxides under oxidizing electron beam irradiation.

Chapter 6. Conclusions and Perspectives

6.1. Thesis Summary

In this thesis, by combining electrochemical characterizations with electron microscopic techniques, we systematically studied the catalytic performance of both Pt-M ORR catalysts and perovskite oxide OER catalysts at various pH values. The stabilities and activities of both catalyst systems are found to be closely related to their atomic and electronic structures. For Pt-alloy ORR catalysts, having transition metal with more positive dissolution potential can lead to better chemical stability in acidic electrolyte but worse activity improvement due to less beneficial electronic structure adjustment (Chapter 2). By controlling the formation of Pt-rich protective shell on the surface of Ptalloy particles, we can further improve the stability by preventing the leaching of transition metal from the core, and therefore keep the initially high ORR activity after voltage cycling (Chapter 3). Meanwhile, for perovskites OER catalysts, if the Fermi level moves closer to the O 2p-band center, the lattice oxygen becomes activated and the formation of lattice oxygen vacancy becomes easier. This on one hand can activate the oxygen redox and lead to higher OER activity (Chapter 4). While on the other hand, the activation of oxygen vacancies causes the worse stability in both neutral and basic electrolytes (Chapter 4), and enables the water uptake into the oxides lattice to initiate the structural oscillation during the OER in ETEM (Chapter 5). The above discoveries revealed the great influence of the electrolyte-catalyst interaction to the stability and activity during the oxygen redox reactions. This work not only provided deeper understandings to the mechanisms of oxygen electrocatalysis and catalyst degradation processes, but also brought us new design principles to make more stable catalysts with higher catalytic activities.

6.2. Outlook

It is interesting to find that for both Pt-M catalysts used for ORR in acidic electrolyte and perovskite catalysts used for OER in neutral or basic electrolyte, the

design guidelines to improve the activity (e.g. more negative $V_{dissolve}$ in Pt-M, or closer distance between Fermi level and O 2p-band in perovskites) often bring worse stability. Therefore, the activity and durability usually cannot be optimized at the same time. The nature of such contradiction, in my viewpoint, is based on the interaction between water/electrolyte and catalysts. For example, in this thesis when we start from a relatively stable catalyst, such as pure Pt and LCO, and try to improve their ORR or OER activities by adjusting their electronic structures, usually we have to tune the chemistry to activate the surface electron transfer, i.e. facilitate the redox of surface active sites. In the case of Pt-M ORR catalysts, the surface adsorption/desorption of oxygen species can be adjusted by alloying Pt with transition metals, such as Ni, which brings beneficial ligand and strain effects to activate the redox on Pt. While in the case of perovskite OER catalysts, the surface adsorption/desorption of oxygen species can be adjusted by replacing La with Sr in LCO to activate the redox on O. This on one hand leads to better OER activity, however on the other hand the newly introduced chemistry (e.g. Ni site in Pt-Ni) and the activated chemistry (e.g. surface O atoms in SCO) can potentially become the new unstable factors in the catalysts. Therefore, for both Pt-M and perovskite systems studied in this thesis, we have to find a balanced point between stability and activity, which brings us an optimization peak, as shown in the Figure 6-1.



Figure 6-1. Competition between activity and stability that leads to optimization peak for the design of new catalysts.

The existence of such optimization peak is not satisfactory, because it limits the best catalytic performance we can potentially approach. Therefore, extended from this thesis, the following research directions can be considered in order to break this limitation and further improve the catalytic performance of the catalysts.

First, the stability of the catalysts may be improved by surface engineering without sacrificing the activity. As an example, in this thesis the surface Pt-rich protective layer outside the Pt-Ni particles has been formed and tuned by different acid and heat treatments to prevent Ni leaching. Similarly, we can always try exposing the more stable element or termination of the catalyst particles to the electrolyte, as long as the catalytic active site is on this stable element/termination. If there is no stable termination in the catalysts, the ion-conductive layer might be used to protect the active material while still carrying the catalytic process.

Second, the additives and buffer molecules in electrolyte may be engineered to prevent the etching effect or reduce the poisoning effect, to improve the stability and activity at the same time. For example, in this thesis we found severe A-site leaching of SCO at pH 7, which might can be prevented by adding high-concentration Sr-salt into the electrolyte. Meanwhile, changing the buffer in pH 7 electrolyte from phosphate to organic molecules may help to decrease the poisoning effects from PO_4^{3-} ions and therefore improve the activity of perovskite OER catalysts without jeopardizing their stability.

In general, both the catalytic and degrading processes for oxygen electrochemical catalysis involve the interaction between electrolyte and electrode. To break the coupling between these two processes, the controlling of electrolyte-electrode interface will become an important direction for future scientific and engineering researches.

References

(1) Lewis, N. S.; Nocera, D. G. *Proc. Natl. Acad. Sci.* **2006**, *103*, 15729.

(2) Gray, H. B. *Nat. Chem.* **2009**, *1*, 7.

(3) Hoogers, G.; Thomsett, D. *Cat. Tech.* **1999**, *3*, 106.

(4) Steele, B. C. H.; Heinzel, A. *Nature* **2001**, *414*, 345.

(5) Habas, S. E.; Lee, H.; Radmilovic, V.; Somorjai, G. A.; Yang, P. *Nat. Mater.* **2007**, *6*, 692.

(6) Kanan, M. W.; Nocera, D. G. *Science* **2008**, *321*, 1072.

(7) McCrory, C. C. L.; Jung, S.; Peters, J. C.; Jaramillo, T. F. *J. Am. Chem. Soc.* **2013**, *135*, 16977.

(8) Lu, Y.-C.; Xu, Z.; Gasteiger, H. A.; Chen, S.; Hamad-Schifferli, K.; Shao-Horn, Y. *J. Am. Chem. Soc.* **2010**, *132*, 12170.

(9) Armand, M.; Tarascon, J. M. *Nature* **2008**, *451*, 652.

(10) Maiyalagan, T.; Jarvis, K. A.; Therese, S.; Ferreira, P. J.; Manthiram, A. *Nat. Commun.* **2014**, *5*, 3949 1.

(11) Lee, S. W.; Carlton, C.; Risch, M.; Surendranath, Y.; Chen, S.; Furutsuki, S.; Yamada, A.; Nocera, D. G.; Shao-Horn, Y. *J. Am. Chem. Soc.* **2012**, *134*, 16959.

(12) Shie, J.-L.; Pai, C.-Y. *Indoor and Built Environment* **2010**, *19*, 503.

(13) Chen, S.; Ferreira, P. J.; Sheng, W.; Yabuuchi, N.; Allard, L. F.; Shao-Horn, Y. *J. Am. Chem. Soc.* **2008**, *130*, 13818.

(14) Nilekar, A.; Xu, Y.; Zhang, J.; Vukmirovic, M.; Sasaki, K.; Adzic, R.; Mavrikakis, M. *Top. Catal.* **2007**, *46*, 276.

(15) Stamenkovic, V. R.; Mun, B. S.; Arenz, M.; Mayrhofer, K. J.; Lucas, C. A.; Wang, G.; Ross, P. N.; Markovic, N. M. *Nat. Mater.* **2007**, *6*, 241.

(16) Stamenkovic, V. R.; Mun, B. S.; Mayrhofer, K. J. J.; Ross, P. N.; Markovic, N. M. *J. Am. Chem. Soc.* **2006**, *128*, 8813.

(17) Hasché, F.; Oezaslan, M.; Strasser, P. J. Electrochem. Soc. **2011**, 159, B24.

(18) Zhang, J.; Lima, F. H. B.; Shao, M. H.; Sasaki, K.; Wang, J. X.; Hanson, J.; Adzic, R. R. *J. Phys. Chem. B* **2005**, *109*, 22701.

(19) Xu, Y.; Ruban, A. V.; Mavrikakis, M. J. Am. Chem. Soc. **2004**, 126, 4717.

(20) Norskov, J. K.; Bligaard, T.; Rossmeisl, J.; Christensen, C. H. *Nat. Chem.* **2009**, *1*, 37.

(21) Wang, D.; Yu, Y.; Xin, H. L.; Hovden, R.; Ercius, P.; Mundy, J. A.; Chen, H.; Richard, J. H.; Muller, D. A.; DiSalvo, F. J.; Abruña, H. D. *Nano Lett.* **2012**, *12*, 5230.

(22) Kim, Y. S.; Jeon, S. H.; Bostwick, A.; Rotenberg, E.; Ross, P. N.; Stamenkovic, V. R.; Markovic, N. M.; Noh, T. W.; Han, S.; Mun, B. S. *Adv. Energy Mat.* **2013**, *3*, 1257.

(23) Chen, C.; Kang, Y.; Huo, Z.; Zhu, Z.; Huang, W.; Xin, H. L.; Snyder, J. D.; Li, D.; Herron, J. A.; Mavrikakis, M.; Chi, M.; More, K. L.; Li, Y.; Markovic, N. M.; Somorjai, G. A.; Yang, P.; Stamenkovic, V. R. *Science* **2014**, *343*, 1339.

(24) Gan, L.; Heggen, M.; O'Malley, R.; Theobald, B.; Strasser, P. *Nano Lett.* **2013**, *13*, 1131.

(25) Selvaganesh, S. V.; Sridhar, P.; Pitchumani, S.; Shukla, A. K. J. *Electrochem. Soc.* **2013**, *160*, F49.

(26) Risch, M.; Stoerzinger, K. A.; Maruyama, S.; Hong, W. T.; Takeuchi, I.; Shao-Horn, Y. *J. Am. Chem. Soc.* **2014**, *136*, 5229.

(27) Stoerzinger, K. A.; Risch, M.; Suntivich, J.; Lu, W. M.; Zhou, J.; Biegalski, M. D.; Christen, H. M.; Ariando; Venkatesan, T.; Shao-Horn, Y. *Energ. Environ. Sci.* **2013**, *6*, 1582.

(28) Grimaud, A.; May, K. J.; Carlton, C. E.; Lee, Y.-L.; Risch, M.; Hong, W. T.; Zhou, J.; Shao-Horn, Y. *Nat. Commun.* **2013**, *4*, 2439 1.

(29) Suntivich, J.; May, K. J.; Gasteiger, H. A.; Goodenough, J. B.; Shao-Horn, Y. *Science* **2011**, *334*, 1383.

(30) Meadowcroft, D. B. *Nature* **1970**, *226*, 847.

(31) Suntivich, J.; Gasteiger, H. A.; Yabuuchi, N.; Shao-Horn, Y. J. *Electrochem. Soc.* **2010**, *157*, B1263.

(32) Lu, Z.; Wang, H.; Kong, D.; Yan, K.; Hsu, P.-C.; Zheng, G.; Yao, H.; Liang, Z.; Sun, X.; Cui, Y. *Nat. Commun.* **2014**, *5*, 4345 1.

(33) Maiyalagan, T.; Jarvis, K. A.; Therese, S.; Ferreira, P. J.; Manthiram, A. *Nat. Commun.* **2014**, *5*.

(34) Mathias, M. F.; Makharia, R.; Gasteiger, H. A.; Conley, J. J.; Fuller, T. J.; Gittleman, C. J.; Kocha, S. S.; Miller, D. P.; Mittelsteadt, C. K.; Xie, T.; Yan, S. G.; Yu, P. T. *Electrochem. Soc. Interface* **2005**, *14*, 24.

(35) Ball, S. C.; Hudson, S. L.; Theobald, B. R.; Thompsett, D. *ECS Trans.* **2007**, *11*, 1267.

(36) Wagner, F. T.; Gasteiger, H. A.; Makharia, R.; Neyerlin, K. C.; Thompson, E. L.; Yan, S. G. *ECS Trans.* **2006**, *3*, 19.

(37) Chen, S.; Gasteiger, H. A.; Hayakawa, K.; Tada, T.; Shao-Horn, Y. J. *Electrochem. Soc.* **2010**, *157*, A82.

(38) Mayrhofer, K. J. J.; Hartl, K.; Juhart, V.; Arenz, M. *J. Am. Chem. Soc.* **2009**, *131*, 16348.

(39) May, K. J.; Carlton, C. E.; Stoerzinger, K. A.; Risch, M.; Suntivich, J.; Lee, Y.-L.; Grimaud, A.; Shao-Horn, Y. *J. Phys. Chem. Lett* **2012**, *3*, 3264.

(40) Risch, M.; Grimaud, A.; May, K. J.; Stoerzinger, K. A.; Chen, T. J.; Mansour, A. N.; Shao-Horn, Y. *J. Phys. Chem. C* **2013**, *117*, 8628.

(41) Nocera, D. G. Accounts Chem. Res. 2012, 45, 767.

(42) Kudo, A.; Miseki, Y. *Chem. Soc. Rev.* **2009**, *38*, 253.

(43) Suntivich, J.; Gasteiger, H. A.; Yabuuchi, N.; Nakanishi, H.; Goodenough, J. B.; Shao-Horn, Y. *Nat. Chem.* **2011**, *3*, 546.

(44) Bockris, J. O. M.; Otagawa, T. J. Electrochem. Soc. **1984**, 131, 290.

(45) Hammer, B.; Norskov, J. K. *Nature* **1995**, *376*, 238.

(46) Nørskov, J. K.; Rossmeisl, J.; Logadottir, A.; Lindqvist, L.; Kitchin, J. R.; Bligaard, T.; Jónsson, H. *J. Phys. Chem. B* **2004**, *108*, 17886.

(47) Greeley, J.; Stephens, I. E. L.; Bondarenko, A. S.; Johansson, T. P.; Hansen, H. A.; Jaramillo, T. F.; RossmeislJ; ChorkendorffI; Nørskov, J. K. *Nat. Chem.* **2009**, *1*, 552.

(48) Man, I. C.; Su, H.-Y.; Calle-Vallejo, F.; Hansen, H. A.; Martínez, J. I.; Inoglu, N. G.; Kitchin, J.; Jaramillo, T. F.; Nørskov, J. K.; Rossmeisl, J. *Chem. Catal. Chem.* **2011**, *3*, 1159.

(49) Han, B.; Carlton, C. E.; Suntivich, J.; Xu, Z.; Shao-Horn, Y. *J. Phys. Chem. C* **2015**, *119*, 3971.

(50) Han, B.; Carlton, C. E.; Kongkanand, A.; Kukreja, R. S.; Theobald, B. R.; Gan, L.; O'Malley, R.; Strasser, P.; Wagner, F. T.; Shao-Horn, Y. *Energ. Environ. Sci.* **2015**, *8*, 258.

(51) Han, B.; Risch, M.; Lee, Y.-L.; Ling, C.; Jia, H.; Shao-Horn, Y. *Phys. Chem. Chem. Phys.* **2015**, *17*, 22576.

(52) Han, B.; Stoerzinger, K. A.; Tileli, V.; Gamalski, A.; Stach, E.; Shao-Horn, Y. **2016**, In preparation.

(53) Gasteiger, H. A.; Kocha, S. S.; Sompalli, B.; Wagner, F. T. *Appl Catal B-Environ* **2005**, *56*, 9.

(54) Stamenkovic, V. R.; Fowler, B.; Mun, B. S.; Wang, G.; Ross, P. N.; Lucas, C. A.; Marković, N. M. *Science* **2007**, *315*, 493.

(55) Wakisaka, M.; Suzuki, H.; Mitsui, S.; Uchida, H.; Watanabe, M. J. Phys. Chem. C 2008, 112, 2750.

(56) Paulus, U. A.; Wokaun, A.; Scherer, G. G.; Schmidt, T. J.; Stamenkovic, V.; Radmilovic, V.; Markovic, N. M.; Ross, P. N. *J. Phys. Chem. B* **2002**, *106*, 4181.

(57) Koh, S.; Leisch, J.; Toney, M. F.; Strasser, P. *J. Phys. Chem. C* **2007**, *111*, 3744.

(58) Strasser, P.; Koh, S.; Anniyev, T.; Greeley, J.; More, K.; Yu, C.; Liu, Z.; Kaya, S.; Nordlund, D.; Ogasawara, H.; Toney, M. F.; Nilsson, A. *Nat. Chem.* **2010**, *2*, 454.

(59) Mukerjee, S.; Srinivasan, S. J. Electroanal. Chem. **1993**, 357, 201.

(60) Mukerjee, S.; Srinivasan, S.; Soriaga, M. P.; Mcbreen, J. *J. Phys. Chem.* **1995**, *99*, 4577.

(61) Antolini, E.; Salgado, J. R. C.; Gonzalez, E. R. *J. Power Sources* **2006**, *160*, 957.

(62) Watanabe, M.; Tsurumi, K.; Mizukami, T.; Nakamura, T.; Stonehart, P. *J. Electrochem. Soc.* **1994**, *141*, 2659.

(63) Jalan, V.; Taylor, E. J. J. Electrochem. Soc. 1983, 130, 2299.

(64) Colón-Mercado, H. R.; Kim, H.; Popov, B. N. *Electrochemi. Commun.* **2004**, *6*, 795.

(65) Wei, Z. D.; Guo, H. T.; Tang, Z. Y. J. Power Sources **1996**, *62*, 233.

(66) Carlton, C. E.; Chen, S.; Ferreira, P. J.; Allard, L. F.; Shao-Horn, Y. *J. Phys. Chem. Lett.* **2011**, *3*, 161.

(67) Erlebacher, J. J. Electrochem. Soc. **2004**, 151, C614.

(68) Erlebacher, J. Phys. Rev. Lett. **2011**, 106, 225504.

(69) *CRC Handbook of Chemistry and Physics, 90th ed*; CRC Press: Boca Raton, 2000; Vol. 8.

(70) Okamoto, H. J. Phase Equilib. **1991**, *12*, 617.

(71) Bharadwaj, S. R.; Tripathi, S. N.; Chandrasekharaiah, M. S. *J. Phase Equilib.* **1995**, *16*, 460.

(72) Okamoto, H. J. Phs. Eqil. and Diff. **2004**, 25, 395.

(73) Okamoto, H. J. Phs. Eqil. and Diff. **2008**, 29, 471.

(74) Abe, T.; Sundman, B.; Onodera, H. J. Phs. Eqil. and Diff. 2006, 27, 5.

(75) Okamoto, H. J. Phase Equilib. 2001, 22, 591.

(76) Wang, B.; Berry, D. C.; Chiari, Y.; Barmak, K. *J. Appl. Phys.* **2011**, *110*, 013903.

(77) Kolb, B.; Müller, S.; Botts, D. B.; Hart, G. L. W. *Phys. Rev. B* **2006**, *74*, 144206.

(78) Nash, P.; Singleton, M. F. *Bulletin of Alloy Phase Diagrams* **1989**, *10*, 258.

(79) Nart, F. C.; Vielstich, W. Handbook of Fuel Cells – Fundamentals, *Technology and Applications, H. A. G. a. A. L. Wolf Vielstich Editor*; John Wiley & Sons, Ltd., 2003.

(80) Ferreira, P. J.; la O', G. J.; Shao-Horn, Y.; Morgan, D.; Makharia, R.; Kocha, S.; Gasteiger, H. A. *J. Electrochem. Soc.* **2005**, *152*, A2256.

(81) Gasteiger, H. A.; Markovic, N. M.; Ross, P. N. *J. Phys. Chem.* **1995**, *99*, 8290.

(82) Marković, N. M.; Ross, P. N. *Electrochim. Acta* **2000**, *45*, 4101.

(83) Antolini, E.; Salgado, J.; Giz, M.; Gonzalez, E. *Int. J. Hydrogen Energ.* **2005**, *30*, 1213.

(84) The US Department of Energy (DOE), Energy Efficiency and Renewable Energy, 2012; Vol. Technical Plan — Fuel Cells.

(85) Debe, M. K. *Nature* **2012**, *486*, 43.

(86) Gan, L.; Heggen, M.; Rudi, S.; Strasser, P. *Nano Lett.* **2012**, *12*, 5423.

(87) Snyder, J.; McCue, I.; Livi, K.; Erlebacher, J. *J. Am. Chem. Soc.* **2012**, *134*, 8633.

(88) Oezaslan, M.; Heggen, M.; Strasser, P. J. Am. Chem. Soc. **2012**, 134, 514.

(89) Cui, C.; Gan, L.; Heggen, M.; Rudi, S.; Strasser, P. *Nat. Mater.* **2013**, *12*, 765.

(90) Choi, S.-I.; Xie, S.; Shao, M.; Odell, J. H.; Lu, N.; Peng, H.-C.; Protsailo, L.; Guerrero, S.; Park, J.; Xia, X.; Wang, J.; Kim, M. J.; Xia, Y. *Nano Lett.* **2013**, *13*, 3420.

(91) Kongkanand, A.; Wagner, F. Annual Merit Review DOE Hydrogen and Fuel Cells and Vehicle Technologies Programs, Washington, DC **2013**, High-Activity Dealloyed Catalysts.

(92) Gasteiger, H. A.; Kocha, S. S.; Sompalli, B.; Wagner, F. T. *Applied Catalysis B: Environmental* **2005**, *56*, 9.

(93) Steinbach, A. General Motors Global Product Development, 2014.

(94) Popov, B. N. Annual Merit Review DOE Hydrogen and Fuel Cells and Vehicle Technologies Programs, Washington, DC **2014**, Development of Ultra-low Doped-Pt Cathode Catalysts for PEM Fuel Cells.

(95) Wagner, F. T.; Yan, S. G.; Yu, P. T. In *Handbook of Fuel Cells*; John Wiley & Sons, Ltd: 2010.

(96) Liu, Z.; Xin, H.; Yu, Z.; Zhu, Y.; Zhang, J.; Mundy, J. A.; Muller, D. A.; Wagner, F. T. *J. Electrochem. Soc.* **2012**, *159*, F554.

(97) Erlebacher, J.; Aziz, M. J.; Karma, A.; Dimitrov, N.; Sieradzki, K. *Nature* **2001**, *410*, 450.

(98) Toda, T.; Igarashi, H.; Uchida, H.; Watanabe, M. *J. Electrochem. Soc.* **1999**, *146*, 3750.

(99) Mukerjee, S.; Srinivasan, S.; Soriaga, M. P.; Mcbreen, J. *J. Electrochem. Soc.* **1995**, *142*, 1409.

(100) Adzic, R. R.; Zhang, J.; Sasaki, K.; Vukmirovic, M. B.; Shao, M.; Wang, J. X.; Nilekar, A. U.; Mavrikakis, M.; Valerio, J. A.; Uribe, F. *Top. Catal.* **2007**, *46*, 249.

(101) Wang, D.; Xin, H. L.; Hovden, R.; Wang, H.; Yu, Y.; Muller, D. A.; DiSalvo, F. J.; Abruña, H. D. *Nat. Mater.* **2013**, *12*, 81.

(102) Jaffary, C. In *Handbook of Fuel Cells: Fundamentals, Technology and Application*; W. Vielstich, A. L., and H. A. Gasteiger, Ed.; John Wiley and Sons: Chichester 2003.

(103) Rincón, R. A.; Ventosa, E.; Tietz, F.; Masa, J.; Seisel, S.; Kuznetsov, V.; Schuhmann, W. *Chem. Phys. Chem.* **2014**, *15*, 2810.

(104) Kuhl, K. P.; Hatsukade, T.; Cave, E. R.; Abram, D. N.; Kibsgaard, J.; Jaramillo, T. F. *J. Am. Chem. Soc.* **2014**, *136*, 14107.

(105) Pei, P.; Wang, K.; Ma, Z. Appl. Energ. **2014**, *128*, 315.

(106) Bai, L.; Gao, L.; Conway, B. E. J. Chem. Soc., Farady Trans. 1993, 89, 243.

(107) Kresse, G.; Furthmüller, J. Phys. Rev. B 1996, 54, 11169.

(108) Perdew, J. P.; Burke, K.; Ernzerhof, M. *Physical Review Letters* **1996**, 77, 3865.

(109) Kresse, G.; Joubert, D. *Phys. Rev. B* **1999**, *59*, 1758.

(110) Rossmeisl, J.; Qu, Z. W.; Zhu, H.; Kroes, G. J.; Nørskov, J. K. *J. Electroanal. Chem.* **2007**, *607*, 83.

(111) Ayers, K. E.; Dalton, L. T.; Anderson, E. B. *ECS Trans.* **2012**, *41*, 27.

(112) Tadanaga, K.; Katata, N.; Minami, T. J. Am. Ceram. Soc. 1997, 80, 1040.

(113) Stoerzinger, K. A.; Hong, W. T.; Azimi, G.; Giordano, L.; Lee, Y.-L.; Crumlin, E. J.; Biegalski, M. D.; Bluhm, H.; Varanasi, K. K.; Shao-Horn, Y. *J. Phys. Chem. C* **2015**, *119*, 18504.

(114) Kuhlenbeck, H.; Shaikhutdinov, S.; Freund, H.-J. *Chem. Rev.* **2013**, *113*, 3986.

(115) Azimi, G.; Dhiman, R.; Kwon, H.-M.; Paxson, A. T.; Varanasi, K. K. *Nat. Mater.* **2013**, *12*, 315.

(116) Paz, Y.; Luo, Z.; Rabenberg, L.; Heller, A. J. Mater. Res. 1995, 10, 2842.

(117) Fujishima, A.; Zhang, X.; Tryk, D. A. Surf. Sci. Rep. 2008, 63, 515.

(118) Lee, K.; Kim, Q.; An, S.; An, J.; Kim, J.; Kim, B.; Jhe, W. *P. Natl. Acad. Sci.* **2014**, *111*, 5784.

(119) Kreuer, K. D. Annu. Rev. Mater. Res. 2003, 33, 333.

(120) Iwahara, H. Solid State Ionics **1996**, 86–88, Part 1, 9.

(121) Kreuer, K. D. Solid State Ionics **1997**, 97, 1.

(122) Malavasi, L.; Fisher, C. A. J.; Islam, M. S. Chem. Soc. Rev. 2010, 39, 4370.

(123) Grimaud, A.; Mauvy, F.; Bassat, J. M.; Fourcade, S.; Rocheron, L.; Marrony, M.; Grenier, J. C. *J. Electrochem. Soc.* **2012**, *159*, B683.

(124) Jung, J.-I.; Risch, M.; Park, S.; Kim, M. G.; Nam, G.; Jeong, H.-Y.; Shao-Horn, Y.; Cho, J. *Energ. Environ. Sci.* **2015**, DOI: 10.1039/C5EE03124A.

(125) Hong, W. T.; Risch, M.; Stoerzinger, K. A.; Grimaud, A.; Suntivich, J.; Shao-Horn, Y. *Energ. Environ. Sci.* **2015**, *8*, 1404.

(126) Lee, Y.-L.; Kleis, J.; Rossmeisl, J.; Shao-Horn, Y.; Morgan, D. *Energy Environ. Sci.* **2011**, *4*, 3966.

(127) Bielanski, A.; Haber, J. *Oxygen in catalysis*; CRC Press, 1990.

(128) Wang, L.; Merkle, R.; Maier, J.; Acartürk, T.; Starke, U. *Appl. Phy. Lett.* **2009**, *94*, 071908.

(129) Stoerzinger, K. A.; Hong, W. T.; Crumlin, E. J.; Bluhm, H.; Biegalski, M. D.; Shao-Horn, Y. *J. Phys. Chem. C* **2014**, *118*, 19733.

(130) Starr, D. E.; Liu, Z.; Havecker, M.; Knop-Gericke, A.; Bluhm, H. *Chem. Soc. Rev.* **2013**, *42*, 5833.

(131) Stoerzinger, K. A.; Hong, W. T.; Crumlin, E. J.; Bluhm, H.; Shao-Horn, Y. *Accounts Chem. Res.* **2015**, *48*, 2976.

(132) Raabe, S.; Mierwaldt, D.; Ciston, J.; Uijttewaal, M.; Stein, H.; Hoffmann, J.; Zhu, Y.; Blöchl, P.; Jooss, C. *Adv. Funct. Mater.* **2012**, *22*, 3378.

(133) Mildner, S.; Beleggia, M.; Mierwaldt, D.; Hansen, T. W.; Wagner, J. B.; Yazdi, S.; Kasama, T.; Ciston, J.; Zhu, Y.; Jooss, C. *J. Phys. Chem. C* **2015**, *119*, 5301.

(134) Xie, D.-G.; Wang, Z.-J.; Sun, J.; Li, J.; Ma, E.; Shan, Z.-W. *Nat. Mater.* **2015**, *14*, 899.

(135) Daio, T.; Bayer, T.; Ikuta, T.; Nishiyama, T.; Takahashi, K.; Takata, Y.; Sasaki, K.; Matthew Lyth, S. *Sci. Rep.* **2015**, *5*, 11807.

(136) Panciera, F.; Chou, Y. C.; Reuter, M. C.; Zakharov, D.; Stach, E. A.; Hofmann, S.; Ross, F. M. *Nat. Mater.* **2015**, *14*, 820.

(137) Yáng, Z.; Harvey, A. S.; Gauckler, L. J. Scripta Mater. 2009, 61, 1083.

(138) Aronova, M. A.; Sousa, A. A.; Leapman, R. D. *Micron (Oxford, England : 1993)* **2011**, *42*, 252.

(139) Miller, L., Purdue University, 2013.

(140) Martin, J. M.; Vacher, B.; Ponsonnet, L.; Dupuis, V. Ultramicroscopy **1996**, 65, 229.

(141) Kosacki, I.; Tuller, H. L. Solid State Ionics **1995**, 80, 223.

(142) Muñoz, A.; de la Calle, C.; Alonso, J. A.; Botta, P. M.; Pardo, V.; Baldomir, D.; Rivas, J. *Phys. Rev. B* **2008**, *78*, 054404.

(143) Takeda, Y.; Kanno, R.; Takada, T.; Yamamoto, O.; Takano, M.; Bando, Y. *Z. Anorg. Allg. Chem.* **1986**, *540*, 259.

(144) Ishigaki, T.; Yamauchi, S.; Mizusaki, J.; Fueki, K.; Tamura, H. *J. Solid State Chem.* **1984**, *54*, 100.