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In situ surface potential evolution along Au/Gd:CeO$_2$ electrode interfaces

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We present an investigation of electroactive Au/gadolinium doped ceria electrode interfaces under CO$_2$/CO co-electrolysis environments using a combination of in situ high temperature scanning surface potential microscopy (HT-SSPM) and modified Poisson-Cahn (PC) models. Here charged surface adsorbate-oxygen vacancy interactions manifested in HT-SSPM potential profiles as small perturbations of opposite sign in reference to the applied biases. The positive deviation of surface potential on Au from applied cathodic biases is attributed to the work function difference between gold ($\phi_{\text{Au}} \sim 5.31$ eV) and graphitic carbon deposits ($\phi_{\text{C}} \sim 5.0$ eV) formed through CO disproportionation. The negative potential deviation from the applied anodic bias is attributed to negatively charged carboxylates. Results of the PC model confirmed the affinity of oxygen vacancies for the surface, thus supporting in situ experimental evidence of surface vacancy accumulation/depletion processes induced by cathodic/anodic biases. © 2017 Author(s). All article content, except where otherwise noted, is licensed under a Creative Commons Attribution (CC BY) license (http://creativecommons.org/licenses/by/4.0/).

Atmospheric greenhouse emissions, especially carbon dioxide (CO$_2$) levels, stimulate research focus in efficiently converting CO$_2$ into production of methane, syngas, and other carbonaceous fuels that require deliberate catalyst design. Due to their high activity, expensive noble metal electrocatalysts remain utilized in industrial battery and electrolyzer device applications, which motivates the pursuit of abundant, earth-friendly, cheaper, alternative materials. Ceria (CeO$_2$) is a rare-earth oxide, used in water-gas-shift, steam reforming, and emissions applications, that is also being explored as a CO$_2$/CO co-electrolysis catalyst.

Understanding the microstructure-electrochemical activity balance within CeO$_2$ requires operando characterization techniques capable of direct measurements under realistic reaction environments. Electron microscopy has resolved real-time phase and structural dynamics during redox reactions in ceria nanoparticles under reactive environments. In situ scanning tunneling microscopy was recently implemented to probe the surface chemistry and electronic structure in Li$_{0.8}$Sr$_{0.2}$CoO$_3$ (LSC) perovskite electrodes under near ambient pressures. In situ ambient-pressure X-ray photoelectron spectroscopy (AP-XPS) studies mapped local potential losses along ceria surfaces during electrochemical operation to define the active region. In situ AP-XPS demonstrates excellent sensitivity to composition and adsorbate/surface chemical states but cannot fully resolve surface potential regions of interest below $\sim 20$ µm, as limited by its synchrotron source.

Most scanning probe microscopy (SPM) studies of solid-oxide electrocatalysts are performed at room temperature, such as ex situ topographic imaging to monitor surface morphology. Advanced SPM methods, such as electrochemical strain microscopy, were used to detect displacements along Pt-yttria-stabilized zirconia (YSZ) triple phase boundaries (TPBs). We recently created a
custom-made sample chamber to scan electroactive materials at intermediate temperatures (400 °C–800 °C) and within gas environments.\textsuperscript{21} We previously performed high temperature scanning surface potential microscopy (HT-SSPM) for the direct, \textit{operando} observation of potential profiles that define active zone and TPB widths of mixed and electronic conducting electrode-electrolyte interfaces,\textsuperscript{22} and to track surface potential evolution in YSZ electrolytes as a function of temperature to yield the locally derived activation energy.\textsuperscript{23} Overall the high temperature \textit{in situ} SPM community continues to grow and progress with real-time studies of electroactive oxides, phase transitions, and mixed conduction.\textsuperscript{24} Models of the surface and near-surface chemistry of ceria must account for defects in high concentrations. As such the Poisson-Cahn (PC) formalism is typically employed,\textsuperscript{25,26} which describes the segregation of defects such as dopant cations and oxygen vacancies to the surface and near-surface region in concentrated solid electrolytes and mixed conductors. Here we combine \textit{in situ} HT-SSPM and PC models to explore the electrochemical activity of the Au/gadolinium doped ceria (GDC) catalyst interface supported on a YSZ electrolyte. HT-SSPM yields the surface potential profile along the Au/GDC interface to define the electroactive region and overpotential gradient. The PC formalism was subsequently applied, yielding a simplified model of the surface defect concentration profiles in ceria to provide qualitative feedback with the experiment.

The sample geometry comprised a 40 nm (20\%) Gd:CeO\textsubscript{2} thin film (GDC) deposited onto 500 µm thick (001) single-crystalline YSZ (MTI) by RF sputtering (Fig. 1(a)) which was annealed at 600 °C for 4 h. X-ray diffraction analysis (X’Pert PRO, PANalytical) showed that only GDC (200) and (400) peaks appear with a single YSZ (200) peak, likely indicative of a heteroepitaxial GDC/YSZ interface (Fig. 1(b)). A lithography-evaporator process yielded a 200 nm Au current-collecting electrode with a sharp, well-defined edge. The entire back of the YSZ substrate was coated by a porous Ag paste counter electrode (Ted Pella Leitsilber\textsuperscript{TM}). HT-SSPM measurements were performed using our custom chamber\textsuperscript{21} that enabled the commercial AFM (Asylum Research MFP-3D) to scan under operating environments. SSPM represents a modified, two-pass local probe technique. The first pass collects topography of the surface, while during the second pass the tip is lifted to a specific separation distance (\(\Delta H = 0\) nm), retraces the topographic profile, and determines the contact potential difference (CPD) by detecting the electrostatic force between a conductive tip (ASYELEC-01, \(f = 70\) kHz) and sample surface under an AC bias (\(V_{\text{AC}} = 3\) V; scan rate 0.6 Hz). A DC bias equivalent to the CPD is applied to compensate for (and nullify) the force on the tip, resulting in the surface potential image. The sample was heated to 500 °C for 1 h to achieve thermal equilibrium. A CO/CO\textsubscript{2} mixture gas balanced with N\textsubscript{2} (Airgas; 0.4\%:20\%:79.6\%) was then introduced into the chamber at a flow rate of 160 ml/min. During HT-SSPM measurement, the porous Ag electrode was maintained at ground potential while external biases were applied to the Au current collector. Here heterogeneous CO/CO\textsubscript{2} redox reactions occurred at the Au/GDC electrode under positive/negative biases applied to the sample, respectively.

Figure 2 shows the results of topographic (Fig. 2(a)) and \textit{in situ} HT-SSPM imaging (Figs. 2(b) and 2(c)) collected at 500 °C under –2 V, 0 V, and 2 V applied bias, respectively. Fig. 2(e) shows the potential line profiles taken from the HT-SSPM images found in Figures 2(b)–2(d). Here the open circuit voltage is considered to be zero as both electrodes are exposed to a uniform gas environment when equilibrium is achieved, thus the electrochemical reduction reaction is described as follows:\textsuperscript{27}

\[
\text{CO}_2(g) + \text{Vo}^- + 2\text{Ce}_{ce}' \rightarrow \text{CO}(g) + \text{Oo}^x + 2\text{Ce}_{ce}^x,
\]

FIG. 1. (a) Illustration of the sample geometry and Au/GDC interface reaction; (b) XRD pattern of the epitaxial GDC film on a YSZ (001) single crystal.
where in the Kröger-Vink notation, $V_{O^\cdot \cdot}$ is an oxygen vacancy with effective 2+ charge, $Ce_{Ce^\cdot}$ is a cerium-localized electron with effective 1–charge, and $O_{Ox}$ and $Ce_{Ce^x}$ are neutral lattice oxygen and cerium, respectively.

The potential profile variation under 0 V (Fig. 2(e); middle) reflects the variation in the work function and surface charge, particularly at the Au/GDC interface. The application of positive or negative bias promotes the electro-oxidation or electro-reduction reactions, respectively, which becomes the dominant contributor to the surface potential measured by HT-SSPM. Note that the surface potential on Au under external bias is appreciably less than the applied voltage 2 V and slightly greater than the applied voltage −2 V. For the positive overpotential, the difference is attributed to the presence of negatively charged adsorbates (e.g., singly charged carboxylates). For negative applied biases ($V_{app} = −2$ V), the observed surface potential difference of ~0.3 V is significantly higher than any expected contribution from positively charged adsorbates. We posit that this feature is likely due to the surface accumulation of graphitic carbon deposits on Au through CO disproportionation under −2 V bias, as the work function of carbon ($\phi_C \sim 5.0$ eV) is slightly lower than that of gold ($\phi_{Au} \sim 5.31$ eV). During SSPM imaging, a lower work function will manifest as a more positive CPD, i.e., $CPD = V_{tip} - V_{sample}$. Here the work function difference between carbon and gold is ~0.31 eV, close to the 0.3 V difference between the measured potential and applied voltage on the Au current collector.

HT-SSPM was also performed under ambient air environments at 500 °C (Fig. 3(a)). Compared to the profiles in the CO/CO$_2$ gas mixture (Fig. 2(e)), the surface potential on Au remained unchanged for an applied bias of 2 V, while Au under −2 V no longer exhibited a positive 0.3 V variation in the surface potential. The trend of the profile under −2 V bias in ambient air starkly contrasts the profile measured in mixture gas; the clear space charge potential observed at the GDC/Au interface within CO/CO$_2$ environments at 500 °C is significantly reduced under ambient air conditions.

Moving on to the ceria electrode from Au, a steep change in the cell potential occurs that is likely attributed to the spillover of adsorbates from ceria onto the gold surface. Under open-circuit conditions, the current increases significantly, indicating a strong adsorbate accumulation. This effect is more pronounced in the mixture gas environment, where the higher oxygen availability facilitates the spillover process.
conditions, the surface potential of ceria is negative under both oxygen-containing (Fig. 3(a)) and CO₂-containing (Fig. 3(b)) atmospheres. This is likely due to the presence of negatively charged adsorbates. The behavior of the surface potential in both environments under cathodic and anodic potentials can be understood via oxygen vacancy considerations: cathodic potentials increase the concentration of positively charged vacancies, which accumulate at the surface in relatively large amounts due to electrostatic contributions along with an energetic affinity for surface segregation. Under anodic potentials, the opposite holds: the system becomes starved of oxygen vacancies, and the surface potential becomes strongly negative.

The macroscopic current vs. voltage (I-V) response was also collected (Fig. 3(c)), both in mixed CO₂/CO (red) and ambient air environments (blue), respectively. The large currents under ambient air result from the oxygen redox reaction. Introduction of the CO/CO₂ mixture dramatically reduced the oxygen partial pressure and the dominant current instead originated from the reaction shown in Equation (1). The limited CO partial pressure in the gas mixture suppressed the reaction to cause the current reduction. The asymmetric I-V character is likely due to the graphitic carbon on the GDC/Au interface under cathodic bias, which enhances the electronic conductivity of the GDC surface and promotes CO₂ reduction in yielding a higher current. This pattern further implies the existence of CO disproportionation under cathodic bias.

A model of the ceria electrode considering a dopant cation, a small-polaron electron localized at cerium ions (leading to a Ce³⁺ state), and oxygen vacancies was derived and implemented. A negatively charged adsorbate state—such as carboxylate—was also considered. The PC formalism was coupled with a zero-dimensional electrochemical model for the cell, which considered (for simplicity) the near-surface space charge region to be in equilibrium. Although the thin film cell does not conform to zero-dimensional symmetry—modeling the potential drop due to charge transport resistance moving away from the current collector requires at least a one-dimensional treatment—and there is no reason to believe that the space charge zone will remain in equilibrium while current is being drawn, this simplified treatment can still offer some qualitative insight.

The equilibrium space charge assumption enables a separation of the nonequilibrium cell model from the Poisson-Cahn model: the cell model can be solved first, yielding bulk defect concentrations and adsorbate concentrations as a function of applied potential, gas composition, and temperature. Then the bulk and surface concentrations can be used as boundary conditions for the space charge model.

The adsorption reactions considered are

\[ \text{CO}_2(g) + \text{Ce}_{ce} \rightarrow (\text{CO}_2)' - \text{Ce}_{ce}^x, \]  

\[ (\text{CO}_2)' - \text{Ce}_{ce}^x + \text{V}_o \rightarrow \text{Ce}_{ce} \rightarrow \text{CO}(g) + 2\text{O}_2^x + 2\text{Ce}_{ce}^x \]  

with \( (\text{CO}_2)' - \text{Ce}_{ce}^x \) the adsorbed carboxylate species. The corresponding rate expressions are

\[ r_a = k_a[p_{\text{CO}_2}a_e(1 - \theta)/\kappa_a], \]  

\[ r_i = k_i[\theta a_e a_e - p_{\text{CO}_2}(1 - \theta)/\kappa_i] \]  

with \( r_a \) the rate of adsorption and \( r_i \) the rate of incorporation, \( k_a \) and \( k_i \) the corresponding rate constants, \( a_e \) and \( a_i \) the activities of electrons and vacancies, respectively, in the bulk, and \( \theta \) the site fraction of carboxylate. With all other processes in the electrode (other than the transport of oxygen vacancies in the electrolyte) considered to be in quasi-equilibrium, the current is controlled by these rate expressions.

Given a solution to the cell model, the free energy functional for the space charge region is written as follows:

\[ F[y, n, v, \phi; \theta, T] = \Phi(y, n, v, \phi) - FN_0 \theta \phi \]

\[ + \int_0^L \left[ W(y, v, n, T) + \frac{1}{2} c_y |\nabla y|^2 + \frac{1}{2} c_v |\nabla v|^2 + \frac{1}{2} c_n |\nabla n|^2 - \frac{1}{2} \epsilon_r \epsilon_0 |\nabla \phi|^2 + F \phi (2N_e v - Nn - Ny) \right] dx \]  

\[ - \frac{1}{2} \epsilon_r \epsilon_0 |\nabla \phi|^2 + F \phi (2N_e v - Nn - Ny) \right] dx \]  

(4)
with \( p \) the electrostatic potential; \( y, n, \) and \( v \) the concentrations of dopant, electrons, and vacancies, respectively, with the subscript \( s \) pertaining to a surface concentration; the functions \( \Phi \) and \( W \) are intensive free energy expressions for the surface and bulk, respectively. \( c_y, c_n, \) and \( c_v \) gradient energy coefficients for dopants, electrons, and vacancies, respectively, \( N, N_v, \) and \( N_s \) are the density of sites for cations in the bulk, vacancies in the bulk, and at the surface, respectively, and \( L \) the length of the space charge region.

Assuming that the dopant is uniformly fixed at the bulk concentration throughout (justifiable due to the low-temperature deposition process), the Euler-Lagrange equations are

\[
c_v \nabla^2 v = \frac{\partial W}{\partial v} + 2N_v F \phi, \tag{5a}
\]

\[
c_n \nabla^2 n = \frac{\partial W}{\partial n} - NF \phi, \tag{5b}
\]

\[
\nabla^2 \phi = -\frac{F}{\epsilon_0 \epsilon_r} (N_n + 2N_v v - N_y), \tag{5c}
\]

\[
\int_0^L (v - \bar{v}) dx = \int_0^L (n - \bar{n}) dx = N_s \theta, \tag{5d}
\]

where the final integral equations are conservation of mass constraints: the integrated difference between the average concentrations (indicated with a bar) and the corresponding concentration profile must be balanced by the number of adsorbed states at the surface.

Many of the model parameters—in particular, those pertaining to the equilibrium constants and activity expressions appearing in Equation (3), which also appear in the functions \( \Phi \) and \( W \)—by fitting to data on surface and bulk concentrations of electrons were measured by Chueh et al.\textsuperscript{16} Other parameters—chiefly those pertaining to the rate constants \( k_a \) and \( k_i \)—were adjusted to approximate the measured cell current.

Model results for \(-2 \text{ V}\) overpotential appear in Fig. 4, which depicts the electrostatic potential and the oxygen vacancy concentration in the vicinity of the space charge region near the ceria surface in the \( z \) (thickness) direction. The simulation shows a highly reduced bulk, as expected for the large applied overpotential, leading to a large electron and oxygen vacancy concentration in the ceria bulk. The surface is further enriched with vacancies due to the affinity of vacancies for the surface, leading to a positive surface potential, in accordance with the experiment. Results from the positive bias case did not converge, as the applied potential of \(+2 \text{ V}\) is too large to accommodate the assumption of equilibrium throughout the surface region used in the present study.

![FIG. 4. Distribution of electrostatic potential and oxygen vacancies along (z) depth direction under cathodic bias (–2 V) simulated with PC models.](image)
The simulation results for the CO$_2$/CO case form a qualitative understanding of the SSPM results in ambient air. Because air is the more oxidizing environment, the degree of reduction—i.e., the concentration of oxygen vacancies and electrons—will be lower. Consequently less oxygen vacancies segregate to the surface and a concomitant decrease in the positive surface potential is observed in the SSPM scans.

In summary, we performed HT-SSPM profiling of electroactive Au/GDC electrode interfaces under a reaction gas environment. The application of cathodic/anodic biases to Au induced the accumulation/depletion of surface oxygen vacancies within GDC. Charged adsorbate-oxygen vacancy interactions along the GDC surface manifested as small HT-SSPM potential perturbations of opposite sign in reference to the applied bias. The resulting work function changes and asymmetrical I-V character suggest that graphitic carbon deposition occurs under cathodic bias. The Poisson-Cahn formalism derived for ceria under cathodic bias estimated the distribution of the electrostatic potential and oxygen vacancies in the depth dimension, further validating the affinity of oxygen vacancies for the GDC surface. We anticipate that the qualitative agreement between in situ microscopy and PC models opens the pathway towards improved combined studies of electroactive species in oxides that disrupt the empirical measure-model cycle to directly yield kinetically relevant material parameters.

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