Mechanistic Studies of Water Electrolysis and Hydrogen Electro-Oxidation on High Temperature Ceria-Based Solid Oxide Electrochemical Cells

Chunjuan Zhang,†,‡ Yi Yu,†,‡ Michael E. Grass,†,‡ Catherine Dejoie,‡ Wuchen Ding,§ Karen Gaskell,† Naila Jabeen,‡ Young Pyo Hong,‡ Andrey Shavorskiy,‡ Hendrik Bluhm,‡ Wei-Xue Li,§ Gregory S. Jackson,‡ Zahid Hussain,‡ Zhi Liu,*,†,∥ and Bryan W. Eichhorn*†

†Department of Chemistry and Biochemistry and Department of Mechanical Engineering, University of Maryland, College Park, Maryland 20742, United States
‡Lawrence Berkeley National Laboratory, Berkeley, California 94720, United States
§State Key Laboratory of Catalysis, Dalian Institute of Chemical Physics, Chinese Academy of Sciences, Dalian 116023, China
∥School of Physical Science and Technology, ShanghaiTech University, Shanghai 200031, China

ABSTRACT: Through the use of ambient pressure X-ray photoelectron spectroscopy (APXPS) and a single-sided solid oxide electrochemical cell (SOC), we have studied the mechanism of electrocatalytic splitting of water (H₂O + 2e⁻ → H₂ + O²⁻) and electro-oxidation of hydrogen (H₂ + O²⁻ → H₂O + 2e⁻) at ~700 °C in 0.5 Torr of H₂/H₂O on ceria (CeO₂−x) electrodes. The experiments reveal a transient build-up of surface intermediates (OH⁻ and Ce³⁺) and show the separation of charge at the gas—solid interface exclusively in the electrochemically active region of the SOC. During water electrolysis on ceria, the increase in surface potentials of the adsorbed OH⁻ and incorporated O²⁻ differ by 0.25 eV in the active regions. For hydrogen electro-oxidation on ceria, the surface concentrations of OH⁻ and O²⁻ shift significantly from their equilibrium values. These data suggest that the same charge transfer step (H₂O + Ce³⁺ ⇌ Ce⁴⁺ + OH⁻ + H⁺) is rate limiting in both the forward (water electrolysis) and reverse (H₂ electro-oxidation) reactions. This separation of potentials reflects an induced surface dipole layer on the ceria surface and represents the effective electrochemical double layer at a gas—solid interface. The in situ XPS data and DFT calculations show that the chemical origin of the OH⁻/O²⁻ potential separation resides in the reduced polarization of the Ce—OH bond due to the increase of Ce³⁺ on the electrode surface. These results provide a graphical illustration of the electrochemically driven surface charge transfer processes under relevant and nonultrahigh vacuum conditions.

INTRODUCTION

Understanding the mechanisms of charge separation and charge transfer at electrochemical interfaces is essential for the rational development of electrochemical devices, such as batteries, fuel cells, electrolyzers, and supercapacitors.1,2 However, the materials and operating conditions employed in real world applications of these technologies are usually quite different from those used in surface science studies on model systems (i.e., the “pressure and materials gap”).3–5 This disconnect is particularly problematic with high temperature electrochemical energy conversion devices with multicomponent materials (e.g., solid oxide fuel cells, electrolyzers, and electrocatalytic fuel processors)6 for which in situ surface experiments at cell operating temperatures (typically >500 °C) are challenging.7 Because of the experimental constraints of most surface science experiments, the knowledge and understanding of the surface processes at relevant conditions are limited and rely on extrapolations from ultrahigh vacuum (UHV) conditions and modeling studies.8 As a result, the electrochemical surface processes are not well understood. For example, the non‐Faradaic electrochemical modification of catalytic activity (NEMCA or EPOC)9 can significantly enhance the rates of catalytic transformation of over 100 reactions,10 yet the origins of this enhancement are not fully understood.5 Even the mechanism of simple hydrogen electro-oxidation and water electrolysis on oxide surfaces of solid oxide electrochemical cells remains controversial with regard to the presence or absence of a double layer (dipole layer) at the gas—solid interface and the rate limiting processes on the oxide surfaces.11

Received: March 18, 2013
Published: July 3, 2013

dx.doi.org/10.1021/ja402604u | J. Am. Chem. Soc. 2013, 135, 11572−11579
In previous publications, we showed how ambient pressure X-ray photoelectron spectroscopy can be used to monitor changes in Ce oxidation states in CeO$_{2-x}$ electrodes, measure local surface potentials across an entire solid oxide electrochemical cell (SOEC), and measure local overpotentials on operating SOEC devices in far-from-equilibrium conditions. These studies laid the groundwork for performing in situ mechanistic studies designed to “observe” charge separation at an SOEC gas—solid interface and monitor changes in chemical intermediates involved in the electrochemical process. Our studies have focused on mixed ionic/electronic conductors (MIEC) such as ceria because of their well-documented catalytic and electrocatalytic properties as well as their ability to extend the electrochemically active region beyond the three-phase boundary. The catalytic behavior of ceria is directly linked to its accessible mixed valence Ce$^{3+}$/Ce$^{4+}$ redox states, its oxygen storage capacity, and surface vacancy concentrations. Recent in situ studies on ceria and doped ceria have shown that surface oxygen vacancies are either linked to underlying Ce$^{3+}$ ions or clustered around Ce$^{3+}$ ions when vacancy concentrations are high. While the oxygen mobility and catalytic behavior of ceria have been directly linked to the surface oxygen vacancy concentration, the mechanisms of catalysis and electrocatalysis remain largely unknown.

In this study, we show that transient intermediates accumulate in the active region of a ceria SOEC as a result of rate-limiting charge transfer processes. The same electrochemical step, H$_2$O + Ce$^{3+}$ ⇔ Ce$^{4+}$ + OH$^-$ + H$, appears to be rate limiting in both the forward (water electrolysis) and reverse (H$_2$ electro-oxidation) reactions. The mechanistic insight was obtained from monitoring the build-up of Ce$^{3+}$ and OH$^-$ at positive and negative biases, respectively. In addition, we observe a separation of local surface potentials of the adsorbed OH$^-$ and incorporated O$^{2-}$ ions due to a build-up of surface Ce$^{3+}$. The in situ XPS data and DFT calculations show that the chemical origin of the OH$^-$/O$^{2-}$ potential separation resides in the reduced polarization of the Ce$^{3+}$/Ce$^{4+}$ build up due to the Ce$^{3+}$ buildup. This charge separation can be viewed as the effective double layer at an electrochemical gas—solid interface and is interpreted in the context of Fleig’s description of surface potential steps on MIEC electrodes. These results provide insight into the high temperature surface chemistry on mixed ionic/electronic conducting ceria (CeO$_{2-x}$) electrodes.

### RESULTS AND DISCUSSION

The single-chamber polycrystalline yttria-stabilized zirconia (YSZ) cell consists of a Pt counter electrode and ceria working electrodes with Au current collectors (Figure 1A). Dense thin ceria films were sputtered on top of Au films with elongated Au pads exposed for electrical connections. Underneath the Au films, 30 nm thick alumina films were sputtered to block the O$^{2-}$ transport between YSZ and Au. Only one ceria edge has direct contact with the YSZ electrolyte, which defines the current flow region. The outer ceria edge is ~300 μm from the nearest Pt electrode edge. In situ APXPS and electrochemical studies were conducted at ~700 °C with 0.5 Torr of 1:1 H$_2$/H$_2$O mixtures. An overview of the cell fabrication process is described in the Experimental Section, and a detailed description can be found in ref 13.

At open circuit voltage (OCV), the ceria surface is at thermal equilibrium with the H$_2$ and H$_2$O gases as described by the following four basic exchange equilibria:

$$H_2O + Ce^{3+} ⇔ Ce^{4+} + OH^- + H^+ \quad (E1)$$

$$OH^- + Ce^{3+} ⇔ Ce^{4+} + O^{2-} + H^+ \quad (E2)$$

$$H^+ + H^+ ⇔ H_2 \quad (E3)$$

$$Ce^{4+} + e^- ⇔ Ce^{3+} \quad (E4)$$

These four exchange reactions represent the interactions between H$_2$O and OH$^-$ (E1), OH$^-$ and O$^{2-}$ (E2), and surface hydrogen atoms H$^+$ and H (E3) and electron transport by way of polaron hopping (E4). Since there is no net current flow in the cell at OCV, the surface cerium redox states and the surface hydroxyl coverage adopt equilibrium concentrations dictated by the cell temperature and gas partial pressures. However, when a bias is applied between the counter electrode (Pt) and working electrode (CeO$_{2-x}$), current flows through the cell and these reactions can be shifted from their equilibrium positions. For example, when Pt is positively biased relative to ceria, O$^{2-}$ ions are driven from the surface of ceria down to the YSZ electrolyte and out to the Pt electrode while electrons move from the gold current collector to the ceria surface. Under these conditions, the forward reactions E1–E4 are favored on ceria, which results in water electrolysis, whereas hydrogen electro-oxidation is promoted on the Pt electrode. The water electrolysis process on ceria is illustrated in Figure 2. When the bias is reversed...
The surface bias and surface concentrations of OH\(^-\) and O\(^{2-}\) on an 800 nm thick ceria electrode were determined through in situ measurements of the O 1s XPS spectra (Figure 3). Two-dimensional (2D) APXPS spectral maps (binding energy (BE) versus position) were constructed by using the differentially pumped electron analyzer installed on beamline 9.3.2 at the Advance Light Source in Berkeley.\(^{24,25}\) Figure 3A shows the second derivative of 2D O 1s XPS intensity spectral maps in the active regions of ceria electrode at +1.2 V applied bias. The three peaks are due to O\(^{2-}\) ions in the ceria electrode (~528 eV), the surface OH\(^-\) (~529.7 eV),\(^{26}\) and gas phase water (533.8 eV) near the electrode.\(^{27}\) To clearly illustrate the bias-induced peak shifts of O 1s spectra, the second derivatives of 2D O 1s XPS intensity spectral maps are plotted in the active regions of ceria electrode. Depth profile studies of the O 1s spectra (Figure S1) confirm that the OH\(^-\) species (BE ≈ 529.7 eV) are on the surface of the ceria electrode while the O\(^{2-}\) signal represents an average of the oxide ions in the solid phase very near the surface (see Experimental Section). The spatially resolved individual XPS spectra can be obtained by taking one-dimensional slices from the 2D intensity spectral maps. The peak fitting of a typical O 1s spectrum is shown in Figure 3B.

We have previously shown that the apparent binding energy of an electron in a surface atom at an applied bias (\(B_{\text{BE}}\)) is a direct measure of the local surface potential of that atom (\(V_L\)) when compared to its binding energy at OCV, where \(V_L = B_{\text{BE}} - B_{\text{BE}_{\text{OCV}}}\).\(^{12,28\text{–}30}\) As such, the 2D XPS data collected at...

\(\text{OH}^-\) and \(\text{O}^{2-}\) on an 800 nm thick ceria electrode were determined through in situ measurements of the O 1s XPS spectra (Figure 3). Two-dimensional (2D) APXPS spectral maps (binding energy (BE) versus position) were constructed by using the differentially pumped electron analyzer installed on beamline 9.3.2 at the Advance Light Source in Berkeley.\(^{24,25}\) Figure 3A shows the second derivative of 2D O 1s XPS intensity spectral maps in the active regions of ceria electrode at +1.2 V applied bias. The three peaks are due to O\(^{2-}\) ions in the ceria electrode (~528 eV), the surface OH\(^-\) (~529.7 eV),\(^{26}\) and gas phase water (533.8 eV) near the electrode.\(^{27}\) To clearly illustrate the bias-induced peak shifts of O 1s spectra, the second derivatives of 2D O 1s XPS intensity spectral maps are plotted in the active regions of ceria electrode. Depth profile studies of the O 1s spectra (Figure S1) confirm that the OH\(^-\) species (BE ≈ 529.7 eV) are on the surface of the ceria electrode while the O\(^{2-}\) signal represents an average of the oxide ions in the solid phase very near the surface (see Experimental Section). The spatially resolved individual XPS spectra can be obtained by taking one-dimensional slices from the 2D intensity spectral maps. The peak fitting of a typical O 1s spectrum is shown in Figure 3B.

We have previously shown that the apparent binding energy of an electron in a surface atom at an applied bias (\(B_{\text{BE}}\)) is a direct measure of the local surface potential of that atom (\(V_L\)) when compared to its binding energy at OCV, where \(V_L = B_{\text{BE}} - B_{\text{BE}_{\text{OCV}}}\).\(^{12,28\text{–}30}\) As such, the 2D XPS data collected at...
an applied bias provide a map of the spatially resolved local surface potentials of all atoms on the SOC surface. In Figure 3C, we show how the local surface potential of OH\(^{-}\) and O\(^{2-}\) shift under applied biases across the active region of the ceria electrode. Across the surface of the SOC, the \(V_L\) values for all of the surface species (i.e., OH\(^{-}\), O\(^{2-}\), Ce\(^{3+}\), Zr\(^{4+}\)) shift by the same amount\(^{13}\) provided that they are outside of the electrochemically active region of the ceria electrode. However, when water-splitting reactions are favored on ceria (positive bias), the \(V_L\) values for OH\(^{-}\) and O\(^{2-}\) are significantly different.

Figure 4. (A) Schematic representation of relative bond polarities (bond dipoles) for the Ce\(^{3+}\)--OH and Ce\(^{4+}\)--OH interactions on the ceria surface. The electrochemically induced build-up in Ce\(^{3+}\) concentration results in a divergence in the local surface potentials of OH\(^{-}\) (red) and O\(^{2-}\) (blue) within the active region denoted by the dashed lines in (A). (B) Interpretation of the potential losses across the gas–solid interface and ceria–YSZ interface showing the surface potential steps (\(\chi\)) and the charge transfer overpotential (\(\eta\)). The schematic is a modified version of Fleig’s model.\(^{19}\) In the scheme above, the local equilibrium potentials of the YSZ electrolyte, the ceria electrode, and hydroxyl adsorbate layers are shown in blue and are labeled \(V_{L(\text{eq})}\), \(V_{L(\text{ads})}\), \(V_{L(\text{ads})}\), respectively. The local potentials observed at an applied cell bias of +1.2 V are shown in green and denoted by \(V_{L(\text{eq})}\), \(V_{L(\text{ads})}\), \(V_{L(\text{ads})}\), respectively. For simplicity, all of the local potentials are normalized to the equilibrium YSZ electrolyte potential. In our single-sided half cell, all equilibrium cell potentials are equal to 0.0 V. See text for definitions.

Figure 5. (A) Spatially resolved cerium redox changes (Ce\(^{3+}\) fraction) calculated from fitted Ce 4d spectra under OCV and ±1.2 V applied biases. (B) Spatially resolved binding energy separations (i.e., surface potential steps) between surface adsorbates (OH\(^{-}\)) and solid surface (O\(^{2-}\)) derived from O 1s spectra under OCV and ±1.2 V applied biases. (C) Example of Ce 4d peak fitting. (D) Correlation between Ce\(^{3+}\) fraction changes and surface potential step changes under +1.2 V applied bias versus OCV. The Ce\(^{3+}\) positions were corrected for a 50 μm experimental shift associated with using different beam energies in different XPS measurements.
in the active regions of the ceria (Figure 3C). Under these conditions, the Ce$^{3+}$/Ce$^{4+}$ ratios are also driven away from equilibrium, showing a large increase in surface Ce$^{3+}$ concentration in the same region (Ce 4d XPS spectra, Figure 5A). Outside the active region, the $V_L$ values for OH$^-$ and O$^{2-}$ once again become equivalent and the Ce$^{3+}$/Ce$^{4+}$ ratios maintain their equilibrium values. This difference in the local surface potentials of OH$^-$ and O$^{2-}$ ($V_L$(OH) − $V_L$(O)) in the active region represents the local potential difference between the surface adsorbates and the ceria electrode. The build-up of surface Ce$^{3+}$ in the active region drives the separation of the potentials (vide infra). When H$_2$ electro-oxidation is promoted on ceria (negative bias), the $V_L$ values for OH$^-$ and O$^{2-}$ show a very small but discernible divergence but in the opposite direction (Figures 3C and 5B). The origins of the divergent $V_L$ values are described below.

The dipole model$^{31-33}$ at gas–solid interfaces$^{34,35}$ can illustrate the divergence of the OH$^-$ and O$^{2-}$ surface potentials in the active regions of the SOC. The chemisorbed OH$^-$ ions are bonded to ceria on the SOC surface with natural bond dipoles, with the negative end pointing to OH$^-$ oxygen and the positive end to the Ce$^{3+}$/Ce$^{4+}$ ions. Reactions E1 and E2 shift the concentrations of charged surface species on either side of the dipole layer and, therefore, modify the magnitude of the surface dipole. At +1.2 V applied bias, the OH$^-$/O$^{2-}$ concentration ratio shows no change in the active region relative to the equilibrium conditions at OCV (Figure 3D). However, the large increase of surface Ce$^{3+}$ ions (i.e., polarons) in the active region (Figure 5A) significantly reduces the Ce$^{3+}$−OH bond polarization relative to Ce$^{4+}$ dominated surface. This electrochemically driven reduction in bond polarization effectively decreases the local surface potentials on the two sides of the dipole layer. Specifically, the hydroxyl adsorbate, $V_L$(OH), is driven to a higher local potential than that of the ceria electrode surface directly beneath it (i.e., the oxide potential, $V_L$(O), Figure 3C). Consequently, the BE difference between hydroxyl adsorbates and electrode oxides becomes larger than that of the OCV condition in the active region (Figure 5B). The correlation of surface Ce$^{3+}$ buildup with divergence of $V_L$(OH) and $V_L$(O) values (Figure 3D) further confirms the origin of this potential separation.

The situation is substantially different at −1.2 V applied bias (H$_2$ electro-oxidation on ceria). Under these conditions, the ceria surface shows little change in Ce$^{3+}$/Ce$^{4+}$ ratios (Figure 5A), yet there is a small but significant increase in the OH$^-$ adsorbate concentration in the active region with an accompanying decrease in surface O$^{2-}$ concentration (Figure 3D).

To elucidate the interplay between surface structure and mechanisms of charge transfer processes at electrochemical interfaces of the ceria electrode, O 1s core level of OH$^-$ and O$^{2-}$ on ceria (111) surface were calculated using spin-polarized total energy calculations, as implemented in the Vienna Ab Initio Simulation Package (VASP), version 5.2.36−40. Though the accurate calculation of the absolute value of the core level remains indeterminable, the relative difference, i.e., the so-called core-level shift (CLS), between different species of interest can be well described.$^{41-43}$ For O 1s considered in the present work the calculated sequence of O 1s (gas H$_2$O) > O 1s (OH$^-$) > O 1s (O$^{2-}$) (Figure S2) indeed agrees well with the experimental results shown in Figure 3B.

The O 1s core level XPS shifts of the surface OH$^-$ and O$^{2-}$ show a strong correlation to the calculated DFT CLS of the OH$^-$ and O$^{2-}$ species under simulated conditions. To compare the O 1s CLSs measured at different experimental conditions, we calculated OH$^-$ CLSs using models containing different types of oxygen vacancies and different oxygen vacancy coverage. We found that the difference between OH$^-$ and O$^{2-}$ in O 1s CLSs increases by 0.3 eV as the O$^{2-}$ vacancy coverage increases from 1/16 to 3/16 ML. The difference also increases by 0.50 eV when a single O$^{2-}$ vacancy is replaced by a dimer oxygen vacancy (one surface vacancy and one subsurface vacancy). Both of these two scenarios agree well with the observation that the BE difference of OH$^-$ and O$^{2-}$ reaches 0.25 eV under +1.2 V applied bias (Figure 3C), where the ceria surface is more reduced. However, the separation between OH$^-$ and O$^{2-}$ in O 1s CLSs decreases by 0.3 eV when a single oxygen vacancy is replaced by a linear surface oxygen vacancy cluster (LSVC).$^{16,20}$ These findings lead us to believe that vacancy clusters are not formed on the ceria electrode surface under +1.2 V applied bias but rather isolated surface vacancies linked with surface Ce$^{3+}$ occur under these conditions, as previously observed in other systems.$^{16}$ In contrast, the value of calculated OH$^-$ O 1s CLS (∼2.7 eV) does not change significantly when the OH$^-$ coverage increases from 1/16 to 3/16 for a given vacancy coverage. This finding agrees well with the measured local potentials under −1.2 V applied bias (Figure 3C), where no significant difference in local potentials between OH$^-$ and O$^{2-}$ is detected. The observed 0.25 V separation of OH$^-$ and O$^{2-}$ surface potentials and the calculated 0.3 eV increases in the CLSs at +1.2 V are also in agreement with the experimental studies of Mullins et al. who showed that there is a 0.3 eV shift of the O$^{2-}$/OH BEs to higher energy for Ce$^{3+}$ oxide relative to Ce$^{4+}$ oxide.$^{26}$

Ce$^{3+}$ and OH$^-$ are both surface intermediates in the ceria-catalyzed electro-oxidation of H$_2$ and H$_2$O electrolysis processes. Shifts in their concentrations provide insight into rate-limiting surface processes. At −1.2 V, the accumulation of OH$^-$ adsorbates in the active region indicates that OH$^-$ consumption is rate-limiting, i.e., the reverse reaction of E1. At +1.2 V, the OH$^-$ maintains its equilibrium concentration while the Ce$^{3+}$ concentration increases significantly. The build-up of surface Ce$^{3+}$ and the lack of changes in OH$^-$/O$^{2-}$ concentration ratio are also consistent with E1 being a rate-limiting process. As such, our results suggest that the first step in water electrolysis (H$_2$O + Ce$^{3+}$ → Ce$^{4+}$ + OH$^-$ + H$^+$) and the last step in hydrogen electro-oxidation (Ce$^{4+}$ + OH$^-$ + H → H$_2$O + Ce$^{3+}$) are rate-limiting steps on the ceria-based SOC electrocatalysts described here. Increases in OH$^-$ concentrations have also been observed in a related study$^{44}$ on YSZ electrolyte surfaces near the three-phase boundary regions in polarized Pt-YSZ-Pt symmetrical electrolysis cells.

The data here can also be described by the Fleig model$^{49}$ for SOC surface reactions associated with MIEC materials such as ceria (Figure 4B). The model highlights the differences between liquid–solid electrochemical interfaces described by classical Butler–Volmer kinetics and gas–solid electrochemical interfaces where double layers involve reactant species. Central to this model is the existence of equilibrium surface potential step ($\chi^*$) describing the effective resistance to charge separation of reaction intermediates at a metal oxide electrode surface (e.g., OH$^-$ + Ce$^{3+}$ → Ce$^{4+}$ + O$^{2-}$ + H$^+$). Physically, this
resistance is equal to the difference between the local surface potentials of the adsorbates and the electrode under equilibrium conditions, described as the equilibrium surface potential step:

\[ \chi^{eq} = V^{eq}_{L(ads)} - V^{eq}_{L(ads)} \]

When the electrode is biased, a modified surface potential step is obtained (\(\chi\)) that represents a shift from equilibrium conditions (Figure 4B). The new \(\chi\) is equal to the potential difference between the surface adsorbates and the electrode under applied bias (\(\chi = V_{L(ads)} - V_{L(ads)} = V_{L(O)} - V_{L(OH)}\)). The difference between the equilibrium potential step and the potential step at bias is defined as \(\Delta \chi = \chi - \chi^{eq}\). This shift in surface potential step drives the net electrochemical reactions and generates current.\(^{19}\) \(\Delta \chi\) is also a direct measure of the electrochemical double layer at the gas–solid interface.\(^{19}\)

The measurements of the divergent \(V_{i}\) values for the OH\(^{-}\) and O\(^{2-}\) at +1.2 V represent the potential drop between the adsorbate (\(V_{L(OH)}\)) and the underlying ceria surface (\(V_{L(O)}\)) and thus a direct measure of \(\Delta \chi = V_{L(OH)} - V_{L(O)}\). In a traditional fuel cell, such as that described by Fleig (Figure 4B), there is a finite equilibrium potential step (\(\chi^{eq}\)) that describes the inherent resistance to surface charge separation resulting from the electrochemical potential of the cell. In our case, all equilibrium potentials are zero because OCV is 0.0 V in a single sided cell, and as a result, \(\Delta \chi = \chi\) in our experiments. The value of \(\Delta \chi\) reaches a maximum of 0.25 V in the center of the active region (Figure 4A). The correlation between surface Ce\(^{3+}\) concentrations and the magnitudes of \(\Delta \chi\) (Figure 3D) confirms that this surface potential step is related to the relative rates of oxygen supply and removal at the surface.

The surface potential steps are different from activation overpotentials (\(\eta\)) associated with charge transfer reactions at phase boundaries. Overpotentials describe barriers to net charge transfer across a double layer,\(^{45,46}\) whereas there is no net charge transfer associated with surface potential steps across the gas–solid interface. However, the changes in bond polarities and the resulting dipoles between surface adsorbates and the electrode surface form an effective double layer at the gas–solid interface, which modifies surface reactions involving charged species. The inherent coupling of reaction intermediate concentration shifts (i.e., OH\(^{-}\) and Ce\(^{3+}\)) and surface potential steps must be included in an accurate kinetic description of gas–solid interfacial reactions involving charge exchange with the underlying surface, as described in Fleig’s model.\(^{19}\) For high-temperature SOC systems, in situ surface studies are the only means of extracting such information, and the results described herein provide a significant advance in these endeavors.

**CONCLUSION**

These experiments provide a picture of charge separation at a gas–solid interface of a working electrochemical device. Similar to electrical double layers between the electrode and the electrolyte, this charge separation leads to an enormous electric field (\(\sim 10^6\) V/m) within a small interface region that greatly affects surface reaction kinetics in electrochemically active materials and in particular oxides. The interplay between this enormous electric field and the chemical reactions at the interface is, in a sense, the essence of high-temperature solid–gas electrochemistry.\(^{47}\)

**REFERENCES**


Estimating the Electric Field at the Dipole Layer. To semiquantitatively estimate the separation between OH− and the O2− surface ions, we used a simple two-layer model to estimate the order of magnitude of such a separation. Assuming an overlayer of Ce(OH) on top of CeO2 bulk, the thickness of such an overlayer, dov, can be estimated using
\[
\frac{d_{ov}}{\cos \alpha} = d = \lambda \ln \left( \frac{n_{ov}}{n_{sub}} R_{ov} + 1 \right)
\]
where d is the distance the photoelectron traveled across the overlayer and \( \alpha \) is the emission angle of electrons relative to the surface normal (\( \alpha = 40^\circ \) and 0° at beamlines 11.0.2 and 9.3.2, respectively). \( R_{ov} \) is the intensity ratio of I(OH−) and I(O2−). \( n_{ov} \) and \( n_{sub} \) are the densities of the overlayer and substrate, and \( \lambda \) is the IMFP of photoelectrons.

Several assumptions have been made: the overlayer has a constant thickness; there is a sharp boundary between the overlayer and the substrate; the overlayer and the substrate have the same IMFP for a given photon energy. Furthermore, we assume \( (n_{ov})/(n_{sub}) = 1 \). We can fit our data with the formula above. We find that \( d = 1 \text{ nm} \) gives the best fit (Figure S5), which leads to a \( d_{ov} \) of 0.8 nm. This will give an average separation of 0.4 nm. This oversimplified model is only used here to estimate the order of magnitude of charge separation. The field strength change then can be estimated to be about \( (0.25 \text{ V})/(0.4 \text{ nm}) = 10^5 \text{ V/m} \).

**Correlation of Surface Ce3+ Fractions and the Surface Dipole.** Under +1.2 V applied bias, the surface cerium oxidation states are largely driven away from equilibrium that leads to a higher Ce3+ concentration in the active region (Figure S5A). There is a striking similarity between the dipole strength change across the cell and Ce3+ similarity change. Our data (Figure S5D) show a strong linear correlation between the changes in Ce3+ concentration (Figure S5A) and changes in OH− BE shift (Figure S5B).

**Theoretical Approaches and Computational Details.** Spin-polarized total energy calculations were performed based on the all-electron projected augmented wave (PAW) method and DFT + U method within the generalized gradient approximation (GGA-PW91) functional as implemented in the Vienna Ab Initio Simulation Package (VASP), version 5.2.19–28. A cutoff of 400 eV was used for the plane wave expansion. The value of the U is set to 5 eV, as used in previous calculations.39,40 A CeO2(111)-p(4×4) slab with three CeO2 layers was used to model the ceria surfaces with different coverage of oxygen vacancy and hydroxyl, and only Γ-points were used to sample the surface Brillouin zone. All atoms in the super cell were relaxed until the residual force on each atom was less than 0.01 eV Å−1. For the core level shift calculations including the final state effect, an electron is removed from the core by generating the corresponding core excited ionic PAW potential in the course of the calculation and remaining core states are relaxed along the self-consistent calculation.41–43

**ASSOCIATED CONTENT**

Supporting Information

XPS depth profile for O 1s spectra (Figure S1), schematic representations of CLSs calculations (Figure S2), and electrochemical characterizations of LSV and EIS (Figure S3). This material is available free of charge via the Internet at http://pubs.acs.org.

**AUTHOR INFORMATION**

*Corresponding Author
*zu2@lbl.gov; eichhorn@umd.edu

**Author Contributions**

*C.Z., Y.Y., and M.E.G. are equal contributors.

**Notes**

The authors declare no competing financial interest.

**ACKNOWLEDGMENTS**

This work was funded by the ONR through Contract N000141110121. The Advanced Light Source is supported by the Director, Office of Science, Office of Basic Energy Sciences, of the U.S. Department of Energy under Contract DE-AC02-05CH11231. We thank the University of Maryland Nanocenter and the University of Maryland Energy Research Center (UMERC) and the National Natural Science Foundation of China (Grants 21173210, 21225315) for support.

**REFERENCES**


dx.doi.org/10.1021/ja402604u/J. Am. Chem. Soc. 2013, 135, 11572–11579


