Lanthanum can be detected using cathodic deposition followed by anodic stripping. The deposition process controls the detection limit. In this work, lanthanum deposition was characterized using an electrochemical quartz crystal microbalance (eQCM), and surface pH near the electrode surface was quantified using microelectrodes. The eQCM was used to correlate the lanthanum mass deposited on the electrode to the applied potential. Two different lanthanum responses were identified based on pH control. In the absence of pH control, the lanthanum film remained on the electrode surface until a large anodic potential was applied (1.8 \( V_{Ag/AgCl} \) or greater). In the presence of pH control, the lanthanum film was stripped off immediately after the applied potential was greater than \(-2.0 \ V_{Ag/AgCl}\). When we measured surface pH near the electrode surface using needle-type microelectrodes, it was found that the pH near the surface increased from 4 to above the detection limit (>10), which indicated that the surface pH was responsible for the two different observed lanthanum responses despite the bulk pH being the same. This is the first study to use eQCM and needle-type microelectrodes to correlate lanthanum deposition with surface pH rather than bulk pH.

The concentrations of lanthanum and other lanthanides are typically measured by depositing them as amalgams with mercury\(^1\) or, more recently, mercury films\(^2\), followed by stripping. As early as 1915\(^3\), mercury pools were used as cathodes that replaced platinum and copper electrodes for the electrolysis of rare earth elements. The reason for this was the fouling of the cathode with insoluble hydroxides, in which the pH at the cathode surface was thought to play a critical role. Recently, similar concerns were raised for lanthanide deposition on mercury-filmed microelectrodes.\(^4\) The authors claimed that pH was responsible for the stability of La deposition. The effect of pH is a consequence of electrolysis or electrochemistry in aqueous solution. Considering the generation of high currents (mA/cm\(^2\) level) on small electrodes during metal deposition, it is expected that pH changes significantly near the electrode surface. Researchers generally control bulk pH, but the pH on an electrode surface has not previously been quantified because the technology for doing this was not available until the present day. Interest in lanthanides stems primarily from electroanalysis and the need for rapid methods of detection\(^2\) and their chemical similarity to the actinides.\(^5\) In addition, the surface pH of deposited La films needs to be characterized in order for us to understand the deposition mechanism. Often, post-treatment analysis via inductively coupled plasma mass spectrometry is used successfully to identify the composition of electrochemically deposited films\(^6,7\) or quantify the amount of material sequestered by the electrochemical method.\(^8\) However, transient processes such as the formation of pH gradients near an electrode surface during deposition limit the usefulness of post-treatment analysis. One particular device, the electrochemical quartz crystal microbalance (eQCM), is suitable for correlating mass accumulation with applied potential. It relies on changes in the resonant frequency of oscillating quartz crystals to detect film formation.\(^9,10\) Electrochemical reactions are activated on electrodes manufactured onto oscillating quartz crystals. Therefore, any electrochemical reactions with products that result in the formation of films on the electrode surface can be studied. The eQCM tracks the resonant frequency shift, which is proportional to the mass attached to the electrode surface (Sauerbrey relation).\(^11\) The electrodes of an eQCM are able to detect ng-level changes in attached mass and can do so within a wide potential window. Thus, film formation can be monitored despite the lack of a voltammetric current peak, such as when background water electrolysis dominates the electrochemical response.

Lanthanum reduction is predicted to occur at \(-2.54 \ V_{Ag/AgCl}\) well outside the polarizable region (in aqueous solution) of typical electrode materials such as platinum, gold, and glassy carbon.\(^12\) At these potentials, current is generated by water electrolysis, which consumes proton equivalents and drives proton flux. The deviation of the surface pH (the solution pH adjacent to the electrode surface) from the bulk pH (the solution pH far from the electrode surface) is commonly underestimated and understated. Early work on cathodic polarization\(^13\) in acids demonstrated that in the absence of added buffering agents, extreme polarization under high current densities resulted in surface pH that approached the pKa of water, ca. pH 12. This conclusion applies generally, in that the dissociation of any buffering agent (including water) controls the surface pH at extreme polarizations. Thus it is expected that attempts to deposit lanthanum on electrodes immersed in simple salt solutions involve surface pH larger than 12. At these pH values, the formation of lanthanum hydroxides is prevalent\(^14\) and becomes a complicating factor in studying lanthanum deposition in aqueous solution.

We hypothesize that surface pH will deviate significantly from bulk pH and affect lanthanum deposition. The extent to which surface pH does this has not been quantified or correlated with mass deposition. Our goal is to determine surface pH using microelectrodes and correlate it to lanthanum deposition using eQCM. New needle-type pH microelectrodes with the ability to measure pH gradients on a polarized surface have been recently developed by our research group and used to detect surface pH.\(^15\) We measured the eQCM response and surface pH response of electrodes polarized as high as \(-2.5 \ V_{Ag/AgCl}\). Mercury was used to quantify the upper limit of the small-load approximation necessary to convert the frequency response of the eQCM to a mass response, similar to calibrations done with copper.\(^16,17\) Lanthanum was deposited in buffered and buffered salt solutions. Additionally, lanthanum deposition on carbon electrodes was compared to deposition on gold electrodes.

Materials and Methods

Chemicals.—The following chemicals were used as is: mercury (II) nitrate monohydrate (83381-50G, Sigma Aldrich), nitric acid (22571-475ML, Sigma Aldrich), lanthanum chloride (203521-25G, Sigma Aldrich), acetic acid (338818-100ML, Sigma Aldrich), sodium acetate (W302406-1KG-K, Sigma Aldrich), and lithium chloride (746460-500G, Sigma Aldrich).
Electrochemical quartz crystal microbalance measurements.— A complete eQCM hardware/software laboratory kit was purchased from Gamry Instruments (992-00083, Gamry Instruments). All experiments were run in a 4-mL Teflon cell (971-00003, Gamry Instruments) with eQCM electrodes mounted at the base of the cell. Carbon electrodes (971-00009, Gamry Instruments) or gold electrodes (971-00006, Gamry instruments) were used. The cell was kept in 3% w/w nitric acid to clean it. Prior to use, the cell was washed three times with 18-MΩ·cm deionized water and subsequently dried. The eQCM electrode was then mounted and the background solution (usually a 100 mM LiCl solution) was added to the assembled cell. A graphite rod counter electrode (496537-43.5G, Sigma Aldrich) and a saturated silver/silver chloride reference electrode (built in-house) were inserted into the filled cell. The resonator that oscillates the eQCM electrode was then turned on. A stable background resonant frequency was obtained prior to all experiments.

Electrochemical setup.— A Gamry Instruments Series G300 potentiostat was used to polarize eQCM electrodes and run all voltammetry experiments. Unless specified, background voltammograms cycling between 2 V \text{Ag/AgCl} and −2.5 V \text{Ag/AgCl} were obtained at 100 mV/s to ensure that each eQCM electrode was working correctly. If a eQCM electrode exhibited a constantly shifting baseline frequency or a poorly defined frequency spectrum, the electrode was discarded. The background solution was then removed and the test solution added to a total volume of 4 mL not including the space taken up by the counter and reference electrodes.

Calibration of the eQCM frequency response.— To ensure that the eQCM frequency response represented the attachment of mass to the electrode, we tested the experimental setup by depositing mercury films onto the electrodes. Two variables were measured, the series frequency shift and the parallel frequency shift. The Sauerbrey mass film deposition (left panel) and removal (right panel) occurred during a potential sweep from 2.0 V \text{Ag/AgCl} to −2.5 V \text{Ag/AgCl} at a scan rate of 50 mV/s. A decreased frequency shift indicates the deposition of lanthanum. At the end of the electrodeposition, ∆F had deviated by 7% from the initial value. Note that the initial ∆F was 5275 Hz and that the frequency shifts shown in Figure SI-1A are offset to zero in the pre-step time interval. Prior experiments using a similar setup with differing films resulted in percentages for copper and polyaniline of 2% and 6%, respectively. Thus, as long as ∆F does not deviate significantly from ~5%, the series frequency shift is a good estimation of the mass attached to the electrode surface. Figure SI-1B compares the total mass estimation from charge and that estimated from series frequency shift. A linear correlation is expected. The theoretical slope should be unity, and our reported slope of 1.103 ± 0.002 deviated by 10%. Linearity with a slope between 0.5 μg and 2 μg indicated the operating region for our eQCM setup.

Measurements of surface pH using pH microelectrodes.— All-in-one pH microelectrodes were constructed following the procedures described previously. These microelectrodes were recently developed and successfully used above polarized surfaces. The pH microelectrode had a liquid ion-exchange (LIX) membrane at the tip and was calibrated in standard buffer solutions (pH 4, 7, and 10) prior to use. The potential difference between the microelectrode tip and the built-in reference electrode was measured using a Keithley 6517A electrometer/high-resistance meter. The LIX sensing tip and the reference electrode were placed very close to each other (300 μm) to prevent artifacts caused by polarization of the working electrode. The microelectrode tip position was controlled using a Mercury Step motor controller PIM-230.10S Part No. M23010SX (Physik Instrumente, Auburn, MA). A Zeiss Stemi 2000 stereomicroscope was used to locate the microelectrode tip. Using the motor and the stereomicroscope, the microelectrode tip was placed at a distance of 100 μm from the electrode surface. Once in position, the surface pH at a bare glassy carbon electrode was directly measured during potential sweeps in solutions of 100 mM LiCl, 50 mM acetate buffer at pH 4.5, and 50 mM carbonate buffer at pH 10. The scan rate was reduced to 1 mV/s to ensure adequate time was allowed for the pH microelectrode to respond. Typical response times were less than 5 seconds.

Results and Discussion

La deposition and monitoring the mass of deposited La using eQCM.— Lanthanum was deposited onto the electrode surface by sweeping the potential from 2 V \text{Ag/AgCl} to −2.5 V \text{Ag/AgCl} in LiCl (Figure 1) and was detected on the eQCM around −1.3 V \text{Ag/AgCl}. As the potential was swept in the negative direction, the frequency shift stabilized at −1.8 V \text{Ag/AgCl}, indicating the completion of lanthanum deposition and monitoring the mass of deposited La using eQCM.— Lanthanum was deposited onto the electrode surface by sweeping the potential from 2 V \text{Ag/AgCl} to −2.5 V \text{Ag/AgCl} in LiCl (Figure 1) and was detected on the eQCM around −1.3 V \text{Ag/AgCl}. As the potential was swept in the negative direction, the frequency shift stabilized at −1.8 V \text{Ag/AgCl}, indicating the completion of lanthanum.

Figure 1. The eQCM response in 1 mM lanthanum in LiCl. Film deposition (left panel) and removal (right panel) occurred during a potential sweep from 2.0 V \text{Ag/AgCl} to −2.5 V \text{Ag/AgCl} at a scan rate of 50 mV/s. A decreased frequency shift indicates the deposition of lanthanum.
deposition. Beyond this potential, frequency shift varied minimally. For three sequential scans (two not shown for clarity), the final frequency shift was $-788 \pm 22$ Hz at $-2.5 \, V_{Ag/AgCl}$. Without lanthanum present, three sequential scans exhibited a final frequency shift of $44 \pm 35$ Hz at $-2.5 \, V_{Ag/AgCl}$. Thus, the net final frequency shift response of $\sim 744$ Hz was a result of lanthanum film formation, depicted as a shaded area in Figure 1. During film formation, the current response increased over the background response. The net current response in Figure 1 (gray line) coincided with film formation. Three sequential scans showed a final net current response of $-1.1 \pm 7.4 \times 10^{-2}$ mA. The cathodic current was consistent with lanthanum reduction and film formation as observed in the literature.2 However, further voltammetric analysis was not possible because of interference of the background response (red dashed line), which highlights the importance of simultaneous eQCM measurements.

**Lanthanum stripping.—**Following deposition during the cathodic sweep, lanthanum was removed by an anodic sweep up to $2.0 \, V_{Ag/AgCl}$. From $-2.5 \, V_{Ag/AgCl}$ to $1.0 \, V_{Ag/AgCl}$, the average frequency shift was $-769 \pm 15$ Hz. For clarity, only the $-0.5 \, V_{Ag/AgCl}$ to $2.0 \, V_{Ag/AgCl}$ region is shown in Figure 1. Once deposited, the lanthanum film persisted over a 3-V window (Figure 1). Beyond $1 \, V_{Ag/AgCl}$, the frequency shift response moved in the positive direction until $2.0 \, V_{Ag/AgCl}$. The scan rate was $10 \, mV/s$. The inset shows a voltammetric peak centered at $1.6 \, V_{Ag/AgCl}$. The scan rate was $10 \, mV/s$.

**Role of deposition time.—**To rule out the possibility that insufficient time was provided for lanthanum accumulation, we cycled the potential five times between $0.6 \, V_{Ag/AgCl}$ and $-2.5 \, V_{Ag/AgCl}$ at a $5 \times$ slower scan rate ($10 \, mV/s$) than that represented in Figure 1. Reduced scan rates maximized lanthanum film formation prior to a removal sweep up to $2.0 \, V_{Ag/AgCl}$. The results are shown in Figure 2. Scan #1 in panel A shows deposition characteristics identical to those in Figure 1. Lanthanum deposition was detected at $-1.3 \, V_{Ag/AgCl}$. Similarly, the frequency shift stabilized near $-1.8 \, V_{Ag/AgCl}$ and remained stable up to the end of scan #1. The final frequency shift during scan #1 was $-1209$ Hz at $-2.5 \, V_{Ag/AgCl}$. This value is $1.5 \times$ larger than that shown in Figure 1. If film formation were diffusion-limited, we would expect Cottrell behavior and a $2.2 \times$ increase in frequency shift, which is the ratio of the scan rates raised to the one-half power ($50^{1/2}/10^{1/2}$). The lower ratio of $1.5 \times (\Delta F_{(10mV/s)})^{1/2}/(\Delta F_{(50mV/s)})^{1/2}$ suggests that coupled reactions limit the rate of film formation. A ratio equal to the scan rate dependence predicted by the Cottrell equation indicates a system that is diffusion limited. A ratio greater than that predicted by the Cottrell equation indicates that convection aided mass transport of analyte to the electrode surface. An additional 1500 Hz was observed during four scans after scan #1. However, panel B shows that the variation in ΔF exceeded our calibration for the frequency shift (see Supplementary Information). Other film processes, such as the ingress/egress of ions into the film,3 potentially contributed to the frequency shift. Thus, we concluded that frequency shift was not representative of film mass beyond scan #1.

Despite this limitation, panel C shows a voltammetric peak indicating film removal during scan #6. Thus, several deposition sweeps with at least $1 \, \mu g$ of film deposited (estimated from the Sauerbrey equation) is required to observe a stripping voltammetric peak on bare carbon.

**Surface pH on the electrode surface.—**Surface pH measurements are shown in Figure 3 with a diagram showing the position of the microelectrode tip. The onset of electrolytic background current was earlier for solutions with lower pH (nitric acid-acetate buffer-LiCl solution-carbonate buffer). Carbonate buffer was added as an additional step for solutions with lower pH.
Figure 3. The variation of surface pH (~100 μm from the electrode surface) during a potential sweep from 0 V_{Ag/AgCl} to ~2.5 V_{Ag/AgCl} at 1 mV/s. Although the LiCl electrolyte had the lowest background current, the surface pH was the least volatile in acetate buffer. A diagram of the microelectrode tip position adjacent to the electrode surface is shown to the right.

additional point to compare with acetate buffer and was not used beyond this. As shown by Figure 3, the surface pH was the most volatile in the unbuffered LiCl electrolyte, with a large pH deviation occurring at ~1.4 V_{Ag/AgCl}. Beyond ~1.5 V_{Ag/AgCl}, the surface pH exceeded pH 10 (out of the calibration range). The buffered acetate solution maintained a surface pH within the calibration range for the duration of the potential sweep. Notably, the pH deviated above pH 6.5 at applied potentials below ~2.0 V_{Ag/AgCl}. In carbonate buffer, the surface pH remained constant until ~1.5 V_{Ag/AgCl}. The nitric acid pH measurements are omitted because the pH microelectrode tip made of LIX membrane was damaged by the low pH. We should note that we used a slower scan rate to ensure that our microelectrode response was comparable to the scan rate (1 mV/s).

With pH beyond 10 in LiCl electrolyte, lanthanum film deposition and the eQCM response are likely caused by the surface pH altering lanthanum speciation. In the cathodic region, the surface pH rises and extends into regions where insoluble lanthanum hydroxides form. Because the pH at the electrode surface increases first, lanthanum hydroxides form on the electrode surface. Once formed, lanthanum hydroxide remains on the electrode surface until a sufficiently acidic surface pH is reached. For La(OH)$_3$, dissolution (shown in Equation 1) was found to be inappreciable above a pH of ~4.3. In a separate experiment, we measured pH changes during anodic stripping and found that the surface pH did not decrease below ~4.3 until an electrode potential of ~1.8 V_{Ag/AgCl} was reached (results not shown). The stability of lanthanum hydroxide under neutral and alkaline conditions explains the persistence of the films formed in the unbuffered LiCl electrolyte, observed in Figure 1 and Figure 2A. The film was removed only when a sufficient anodic current drove the surface pH below ~4.3 where La$^{3+}$ (aq) is stable.

$$\text{La(OH)}_3 + 3\text{H}^+ \rightarrow \text{La}^{3+} + 3\text{H}_2\text{O}$$

Comparing carbon and gold surfaces on La deposition.—Since the behavior of electrochemical reactions is often dependent on the electrode surface material (i.e. platinum, gold, carbon, etc.), we also tested gold surfaces. Figure 4 shows a side-by-side comparison of the lanthanum response on carbon (left panel) and that on gold (right panel) in 100 mM acetate buffer at a scan rate of 100 mV/s. CVs are shown in a separate panel above, sharing the same potential axis as

Figure 4. Side-by-side comparison of the eQCM responses for lanthanum in acetate buffer between a carbon surface (left) and a gold surface (right).
the corresponding frequency shift curves. Both the series frequency shift and the parallel frequency shift are also presented, similar to Figure S1-1. The vertical arrows in the carbon and gold responses indicate the potentials at which a significant cathodic current (>100 μA) was observed. A difference of 300 mV was observed, which reflects the difference in activation overpotential for water electrolysis between gold and carbon materials. Similarly, we observed a 550-mV difference in the onset potential (point I) of lanthanum deposition, with the gold response starting at $-1.55 \, V_{\text{Ag/AgCl}}$. For point II, a 660-mV difference was observed, with the gold response starting at $-1.44 \, V_{\text{Ag/AgCl}}$. These results demonstrate that the film response was not specific to carbon surfaces.

The primary difference between the carbon response and the gold response was a shift in the activation overpotential of film deposition. The shape of the responses was nearly identical except that more film was formed for gold than for carbon. The reason for this is that more time was allotted for deposition on gold than on carbon because of its lower activation potential. From point I to the lower bound of $-2.5 \, V_{\text{Ag/AgCl}}$, the scan time was 4 s for carbon and 10 s for gold. Including the return scan, 12 s of additional deposition time was allowed for the gold surface. The result was maximum frequency shifts (point II) of $-610 \, \text{Hz}$ and $-1390 \, \text{Hz}$ for carbon and gold, respectively. Additionally, we found that it was consistently easier to notice a faradaic response (current peak) during deposition on gold than it was on carbon. A pair of current peaks was observed superimposed onto a significant background. The midpoint potential of the peaks was estimated by taking the difference between the anodic and cathodic currents at each potential. Shown as a gray dashed curve, the midpoint potential was estimated graphically to be $-1.34 \, V_{\text{Ag/AgCl}}$. The presence of these current peaks suggests that using gold surfaces may be more advantageous. However, more mechanistic work is required to link the peaks to the state of lanthanum in the film. The parallel frequency shift mirrored the series frequency shift in both responses but at a smaller maximum frequency shift. ΔF at point II deviated from the initial value by 4% for carbon and 10% for gold. The difference was caused by the differing amounts of film deposited. At a series frequency shift of $-610 \, \text{Hz}$, the ΔF for gold was 3%, which is comparable to the maximum response for carbon. Furthermore, as a point of reference, the ΔF for both carbon and gold was typically $>50\%$ at scan rates of 10 mV/s or lower, which is similar to the sequential scans in Figure 2.

**Conclusions**

In this work, we studied the effect of the surface pH on both the electrochemical and eQCM responses of lanthanum deposition onto an electrode surface in aqueous solution. Two different lanthanum deposition responses were identified using an electrochemical eQCM setup. These responses were identified by the stability of the deposited lanthanum film mass in relation to the applied potential. In the absence of pH control, the lanthanum film remained on the electrode surface until an extreme anodic potential was applied (1.8 $V_{\text{Ag/AgCl}}$ or greater). In the presence of pH control, the lanthanum film stripped off immediately after the applied potential was greater than $-2 \, V_{\text{Ag/AgCl}}$. This 4-V difference in film stability was caused by the ability of the buffer to maintain pH near the electrode surface. Even if the same bulk pH were employed for all of the measurements, stable measurements could only be performed when the pH on the surface of the electrode remained under buffer control. When gold and carbon electrodes were compared for lanthanum deposition, we found that the shape of the responses was nearly identical except that more film was formed on gold than on carbon. The reason for this is that more time was allotted for deposition on gold than on carbon because of its lower activation potential. These results demonstrate that the film response was not specific to carbon surfaces.

**Acknowledgments**

This work was funded by HDTRA-1-10-1-0111. The authors thank Erhan Atci for providing the pH microelectrodes. A. M. acknowledges NIGMS training grant T32 GM008336 and the ARCS Foundation of Seattle.

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