

Silicon Oxide-Encapsulated Platinum Thin Films as Highly Active Electrocatalysts for Carbon Monoxide and Methanol Oxidation

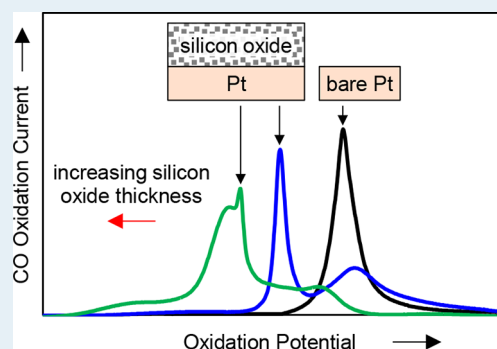
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Supporting Information

ABSTRACT: Direct alcohol fuel cells (DAFCs) have the potential to provide high power densities for transportation and portable applications. However, widespread use of DAFCs is greatly hindered by the lack of anode electrocatalysts that are inexpensive, stable, resistant to CO poisoning, and highly active toward alcohol oxidation. One promising approach to overcoming these challenges is to combine transition metal catalysts with oxide supports, such as SiO₂, which are known to enhance alcohol oxidation by promoting CO oxidation at oxidelmetal interfacial regions through the so-called bifunctional mechanism. Herein, we report on a membrane-coated electrocatalyst (MCEC) architecture for alcohol oxidation, in which a thin, permeable silicon oxide (SiO_x) nanomembrane encapsulates a well-defined Pt thin film (SiO_x/Pt). A key advantage of the MCEC design compared to oxide-supported nanoparticles is that the oxide encapsulation maximizes the density of oxidelmetal interfacial sites between the SiO_x and Pt catalyst. A series of electroanalytical measurements indicates that the SiO_x overlayers provide proximal hydroxyls, in the form of silanol groups, which can enhance alcohol oxidation by interacting with adsorbed intermediates at SiO_x/Pt interfaces. Thanks to these interactions, the SiO_x/Pt electrocatalysts exhibit significantly enhanced CO oxidation activity and roughly a 2-fold increase in the maximum methanol oxidation current density compared to bare Pt. Overall, these demonstrations highlight the potential of using SiO_x-based MCECs for CO tolerant and highly active methanol oxidation electrocatalysts.

KEYWORDS: electrocatalysis, confined catalysis, carbon monoxide oxidation, methanol oxidation, membrane-coated electrocatalyst, bifunctional mechanism, overlayers, silicon dioxide



1. INTRODUCTION

Small alcohol fuels, such as methanol and ethanol, are attractive energy carriers for a sustainable energy future because of their high energy densities, ease of storage as liquids, and the ability to produce them electrochemically from carbon dioxide (CO₂) and water (H₂O) using electricity from renewable resources.^{1–4} These alcohol fuels can be converted back into electricity for various applications using direct alcohol fuel cells (DAFCs), where alcohol oxidation at the anode is coupled with the oxygen reduction reaction (ORR) at the cathode.^{5,6} Despite recent advances in the performance of DAFCs,⁵ their power densities (≈ 0.01 – 10 W cm^{-2}) are still significantly lower than hydrogen fuel cells (HFCs), which typically achieve power densities of ≈ 10 – 100 W cm^{-2} .⁷ Major reasons for the performance gap between DAFCs and HFCs are voltage losses that originate from (i) fuel crossover to the cathode and (ii) sluggish reaction kinetics associated with alcohol oxidation at the DAFC anode.^{8,9} The state-of-the-art anode catalysts in acidic medium are based on nanoparticles of platinum (Pt) or Pt alloys that are supported on high surface area carbon (Pt/C).^{10–12} The performance of DAFC anodes can also suffer from degradation of the electrocatalyst and carbon support, which can lead to dissolution, detachment,

migration, and/or agglomeration of the catalytic nanoparticles.^{13–15}

In order to reduce kinetic overpotential losses associated with the methanol oxidation reaction (MOR) and ethanol oxidation reaction (EOR), significant research efforts have been made to better understand the mechanisms that underlie these reactions. It is now well understood that the MOR and EOR are complex multistep reactions that require catalytic sites for alcohol adsorption and dehydrogenation, as well as sites that facilitate oxidation of carbonaceous intermediates to the desired end product, carbon dioxide (CO₂).^{2,16–20} Many studies have highlighted the importance of efficiently oxidizing carbon monoxide (CO), a commonly observed intermediate in alcohol oxidation that can “poison” active sites that bind CO too strongly.^{5,21} Others have found that CO oxidation is more favorable when oxygen-containing coreactants such as adsorbed hydroxyl groups (OH_{ad}) are located in close proximity to the adsorbed CO.^{22–24} The two most common methods to introduce oxygen-containing species near active

Received: September 8, 2018

Revised: October 19, 2018

Published: October 24, 2018

sites, and thereby improve CO tolerance, are (i) to alloy Pt-based catalysts with a second metal that has a higher affinity for oxygen (more oxophilic), such as ruthenium (Ru)^{25,26} or tin (Sn),^{27,28} and (ii) to support metal nanoparticles on metal oxide supports that contain hydroxyl groups.^{28–36} The enhanced electrocatalytic activity of Pt electrocatalysts for the MOR and EOR by these two modifications is attributed to the so-called bifunctional mechanism whereby metallic Pt provides sites to initially adsorb and dehydrogenate the alcohol while the oxophilic material supplies oxygen-containing species that subsequently oxidize the adsorbed carbonaceous intermediates to CO₂.³⁷ Alloying Pt with Ru or Sn has proven to be effective for alleviating CO poisoning issues,^{25–28} but it does not address the issue of carbon support oxidation. As a result, oxide materials have attracted considerable attention as supports for alcohol oxidation electrocatalysts due to their: (i) higher corrosion resistance than carbon, (ii) abundance of hydroxyl groups to facilitate CO removal, and (iii) potential to suppress catalyst particle migration thanks to partial encapsulation and/or stronger bonding between the oxide material and the metal nanoparticles.^{38–41} In particular, metal oxide supports, such as CeO₂,^{42,43} MgO,⁴⁴ WO₃,⁴⁵ SnO₂,²⁸ and TiO₂,^{30–32} have demonstrated enhanced activity toward alcohol oxidation when paired with Pt nanoparticles.

Motivated by prior studies on metal oxide supports for alcohol oxidation, the current paper investigates oxidelmetal electrocatalysts for methanol oxidation that are composites of silicon oxide (SiO_x) and Pt. Similar to many other oxides supports, SiO_x contains hydroxyl groups, in the form of silanols (Si–OH),^{46–48} which have been shown to promote CO oxidation on Pt electrocatalysts. Additionally, silica (SiO₂) is known to have excellent chemical stability in acidic and neutral pHs.⁴⁹ Many studies have demonstrated improved MOR activity and stability with SiO₂ supported Pt catalysts, with most suggesting that silanol groups suppress CO poisoning and thereby enhance MOR activity through the bifunctional mechanism.^{50–54} Pt/SiO₂ catalysts have also shown enhanced EOR activity compared to Pt/graphite.⁵⁵

Despite the promising reports of high alcohol oxidation activity with Pt/oxide composite electrocatalysts, two common concerns are the lower surface areas and electrical conductivities of oxides such as silica compared to conventional carbon supports.⁵⁴ Consequently, studies that involve oxide supports typically require intricate modifications to improve their low electrical conductivity and surface area. To improve the electrical conductivity, TiO₂ is commonly doped with Nb,^{56,57} C,⁵⁸ or N.⁵⁹ For SiO₂ supports, unique architectures have been employed to increase conductivity and surface area such as incorporating Pt/silica into mesoporous conductive carbon supports⁶⁰ and functionalizing hollow SiO₂ spheres with amino acids to help anchor Pt onto SiO₂ and SiO₂ onto conductive supports.⁵⁴ Although these approaches can effectively improve CO tolerance, they often require complex, high temperature synthesis methods to produce the precise composition, structure, and loading. Moreover, methods that involve high temperature treatment could ultimately decrease the specific surface area of the support and catalyst.

In order to compensate for the low surface areas of oxide supports and minimize catalyst loading, researchers have also tried to minimize catalyst nanoparticle size, albeit at the expense of accelerated dissolution of the smaller nanoparticles.^{61,62} If smaller (<5 nm) Pt nanoparticles could be

stabilized on oxide supports, Ting et al. suggested that they could better take advantage of the bifunctional mechanism compared to larger particles because a higher percentage of the Pt sites would be located in close proximity to the hydroxyl-containing oxide support.⁶² Extending this logic further, we hypothesize that the most active alcohol oxidation electrocatalysts are those that are designed to maximize the number of active sites for alcohol adsorption/dehydrogenation that are in close proximity to hydroxyl sites for CO oxidation.

Toward this end, we explore SiO_x/Pt alcohol oxidation electrocatalysts based on the membrane-coated electrocatalyst (MCEC) architecture,⁶³ in which the active metal electrocatalyst (Pt) is encapsulated by an ultrathin (<10 nm thick) oxide layer that can exhibit membrane-like transport properties.⁶⁴ The SiO_x overlayers used in this study are fabricated with a low-temperature ultraviolet ozone (UV ozone) photochemical synthesis procedure to deposit ultrathin (<10 nm), permeable silicon oxide nanomembranes over well-defined Pt thin film electrocatalysts (SiO_x/Pt), as depicted schematically in Figure 1. The underlying motivations for

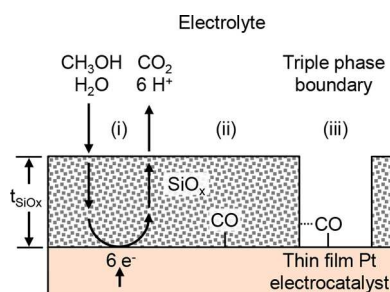


Figure 1. Schematic side view illustrating methanol oxidation at a planar Pt electrocatalyst encapsulated by an ultrathin, permeable SiO_x overlayer with thickness t_{SiO_x} that enables (i) diffusion of electroactive species to and from the electrocatalytic SiO_x/Pt buried interface. Also shown are adsorbed CO intermediates located at (ii) the buried interface and (iii) an opening in the SiO_x film which can create a triple phase boundary site.

investigating these SiO_x/Pt MCECs are their potential to (i) maximize interfacial contact between the Pt catalyst and hydroxyl-containing SiO_x overlayer, (ii) suppress corrosion of the metal nanoparticles and the underlying conductive support, and (iii) create unique active sites at the oxidelmetal buried interface through confinement effects.^{65–67}

MCEC-type architectures have been previously employed to stabilize nanoparticles or molecular catalysts in fuel cells^{68–76} and photoelectrochemical cells.^{77–79} Takenaka et al. demonstrated that silica coatings on Pt nanoparticle catalysts improved durability and minimized particle agglomeration and dissolution for the ORR but found that the same electrodes exhibited poor activity for the MOR and EOR compared to uncoated Pt/C nanoparticle catalysts.⁷³ The poor alcohol oxidation activity was attributed to suppressed transport of small polar alcohols across the hydrophobic silica used in that study. In contrast, we report herein on the use of hydrophilic SiO_x/Pt MCECs that enhance alcohol oxidation. We have recently shown that SiO_x overlayers, fabricated with the UV ozone method, are effective at suppressing Pt nanoparticle migration⁷⁹ and facilitating transport of protons (H⁺) and hydrogen molecules (H₂) between the bulk electrolyte and SiO₂/Pt buried interface.⁶⁴ In the current paper, we extend the use of these hydrophilic SiO_x overlayers,

deposited on planar Pt films, to study CO oxidation and MOR at SiO_x/Pt interfaces (Figure 1). These model thin film electrodes are an attractive platform for studying these reactions because they have very well-defined catalyst surface areas, avoid complexities/nonuniformities associated with nanoparticles, and allow for detailed characterization of the buried oxidelmetal interface. The thin film SiO_x/Pt electrodes in this study demonstrate that the MCEC design leverages the high density of reaction sites at SiO_x/Pt interfaces to readily oxidize intermediates and increase MOR activity compared to bare Pt electrodes. Furthermore, the impact of varied potential and pH conditions on Pt–OH_{ad}, PtO_x, and Si–OH formation are evaluated to elucidate the role of hydroxyl groups on Pt and SiO_x during the MOR. Overall, this study shows that the SiO_x-encapsulated Pt electrocatalysts can enhance methanol oxidation with minimal diffusion barrier to methanol transport to SiO_x/Pt interfaces.

2. EXPERIMENTAL METHODS

2.1. Electrode Preparation. A detailed description of the procedure for synthesizing Pt and SiO_x/Pt thin film electrodes can be found in our previous publication.⁶⁴ Briefly, a 4.5 nm thick Ti adhesion layer and 50 nm thick Pt film were sequentially deposited by electron-beam evaporation onto degeneratively doped Si(100) conductive substrates (p⁺Si, WRS materials). Next, a mixture of the trimethylsiloxy terminated polydimethylsiloxane (PDMS) precursor dissolved in toluene^{80,81} (1.2 and 3.0 mg mL^{−1} for SiO_x films with final thicknesses of ≈2 and ≈5 nm, respectively) was spin coated onto the metal-coated samples for 2.5 min at 4000 rpm. After drying in a vacuum oven, the PDMS was converted into SiO_x under UV light in air for 2 h within a UV ozone cleaning system (UVOCS, T10X10/OES).^{80,82} Electrical contacts were made by soldering a Cu wire to the back side of the electrode substrate. Electrodes were then sealed with vinyl 3M Electroplating Tape 470, which possessed circular openings with an area of 0.246 cm² through which the electrode was exposed to the electrolyte. All current densities reported herein were normalized by the geometric area of this opening.

2.2. Structural Characterization. The thicknesses of the SiO_x overlayers were measured using a Woollam alpha-SE ellipsometer. Raw ellipsometry data was fit with a Cauchy model, and a standard error in thickness was determined for all of the ≈2 nm (sample size *N* = 2) and ≈5 nm (*N* = 6) thick samples used in this study. The morphology of the SiO_x thin films was analyzed with a Bruker Dimension Icon atomic force microscopy (AFM) using the identical imaging parameters previously reported.⁶⁴ X-ray photoelectron spectroscopy (XPS) characterization was performed with a Phi XPS instrument equipped with a monochromatic aluminum Kα X-ray source (15 kV, 20 mA) and operated with a pass energy of 23.5 eV and a charge neutralizer. The charge neutralizer was calibrated to give a C 1s peak center of 284.5 eV, after which the Si 2p, O 1s, and Pt 4f spectra were shifted by the same value. Overlayer composition and atomic ratios were determined on the basis of peak areas and tabulated atomic sensitivity factors (ASF_{*i*}).⁸³ An ASF_{Si} of 0.339 was used for Si to account for differences in density and attenuation lengths of metallic Si and SiO₂.

2.3. Electroanalytical Measurements. A SP-200 Bio-Logic potentiostat was used for conducting all electroanalytical measurements. A carbon rod (Saturn Industries) counter electrode and a Ag/AgCl/sat. 3 M KCl reference electrode (*E*^o

= 0.21 V vs NHE, Hach, E21M002) were used in a standard three electrode configuration. Cyclic voltammetry (CV) measurements used to determine the electrochemically active surface areas (ECSAs) from hydrogen underpotential deposition (*H*_{upd}) signal were performed in deaerated 0.5 M sulfuric acid that was prepared from 18 MΩ deionized water and concentrated sulfuric acid (H₂SO₄, Fisher Scientific, ACS grade). The ECSAs were calculated as previously described⁶⁴ and are based on a conversion factor of 210 μC *H*_{upd} signal per cm^{−2} Pt for polycrystalline Pt.⁸⁴ The reported *H*_{upd}-derived ECSAs are average values determined from analysis of CV cycles 100–150. CO stripping voltammetry experiments were also performed in 0.5 M H₂SO₄. First, CO was adsorbed from a CO-saturated 0.5 M H₂SO₄ electrolyte onto the electrode surface at +0.05 V vs RHE for 3 min. While the electrode was held at this potential, excess CO in solution was subsequently removed by purging the solution with N₂ gas for 20 min. Adsorbed CO was then stripped (oxidized) from the electrode surface by scanning the applied potential from 0.22 V to 0.0 V to 1.2 V vs RHE at 20 mV s^{−1}. Upon reaching the positive scan vertex, the scan direction was reversed to complete the first CV cycle. A second CV cycle was subsequently recorded over the same potential range to verify that no CO remained adsorbed on the electrode after the first cycle. The moles of adsorbed CO initially present on the electrode surface were then calculated on the basis of the difference in the integrated charge recorded during the positive scan segments of the first and second CV cycles. Methanol oxidation experiments were performed in 0.5 M H₂SO₄ with 0.5 M methanol (CH₃OH, Fisher Chemical, ACS grade). CVs were performed for 100 cycles and typically reached a steady state by cycle 15. In examining the effect of the CV vertex on electrochemical activity, the upper vertex potential was increased from 0.8 to 1.2 V vs RHE in 100 mV increments. Each upper vertex was maintained for 15 cycles to allow the sample to reach a steady state. Following the last cycle with an upper vertex potential of 1.2 V vs RHE, the vertex was decreased back to 0.8 V vs RHE to evaluate any discrepancy from the beginning of cycling. Potassium hydroxide (KOH, Sigma-Aldrich, ACS reagent) was used to remove SiO_x from Pt for control experiments, in which samples were exposed to SiO_x synthesis conditions. KOH etching was performed in 20 wt % KOH with 3 v/v % isopropyl alcohol (C₃H₈OH, Fisher Chemical, ACS reagent) for 10 min at 75 °C. Experiments in neutral pH electrolytes were performed in a 0.1 M sodium phosphate buffer solution (Na₂HPO₄/NaH₂PO₄, Sigma-Aldrich, Reagent Plus).

3. RESULTS

3.1. Characterization of SiO_x Overlayer. As-made SiO_x/Pt and Pt thin films were first characterized by ellipsometry, AFM, and XPS to evaluate their composition and structure. The thicknesses of SiO_x overlayers were determined by ellipsometry and found to be 2.4 ± 0.2 and 5.4 ± 0.3 nm. For simplicity, these samples are referred to herein as 2 nm SiO_x/Pt and 5 nm SiO_x/Pt. As-made samples were also characterized with AFM to view differences in the topology of SiO_x overlayers and bare Pt films. All samples possessed uniform and smooth topologies that were characterized by root mean squared (rms) surface roughness values of 0.95, 0.55, and 0.41 nm for the bare Pt, 2 nm SiO_x/Pt, and 5 nm SiO_x/Pt electrodes, respectively (Figure S1). AFM images indicated that microscopic holes were not present on these SiO_x overlayers. SiO_x/Pt electrodes were further characterized with

XPS (Figure S2), which showed that the SiO_x overlayers made by the UV ozone process were primarily comprised of silicon dioxide (SiO_2), as evidenced by the Si 2p peak center located at 103.5 eV and relatively low concentration of carbon (C) (≈ 8 atomic % C). These results are consistent with previously reported XPS characterization of SiO_x layers synthesized using the UV ozone photochemical conversion process.^{80,82}

The electrochemically active surface areas (ECSAs) of Pt and SiO_x/Pt electrodes were evaluated from the integrated H_{upd} signal recorded during CV cycling in deaerated 0.5 M H_2SO_4 . The steady state voltammograms for the 0 nm (bare Pt), 2 nm, and 5 nm SiO_x/Pt samples are provided in Figure 2. All samples

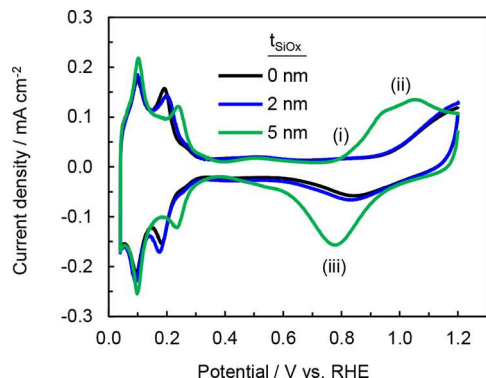


Figure 2. CV curves (30th cycle) recorded at 100 mV s^{-1} in deaerated 0.5 M H_2SO_4 for SiO_x/Pt electrodes containing: $t_{\text{SiO}_x} = 0 \text{ nm}$ (black), $t_{\text{SiO}_x} = 2 \text{ nm}$ (blue), and $t_{\text{SiO}_x} = 5 \text{ nm}$ (green) SiO_x films.

exhibit H_{upd} signal and Pt–oxide formation/reduction peaks that are characteristic of polycrystalline Pt electrodes in sulfuric acid.^{85,86} Analysis of the integrated H_{upd} signal of CV cycles 100–150 gives average ECSA values of 1.011 ± 0.002 , 1.064 ± 0.001 , and $1.22 \pm 0.001 \text{ cm}^2 \text{ Pt per cm}^2$ geometric area for the 0, 2, and 5 nm samples, respectively. Similar to other publications,^{64,73,87} the fact that the ECSA does not decrease for SiO_x/Pt electrodes attests to the ability of protons to transport through the SiO_x overlayer and confirms that the buried interface between the SiO_x and Pt thin film is electrochemically active. Despite having a similar H_{upd} -determined ECSA to the bare Pt control, the CV curve for the 5 nm SiO_x/Pt sample shows some key differences from bare Pt. In addition to slight shifts in the H_{upd} peak locations, Figure 2 reveals significant differences in the features at more positive potentials associated with (i) formation of adsorbed oxygen species such as O_{ad} and OH_{ad} , (ii) their subsequent oxidation to form Pt–oxides, and (iii) reduction of these species during the negative scan. Notably, the onset of Pt oxidation shifts to slightly less positive potentials with increasing SiO_x thickness. Similar shifts in the Pt–OH/PtO_x formation features have been observed for Pt electrodes coated with thin SiO_2 overlayers made by atomic layer deposition.⁸⁷ One possible explanation for these observations is that the SiO_x overlayer alters the adsorption of sulfate ions, which are known to suppress the onset of surface oxidation of noble metal electrodes due to competitive adsorption.⁸⁶ However, it is also possible that SiO_x overlayers can alter Pt–OH/PtO_x dynamics at the SiO_x/Pt buried interface as a result of structural changes in the Pt surface caused by the highly oxidizing UV ozone conversion process and/or changes to the

electrochemical double layer (EDL) structure and, hence, the local electric field.

3.2. CO Stripping Voltammetry. Carbon monoxide (CO) stripping voltammetry was performed on SiO_x/Pt and bare Pt to simultaneously measure their ECSA and evaluate their ability to oxidize CO. Figure 3 compares the CO

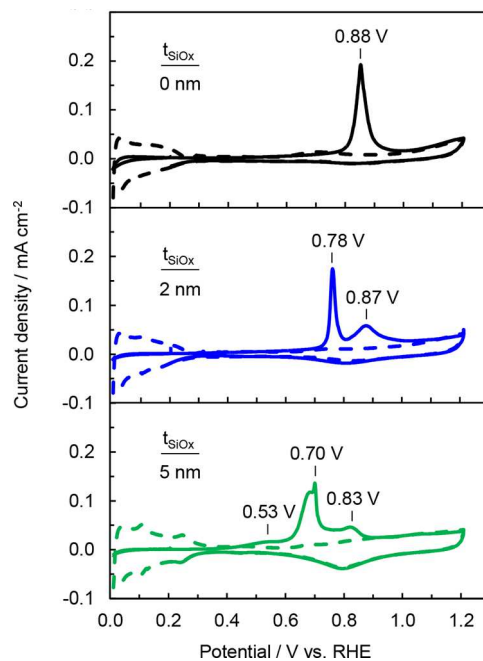


Figure 3. CO stripping voltammetry curves measured in 0.5 M H_2SO_4 at a scan rate of 20 mV s^{-1} for Pt (black), 2 nm SiO_x/Pt (blue), and 5 nm SiO_x/Pt (green). Solid curves represent the first CV cycle that was carried out with CO adsorbed on the electrode surface, while dashed curves represent the second CV cycle that was performed after CO was stripped from the electrode surface during the first cycle.

stripping curves for 0 nm (bare Pt), 2 nm SiO_x/Pt , and 5 nm SiO_x/Pt electrodes. For all the electrodes, no H_{upd} signal is observed in the first cycle (solid curves), indicating that almost all electroactive sites are occupied by adsorbed CO. As the potential is scanned to more positive potentials, distinct peaks associated with CO oxidation are observed for all electrodes. The second cycle (dashed curves) shows only H_{upd} peaks and minor features associated with Pt–oxide formation and reduction, indicating that all of the adsorbed CO was fully oxidized and stripped from the electrode surface during the first cycle.

Although the integrated CO oxidation charge was similar for each sample, the location and number of peaks observed for each sample varied substantially. The peak centers of the main CO oxidation peak for the bare Pt and UV ozone treated bare Pt control samples (Figure S3) are located at 0.88 and 0.87 V vs RHE, respectively. These values are in good agreement with those reported in literature^{30,33} and are consistent with the fact that Pt has a strong binding energy for CO. The 2 nm SiO_x/Pt and 5 nm SiO_x/Pt electrodes exhibit CO oxidation peaks that are shifted to more negative potentials, with peak centers located at 0.78 and 0.72 V vs RHE, respectively. Catalysts that require smaller overpotentials for CO oxidation are commonly described as “CO tolerant” because they require a smaller driving force to remove CO intermediates.^{20,35} This enhanced ability to oxidize CO is often associated with the bifunctional

mechanism of methanol oxidation, especially for composite electrocatalysts in which Pt is combined with oxophilic materials.^{26,33,50}

In addition to the primary CO oxidation peaks observed in Figure 3, smaller but distinct oxidation peaks are also observed at more positive potentials for the 2 and 5 nm SiO_x/Pt electrodes at 0.87 and 0.83 V vs RHE, respectively. These peak locations are similar to those observed for CO oxidation on bare Pt and may suggest that a small fraction of the Pt on the SiO_x/Pt electrodes still exhibit bare Pt-like behavior for CO oxidation. Another minor peak, shifted even more negative than the primary CO oxidation peaks for the SiO_x/Pt electrodes, is present at ≈0.53 V vs RHE. Importantly, the presence of this peak and the negative shift of the primary CO oxidation peaks strongly suggest that the reactive environments at the buried SiO_x/Pt interface and/or SiO_x/Ptelectrolyte triple phase boundary sites are very different from that at the electrolyte/bare Pt interface. The negative shifts in the CO oxidation features of the SiO_x/Pt electrodes with respect to those of the bare Pt control samples indicate that the SiO_x/Pt is able to more easily oxidize adsorbed CO than Pt. Numerous studies on MOR electrocatalysts have connected a negative shift in the CO oxidation features to enhanced MOR activity, hypothesizing that the high activity is explained by lower CO binding energy and, therefore, lower susceptibility to CO poisoning.^{33,35,50}

3.3. Cyclic Voltammetry in Methanol. The electrocatalytic activity of Pt and SiO_x/Pt electrodes toward the electrooxidation of methanol was evaluated by performing 100 CV cycles in 0.5 M CH₃OH in a deaerated 0.5 M H₂SO₄ supporting electrolyte. Figure 4 compares the CVs for 0, 2, and 5 nm SiO_x/Pt electrodes in 0.5 M methanol, for which the methanol oxidation half reaction is⁸⁸

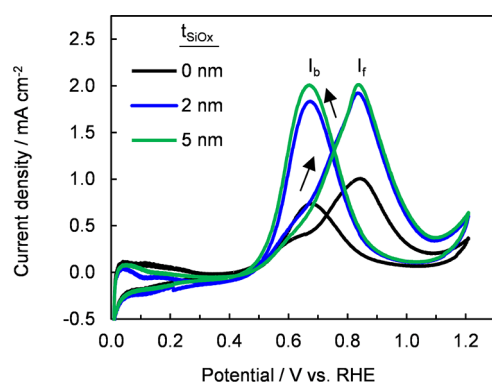
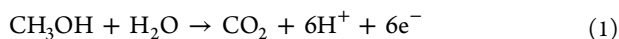


Figure 4. Cyclic voltammetry curves measured in 0.5 M CH₃OH at a scan rate of 100 mV s^{−1} for bare Pt (black), 2 nm SiO_x/Pt (blue), and 5 nm SiO_x/Pt (green) in deaerated 0.5 M H₂SO₄ supporting electrolyte.

The MOR CV curves for all samples possess two primary oxidation peaks, which occur in the positive (forward) and negative (backward) scan directions and are centered at 0.84 and 0.65 V vs RHE, respectively. The magnitude of the current density in the forward direction, I_f , is seen to be ≈2 times larger for the SiO_x/Pt electrodes compared to the bare Pt control sample, despite having similar ECSAs based on the H_{upd} signal. The SiO_x/Pt electrodes also exhibit significantly

higher current densities than bare Pt throughout 15 min chronoamperometry (CA) measurements at both +0.6 V vs RHE and +0.8 V vs RHE (Figure S4), confirming that their higher activity seen in CV measurements is not a transient phenomenon.

Another difference in the CV curves for the SiO_x/Pt and bare Pt electrodes is the relative magnitude of I_f to the peak current density recorded during the backward scan, I_b . Recent studies have demonstrated that both of these peaks have the same chemical origin and can be primarily attributed to oxidation of methanol, as opposed to earlier studies suggesting that most of the current observed in negative scan originated from oxidation of residual carbon intermediates.^{89,90} The hysteresis in the MOR peaks for Pt electrodes is now understood to arise from differences in Pt surface oxidation state during the positive and negative scan directions.⁸⁹ In the positive (forward) scan, methanol oxidation occurs on Pt before it is suppressed by the formation of a high coverage of Pt–hydroxides (Pt–OH_{ad}) and/or Pt–oxides (PtO_x) at more positive potentials. After the scan direction is reversed at the positive scan vertex, methanol oxidation gradually increases again as Pt–OH_{ad} and PtO_x species are reduced to free up metallic Pt sites that are known to be more active for methanol decomposition. By this means, the extent of Pt oxidation that occurs during the scan to positive potentials greatly impacts the peak MOR current density that occurs during the negative (backward) scan (I_b) as well as the ratio of the forward peak current (I_f) to I_b . Due to the important role of Pt–oxides, the ratio of MOR peak current densities (I_f/I_b) can be used as an indicator of the catalyst oxophilicity, which is described as the metallic (M) catalyst's susceptibility to form M–OH or MO_x species.^{89,91} Electrocatalysts with large I_f/I_b are those with a high affinity for oxygen (oxophilic), while those with small I_f/I_b are less readily oxidized or are more easily reactivated by reducing the oxidized form back to the metallic state.^{89,91} From the CV curves in Figure 4, I_f/I_b ratios of 1.32 ± 0.02 , 1.06 ± 0.01 , and 1.00 ± 0.02 are computed for the 0, 2, and 5 nm SiO_x/Pt electrodes, respectively. The differences in I_f/I_b between samples suggest that there are differences in the oxophilicity between the SiO_x/Pt and Pt electrodes. The relationship between the I_f/I_b ratios, catalyst oxophilicity, and Pt–OH_{ad} and PtO_x coverage are discussed further below.

Because the CV curves in Figure 4 were recorded in a sulfuric acid supporting electrolyte, it must be pointed out that sulfate/bisulfate anions are known to suppress methanol oxidation activity of Pt electrocatalysts due to their ability to compete with OH adsorption on the electrocatalyst surface.^{92–94} Because of this effect, peak methanol oxidation current densities recorded for Pt electrocatalysts in sulfuric acid are always lower than those recorded in perchloric acid, for which perchlorate anions adsorb much more weakly to the Pt surface than (bi)sulfate anions.⁹⁵ Given that previous studies have shown SiO_x overlayers capable of serving as selective transport barriers,^{64,96} it is plausible that the enhanced methanol oxidation activity of SiO_x/Pt electrodes could arise from the ability of SiO_x overlayers to block (bi)sulfate ions from reaching the active sites at the SiO_x/Pt buried interface. This hypothesis was tested by performing methanol oxidation CVs with bare Pt and 5 nm SiO_x/Pt electrodes in 0.5 M H₂SO₄ and 0.5 M HClO₄ (Figure S5). Two identical samples were tested for each sample type to avoid sample history effects. Figure S5 shows that the peak methanol oxidation current densities in the perchloric acid supporting electrolyte increased

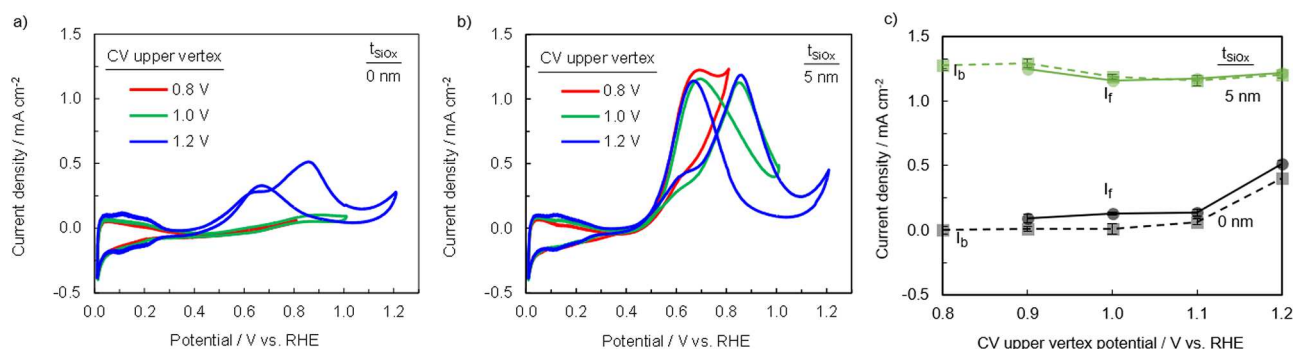


Figure 5. Methanol oxidation CVs (steady state cycle 15) with different upper scan vertices for (a) $t_{\text{SiO}_x} = 0$ nm and (b) $t_{\text{SiO}_x} = 5$ nm SiO_x/Pt MCEC. (c) Peak MOR current densities recorded during the forward (I_f) and backward (I_b) scan segments as a function of upper vertex potential. CVs were performed in 0.5 M H_2SO_4 containing 0.5 M CH_3OH and measured at 100 mV s^{-1} .

by $\approx 65\%$ compared to those recorded in sulfuric acid for both bare Pt and SiO_x/Pt electrodes. The observation of similar “anion effects” for both bare Pt and SiO_x/Pt electrodes indicates that (i) sulfate anions are still capable of reaching the buried SiO_x/Pt interface and (ii) the SiO_x overlayer must be impacting the methanol oxidation activity in other ways besides blocking sulfate ions. The ability of sulfate ions to permeate into the SiO_x overlayers can be understood by the need to maintain electroneutrality within the SiO_x overlayer and is consistent with our previous study that looked at SiO_x/Pt thin film electrodes for the hydrogen evolution reaction in 0.5 M H_2SO_4 .⁶⁴ Regardless of the extent that SiO_x suppresses the adsorption of (bi)sulfate anions, Figures 4 and S5 demonstrate that SiO_x/Pt electrodes possess superior MOR activity compared to bare Pt.

3.4. Role of $\text{Pt}-\text{OH}_{\text{ad}}$ and PtO_x on Methanol Oxidation Activity. Several studies have shown that the extent of Pt oxidation can influence CO oxidation and MOR activity. While the formation of Pt–oxides (PtO_x , $x = 1$ or 2)⁹⁷ has a prohibitive effect on MOR activity,^{89,91,98} the presence of intermediate coverages of Pt–hydroxides, $\text{Pt}-\text{OH}_{\text{ad}}$, is believed to assist in CO removal to allow continual MOR.⁸⁹ To investigate the role of Pt–oxides on the MOR for bare Pt and SiO_x/Pt electrodes, MOR CVs were carried out where the upper vertex potential was incrementally increased. Upper scan vertices ranging between 0.8 and 1.2 V were chosen to transition between conditions where Pt oxidation would be avoided or favored, on the basis of the $\text{Pt}-\text{OH}_{\text{ad}}$ and PtO_x features observed in the control CV curves performed in 0.5 M H_2SO_4 without methanol (Figure 2). Figure 5 shows MOR CVs for bare Pt and 5 nm SiO_x/Pt electrodes with upper vertices of 0.8, 1.0, and 1.2 V vs RHE. The effects of the positive vertex potential on the forward and backward scan peak currents are summarized in Figure 5c, with the complete set of CV curves provided in Figure S6. Figure 5a shows that the bare Pt electrode exhibits very low MOR activity for CVs with positive vertex potentials less than 1.1 V vs RHE but that a sudden jump in MOR activity is achieved once the scan vertex is more positive than 1.1 V vs RHE. In contrast, Figure 5b shows the SiO_x/Pt electrode achieves high MOR activity regardless of upper vertex potential. Interestingly, when the potential vertex was changed back to 0.8 V vs RHE (Figure S4), the bare Pt showed an increased MOR activity similar to the CV performed at 1.2 V vs RHE, while the MOR activity of the SiO_x/Pt remained high for all CV scans. These results demonstrate the formation of $\text{Pt}-\text{OH}_{\text{ad}}$ and PtO_x specifically

at more oxidizing potentials, has a strong effect on initiating MOR activity for bare Pt but has essentially no effect for SiO_x/Pt . For bare Pt, the upper potential vertex that leads to an increase in MOR activity approximately coincides with the onset potential for Pt oxidation, as observed in Figure 2. This result is consistent with many previous studies on Pt-based MOR electrocatalysts that have shown the importance of having some $\text{Pt}-\text{OH}_{\text{ad}}$ species in order to facilitate removal of adsorbed CO intermediates.^{89,99} Meanwhile, for SiO_x/Pt , the lack of dependency of the MOR peak currents on the upper scan rate suggests that the formation of $\text{Pt}-\text{OH}_{\text{ad}}$ may not be necessary to accelerate methanol oxidation.

3.5. Electrocatalyst Stability. Figure 6 contains the 1st, 10th, 50th, and 100th CV cycles for bare Pt and 5 nm SiO_x/Pt electrodes during MOR. The MOR peak currents for bare Pt

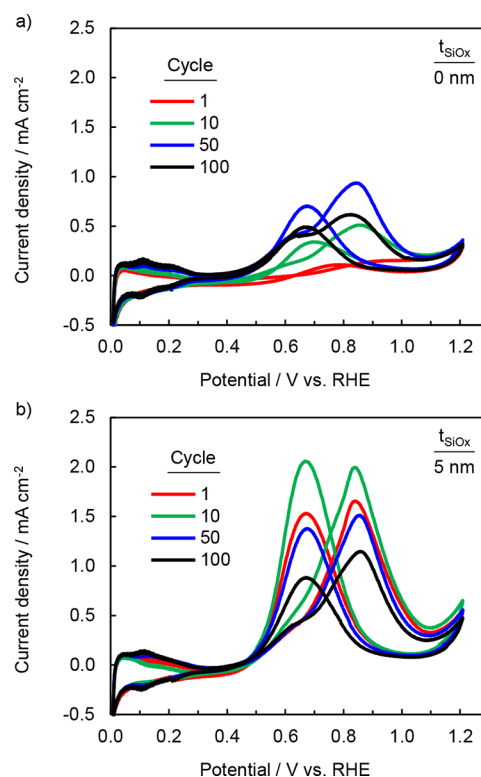
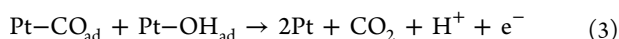
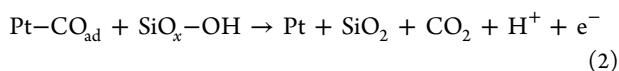


Figure 6. 1st (red), 10th (green), 50th (blue), and 100th (black) CV cycles for (a) bare Pt and (b) 5 nm SiO_x/Pt in 0.5 M H_2SO_4 containing 0.5 M CH_3OH and measured at 100 mV s^{-1} .

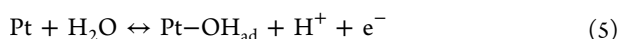
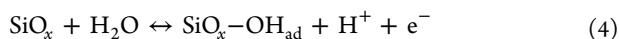
rapidly increase for the first 10 cycles before reaching maximum values between 10 and 50 cycles. Some decline in MOR peak current is observed toward the end of CV cycling, possibly due to the gradual depletion of methanol from the bulk electrolyte caused by slow evaporation of methanol into the headspace. The transient nature of the MOR peak current densities during CV cycling was very different for the SiO_x/Pt electrodes, which show very high initial MOR peak current densities that gradually decrease with cycle number (Figure 6b). Despite the decreasing MOR current densities, the peak current densities of the SiO_x/Pt electrodes still exceeded those of the bare Pt electrode at the end of CV cycling. Control MOR experiments on KOH etched bare Pt and 5 nm SiO_x/Pt, in which no SiO_x remained after the KOH etch, show no difference in MOR activity, confirming that the presence of the SiO_x film is necessary for enhanced MOR current densities, relative to bare Pt (Figure S7). This result suggests that (some) SiO_x must still be present on the electrode at the end of CV cycling to maintain higher currents than Pt. In addition to methanol depletion, the gradual decrease in SiO_x/Pt activity may be related to changes in the SiO_x structure, as evidenced by AFM and XPS analysis of MCEC samples after CV cycling (Figures S8 and S9) that show possible SiO_x delamination and/or SiO_x “island” formation. Although the SiO_x/Pt electrocatalysts appear to be susceptible to degradation during extended cycling, the repeated oxidation/reduction of Pt/PtO_x during CV cycling is likely to cause stress at the SiO_x/Pt interface. The repeated restructuring of the SiO_x/Pt interface may lead to gradual delamination of the SiO_x overlayer, especially for thin film electrodes where the SiO_x is only attached to Pt. In fuel cell-relevant nanoparticle/support systems, SiO_x will primarily be adhered to an inert support material such as carbon for which delamination should be less of an issue in the absence of significant electrochemistry at the SiO_x/support buried interface.

4. DISCUSSION

The results in Figures 3 and 4 demonstrate that deposition of SiO_x onto Pt thin films significantly enhances their catalytic activity toward methanol oxidation compared to bare Pt. Similar observations have been made in prior studies of silicon oxide supported Pt nanoparticle electrocatalysts, with the improved performance most commonly attributed to hydroxyl-facilitated removal of CO intermediates through the aforementioned bifunctional mechanism.^{50–54,100} In order to design catalysts that are more CO tolerant, it is important to understand the source of the hydroxyl groups that are responsible for aiding in the removal of adsorbed CO intermediates on Pt (Pt–CO_{ad}). As expressed in eqs 2 and 3, CO oxidation may be achieved through reactions with silanol groups attached to SiO_x (SiO_x–OH) or hydroxyls on Pt (Pt–OH).^{8,12,61,101}



where, in both cases, hydroxyls must be regenerated through an additional oxidation step.



Prior studies on SiO₂-supported MOR catalysts have suggested that silanol groups may enhance MOR activity by accelerating CO oxidation as a part of the bifunctional (2-site) mechanism.^{50–54,100} In this study, Figure 2 shows that the presence of SiO_x overlayers can also affect Pt oxophilicity and, likely, the coverage of Pt–OH_{ad} at a given applied potential. If CO and methanol oxidation occur at the buried interface of MCECs, it is expected that the presence of the SiO_x may also indirectly influence reaction energetics at the buried interface through confinement (steric) effects, varying concentrations of reactants and spectator ions near active sites, and alteration of electric fields caused by disruption of the electrochemical double layer. A density functional theory study investigating confined catalysis determined the adsorption energy of CO on Pt was lowered due to the presence of a graphene overlayer which destabilized the CO_{ad} molecule.⁶⁷ That study indicates that the confined environments at the buried interface between graphene and Pt can greatly alter the interactions and energetics between molecules and the active electrocatalyst. Similarly, the SiO_x overlayers studied in this work may directly and/or indirectly influence alcohol oxidation kinetics. If the mechanisms by which the SiO_x overlayers influence electrocatalysis of SiO_x/Pt electrodes can be better understood, that information can be used to guide the design of MCECs with even better CO tolerance and alcohol oxidation activity.

The CO stripping results in Figure 3 showed that the presence of 5 nm of SiO_x on Pt shifts CO oxidation features by 100 and 200 mV relative to those for the 2 nm SiO_x/Pt and bare Pt electrodes, respectively. Despite the very positive oxidation potential required to form hydroxyls on bare Pt (>0.85 V vs RHE),^{86,102} SiO_x/Pt is still able to achieve high MOR currents at moderate oxidation potentials (Figure 5b), which suggests hydroxyls are readily available at lower oxidation potentials for the bifunctional mechanism. The silanol groups on SiO_x that are present in acidic environments^{46–48} may serve as an abundant source of hydroxyls that are in close proximity to Pt–CO_{ad} at the SiO_x/Pt interface. We also hypothesize that the SiO_x may change the Pt oxophilicity to make Pt–OH formation more energetically favorable at lower overpotentials, as suggested by the negative shift in the onset potential of Pt oxidation with increasing SiO_x thickness. This trend in the Pt oxidation onset potential may be related to the negative shift in the CO oxidation onset potentials for the 2 and 5 nm SiO_x/Pt samples (0.70 to 0.60 V vs RHE, respectively). However, it must also be noted that the onset for CO oxidation for the 5 nm SiO_x/Pt occurs at 200–300 mV more negative than the onset of Pt-oxidation features, meaning that it is unlikely that Pt–OH alone can explain the enhanced CO oxidation activity at more negative than 0.8 V vs RHE.

Hydroxyl species formed on Pt surfaces can enhance the MOR by promoting the bifunctional mechanism, as suggested by the initiation of MOR activity only after Pt–oxide (Pt–OH_{ad} and PtO_x) formation (Figure 5a). Additional insights into the role of Pt–OH species can be obtained by analyzing the ratio of the peak current densities during methanol oxidation CVs (*I_f*/*I_b*), as mentioned in Section 3.3. In studies on PtRu MOR electrocatalysts, a high *I_f*/*I_b* ratio greater than 1 is commonly associated with a catalyst that is oxophilic.^{25,38} A study focused on the origin of the low *I_b* concluded that the propensity for PtRu catalysts to more easily form oxygenated species during CV excursions to the positive scan vertex inhibits the MOR during the negative (backward) scan segment because the high OH_{ad} and oxide coverage blocks

catalytic sites and thereby lowers I_b .⁸⁹ In other words, hydroxyls are necessary for the promotion of MOR, but excessive OH_{ad} and/or oxide coverage on catalytic sites hinders further MOR due to the low abundance of metallic active sites. As a result, electrocatalysts that are more oxophilic tend to achieve high MOR activity in the positive (forward) scan, I_f , but lower MOR activity in the negative (backward) scan, I_b . This is why PtRu catalysts often have high I_f/I_b , especially compared to Pt. In contrast, SiO_x/Pt electrodes showed higher I_f and lower I_f/I_b than Pt in Figure 3 (I_f/I_b of 1.0 and 1.4, respectively). When the interpretation of the role of PtRu oxophilicity on MOR kinetics is extended to SiO_x/Pt electrocatalysts, the low I_f/I_b for SiO_x/Pt electrodes suggests these electrodes are less oxophilic than bare Pt. However, this statement seems to contradict the observations of more facile $\text{Pt}-\text{OH}_{\text{ad}}/\text{PtO}_x$ formation for 5 nm SiO_x/Pt in the CV curves in the 0.5 M H_2SO_4 supporting electrolyte (Figure 2).

The different relationships between metal oxophilicity and MOR I_f/I_b peak ratios for SiO_x/Pt electrocatalysts compared to PtRu electrocatalysts suggests that metal oxophilicity plays different roles in promoting MOR in these two types of electrocatalysts. Despite the higher oxophilicity, the high I_b suggests that the SiO_x/Pt electrodes have a relatively moderate coverage of $\text{Pt}-\text{OH}_{\text{ad}}$ species during the backward scan that is conducive to higher MOR currents. Furthermore, the onset of I_b has been shown to coincide with the reduction of $\text{Pt}-\text{OH}_{\text{ad}}$ and PtO_x .⁹¹ Consistent with these observations, this study on SiO_x/Pt electrocatalysts suggests that oxophilic electrocatalysts may still exhibit high I_f and I_b so long as the kinetics of $\text{Pt}-\text{OH}$ and PtO_x reduction are fast enough to reactivate enough active sites for methanol decomposition during the backward scan. In other words, the I_f/I_b ratio correlates strongly with the ability of the metallic catalyst to regenerate hydroxyl species and/or metallic Pt sites, which can be referred to as a reactivation efficiency. Following this logic, the SiO_x/Pt catalysts are oxophilic but also have a relatively high reactivation efficiency compared to bare Pt.

We hypothesize that the high oxophilicity and reactivation efficiency of the SiO_x/Pt catalysts is due to hydroxyls from $\text{Si}-\text{OH}$ that are not actually adsorbed onto the Pt surface but only share a proximity. Such proximal hydroxyls would not block Pt sites from methanol decomposition but instead would still be available to facilitate oxidation of CO intermediates through the bifunctional mechanism. Furthermore, proximal hydroxyls provided by $\text{Si}-\text{OH}$ would allow for all of the Pt sites to be utilized for methanol decomposition, as opposed to conventional Pt electrocatalysts, where some fraction of the Pt surface must be occupied by $\text{Pt}-\text{OH}_{\text{ad}}$ (or $\text{Ru}-\text{OH}_{\text{ad}}$ in the case of PtRu alloy). This difference in available catalytic Pt sites may help explain the 2-fold increase in methanol oxidation current of SiO_x/Pt compared to Pt (Figure 4). Accordingly, the bifunctional mechanism is expected to proceed predominantly through silanol-mediated CO removal (eq 2) rather than CO oxidation by $\text{Pt}-\text{OH}_{\text{ad}}$ (eq 3). Therefore, the change in Pt oxophilicity observed for 5 nm SiO_x/Pt (Figure 2) may be a secondary effect of SiO_x encapsulation that does not play a key role in determining MOR activity.

To better understand the role of SiO_x overlayers in facilitating the electrocatalytic properties of the SiO_x/Pt thin films, CO and methanol oxidation experiments were performed in a pH 7 sodium phosphate buffer solution in which silanol groups may become deprotonated. Silica is known to have two different types of silanol groups, each with

a different pK_a .^{46–48,103} Silanol groups form when the solution pH is below the pK_a of $\text{Si}-\text{OH}$ ($\text{pK}_{a1} \approx 4$ and $\text{pK}_{a2} \approx 9$).^{46,47} Figure 7a shows CO stripping CVs for the bare Pt and 5 nm

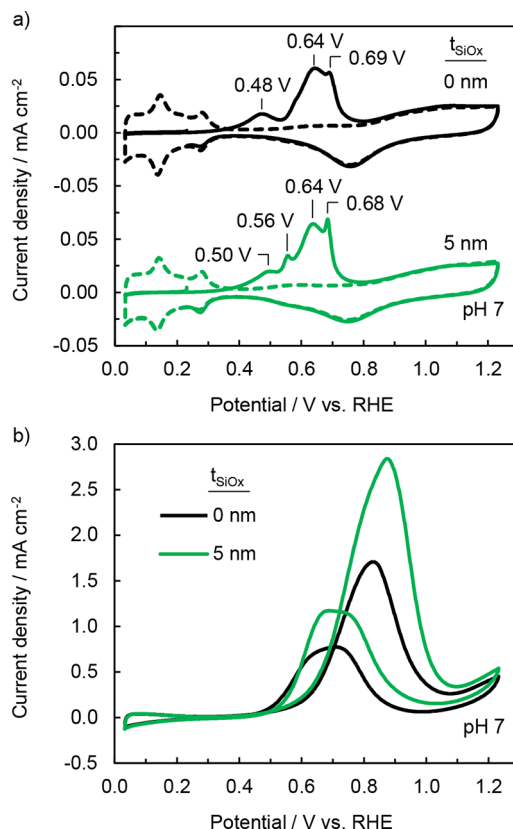


Figure 7. (a) CO stripping and (b) methanol oxidation CVs (cycle 30) in pH neutral electrolyte, 0.1 M sodium phosphate (buffered), with 0.5 M methanol for (b), for bare Pt (black) and 5 nm SiO_x/Pt (green) electrodes at a scan rate of 100 mV s^{-1} .

SiO_x/Pt at pH 7, for which the low- pK_a silanol groups should be deprotonated. Both electrodes exhibit multiple CO oxidation peaks with similar onset potentials (0.40 and 0.44 V vs RHE) that are shifted more negative than in acidic media (Figure 3). These features and differences between acidic and neutral pH are consistent with CO oxidation on multifaceted Pt in alkaline electrolytes.^{104,105} Importantly, the CO stripping curves are nearly identical for the SiO_x/Pt and Pt electrodes. If SiO_x/Pt was more active for CO oxidation than bare Pt in neutral pH, we would expect to observe a higher fraction of CO oxidation charge (i.e., a larger peak) at lower overpotentials.^{105,106} In Figure 7a, the extent of CO oxidation at lower overpotentials ($<0.6 \text{ V}$ vs RHE) is nearly equivalent for both the SiO_x/Pt and Pt electrodes, indicating that the CO oxidation activity is similar for both electrocatalysts. This finding is consistent with the hypothesis that silanol groups on the SiO_x overlayer boost CO oxidation activity, although differences in the structure of adsorbed CO layers in acidic and pH neutral environments may also be important factors in explaining why the CO oxidation curves converge.

Despite showing nearly identical CO stripping behavior as bare Pt in the pH neutral electrolyte, the SiO_x/Pt electrode still displayed significantly larger methanol oxidation activity in CV measurements conducted in the same pH = 7 supporting electrolyte (Figure 7b). It should also be noted that the ratio of

peak MOR currents, I_f/I_b , increased for both electrodes compared to those seen in the acidic electrolyte, from 1.4 to 2.3 for bare Pt and 1.0 to 2.5 for 5 nm SiO_x/Pt , consistent with observations of methanol oxidation in more alkaline media.^{107–109} The observed increase in I_f/I_b for SiO_x/Pt in neutral pH to a value that is similar to that for silanol-free bare Pt lends further support to the hypothesis that proximal silanols were responsible for the low I_f/I_b ratio for SiO_x/Pt in the acidic electrolyte. However, it does not explain why the supposedly silanol-stripped SiO_x/Pt electrodes still maintain a higher MOR activity than bare Pt at neutral pH. One explanation is local acidification at the buried SiO_x/Pt interface, which might arise from suppressed diffusion of protons back to the bulk electrolyte that were generated by the MOR (eq 1). Local acidification could help to keep silanol groups protonated even though the pH of the bulk electrolyte is above the silanol $\text{pK}_{\text{a}1}$. It is also possible that silanol groups associated with $\text{pK}_{\text{a}2}$ of SiO_2 , which are still protonated at $\text{pH} = 7$, are still able to participate in the MOR at more positive potentials, even though they do not appear to influence CO oxidation at less positive potentials (Figure 7a). However, the enhanced MOR current for SiO_x/Pt compared to bare Pt at the neutral pH might also result from the aforementioned “indirect” mechanisms by which the SiO_x overlayer can alter reaction energetics without directly being involved as an active site. Although this study was not able to fully deconvolute the influences of the SiO_x overlayer on methanol oxidation, we expect that in situ spectroscopies and computational tools will be of great value in future studies aimed at a deeper molecular understanding of electrocatalysis at buried interfaces.

5. CONCLUSIONS

The planar MCEC architecture investigated in this work provided a well-defined platform to investigate the unique electrocatalytic properties of the oxide-encapsulated metal electrocatalyst. In this study, we examined the effect of 2–5 nm thick SiO_x overlayers on Pt catalyst films for alcohol oxidation in acidic media. These SiO_x MCECs demonstrated lower CO oxidation onset potentials during CO stripping voltammetry than Pt in an acidic supporting electrolyte. The increased CO tolerance is likely due to the ability of silanol groups on SiO_x to promote oxidation of adsorbed CO on Pt. Furthermore, the SiO_x/Pt MCECs exhibit a 2-fold increase in the maximum peak current densities for alcohol oxidation compared to Pt. The enhanced performance toward alcohol oxidation, in acidic electrolyte, is largely attributed to the interactions between proximal hydroxyls from silanol groups and adsorbed intermediates on Pt. These interfacial regions are maximized with the MCEC design, such that an abundance of hydroxyl groups is readily provided at SiO_x/Pt interfaces where they can accelerate alcohol oxidation by the bifunctional mechanism. Varied CV vertex potential and pH measurements suggest that silanol groups, which are present at all relevant potentials in acidic pH, are active participants in CO and methanol oxidation. Although the MOR activity of SiO_x/Pt electrodes decreases during long-time cycling, this study demonstrates the MCEC design is a promising approach for CO tolerant and highly active alcohol oxidation electrocatalysts.

■ ASSOCIATED CONTENT

● Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acscatal.8b03626.

AFM and XPS characterization of SiO_x films, CO stripping on UV ozone treated Pt, methanol oxidation chronoamperometry, CV in methanol and perchloric acid, CV behavior for varied CV upper vertex potentials, methanol oxidation on etched electrodes, and AFM and XPS characterization of SiO_x/Pt electrodes postmethanol CV measurements (PDF)

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Notes

Any opinions, findings, and conclusions or recommendations expressed in this material are those of the author(s) and do not necessarily reflect the views of the National Science Foundation.

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

The authors would like to acknowledge Xiangye Liu for helpful discussions and suggestions and the Columbia Nano Initiative (CNI) staff for assistance with deposition and characterization tools. D.V.E., J.E.R., and N.Y.L. acknowledge financial support from Columbia University start-up funds, Société de Chimie Industrielle (2017 Seifi Ghasemi/Air Products Scholarship), and the National Science Foundation (NSF) (CBET-1752340).

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