Electrochemical Preconcentration Mechanism of Trivalent Lanthanum

Adan Schafer Medina, Cornelius F. Ivory, Nathalie A. Wall, Sue B. Clark, and Haluk Beyenal

The goals of this work were 1) to demonstrate lanthanum preconcentration/deposition on electrodes, 2) to elucidate the mechanism of deposition, and 3) to use electrodeposition to detect lanthanum on carbon fiber microelectrodes. Lanthanum was preconcentrated via electroprecipitation on carbon electrodes using unbuffered electrolyte. To measure the amount of La deposited on the surface, we used eQCM to observe the mass change (quantified as frequency change) while La precipitated on the surface of the electrode. The chemical state of the deposited film was determined using X-ray photoelectron spectrometry and Auger electron spectrometry. We used a pH microelectrode with a tip diameter of less than 20 μm near the electrode surface to determine surface pH changes. We found that lanthanum preconcentration on electrodes is a result of pH changes at the electrode surface due to water electrolysis. La(OH)₃ was determined to be the predominant state of the film, with La and O atoms colocalized in the precipitates. Based on this discovery, the current responses to lanthanum electroprecipitation on carbon fiber microelectrodes and a mercury-filmed carbon fiber microelectrode were compared. We found that both microelectrode responses were concentration-dependent.

Lanthanum serves as a chemical analog for the trivalent lanthanides and actinides and can therefore be used to study the radioactive actinides. The lanthanides are of interest to researchers due to their importance in a wide variety of industries including manufacturing/fabrication (electronics, catalysts, and alloys), and nuclear waste management. Lanthanum is a trivalent rare earth element which is difficult to electrodeposit in water because of its low standard reduction potential of −2.57 VAg/AgCl. The reactivity of metallic lanthanum in aqueous solution makes the electrodeposition of the metal in mercury amalgams a useful alternative. Thus, mercury-filmed electrodes have shown promise in preconcentrating lanthanum using a rotating disk electrode and a mercury-filmed microelectrode. For example, Schumacher used a 3-mm mercury-filmed glassy carbon rotating disk electrode to obtain a 20-fold reduction in volume for follow-on analysis. In a subsequent work, Schumacher used a 10-μm mercury-filmed carbon fiber microelectrode tip to preconcentrate 5 picograms/L of La on the electrode. In this study, quantitative electrochemical peaks were observed when the electrode was scanned from 0 VAg/AgCl to −2.65 VAg/AgCl. During the scan, the current at −2.65 VAg/AgCl was determined to be positively correlated to the concentration of La in the solution, while the peak at −2.25 VAg/AgCl was determined to be negatively correlated to the concentration of La in solution. The authors concluded that the peak at −2.25 VAg/AgCl was due to the formation of soluble lanthanum hydroxides, whose concentration decreases in favor of insoluble lanthanum hydroxide as the total concentration of lanthanum increases. However, Schumacher did not provide further clarification on the mechanism of lanthanum preconcentration.

Doyle extended this work by optimizing the preconcentration of lanthanum on the mercury-filmed carbon fiber microelectrode with respect to the accumulation potential, ionic strength, and pH. The optimal accumulation potential was selected based on the largest current response from a chronocoulometric potential step and was determined to be −2.0 VAg/AgCl. Similarly, the optimal ionic strength was determined to be 1–2 M. The optimal pH was selected to be pH 4—the lanthanum response was masked by the reduction of hydronium species at lower pH and the chronocoulometric response was more uncertain at higher pH. In addition, the authors attempted to determine the mechanism of lanthanum preconcentration by observing the current response of the electrode to various conditions, including the absence of in situ mercury, differing electrolytes, and the use of buffers. The current response vanished in the absence of mercury, indicating a mercury-dependent mechanism. Firstly, lanthanum adsorption on the mercury film was ruled out because of the lack of increased adsorption upon the use of electrolytes with greater affinity for mercury, the so-called “anson effect.” Secondly, the hydroxide formation mechanism was not supported, as the use of an acetic acid buffer did not inhibit the current response to lanthanum of the mercury-filmed electrode. Lastly, the authors found the current response of the mercury-filmed electrode to increase as the lanthanum concentration increased. Therefore, the mechanism was hypothesized to be the amalgamation of lanthanum into the mercury film. However, the authors did not have knowledge of any surface pH changes near the mercury-filmed electrode surface. If the buffer strength was insufficient to preclude an alkaline environment near the electrode surface, the hydroxide formation mechanism may still have been possible. Although the mercury-filmed electrode preconcentration of lanthanum was successful in these studies, there are environmental concerns due to the toxicity of aqueous mercury to aquatic wildlife.

On the other hand, lanthanum film formation on carbon and gold electrode surfaces has been demonstrated previously using an electrochemical quartz crystal microbalance (eQCM). The eQCM correlates mass accumulation on the electrode surface with applied potential, relying on changes in the resonant frequency of the oscillating crystal to detect changes in adhered mass. The Sauerbrey relation states that the frequency shift is proportional to the negative of the change in mass on the crystal, and is capable of detecting ng-level changes in the deposited film. Babauta observed a lanthanum film gravimetrically while the electrode potential was swept to −2.5 VAg/AgCl. The film onset potential was found to be −1.3 VAg/AgCl and the film stabilized at −1.8 VAg/AgCl in unbuffered 100 mM LiCl aqueous solution at pH 4.5. Stripping of the film was delayed until the onset of anodic current at 1.8 VAg/AgCl and was observed gravimetrically. When the solution was buffered with acetate, the resulting film was no longer stable during the reverse scan. The instability of the deposited lanthanum film in buffered solutions led the authors to hypothesize that increasing surface pH during cathodic sweeps causes La to electroprecipitate.

© The Author(s) 2018. Published by ECS. This is an open access article distributed under the terms of the Creative Commons Attribution 4.0 License (CC BY, http://creativecommons.org/licenses/by/4.0/), which permits unrestricted reuse of the work in any medium, provided the original work is properly cited. [DOI: 10.1149/2.031813jes]
Electroprecipitation is described as the hydrolysis and subsequent precipitation of the free ion onto an electrode surface that features a high surface pH due to the water electrolysis reaction. It involves the generation of hydroxide at a cathode through the hydrolysis of water. In the presence of nitrate, the hydrogen reduction reaction (HER) is responsible for the pH increase. The alkaline conditions at pH, but in the absence of nitrate ions, the hydrogen reduction reaction to ammonia results in an increase in surface hydroxide at a cathode through the hydrolysis of water. In the presence of nitrate, reduction to ammonia results in an increase in surface pH. Monk was successful in electroprecipitating a mixture of copper and lanthanum, forming a mixed metal hydroxide species that was validated through speciation modeling. However, surface pH changes near the electrode surface was not included in this study. Additionally, quantification of surface pH changes during electroprecipitation reactions may improve the preparation of lanthanide hydroxide-modified surfaces in the protection of surfaces/nanoparticles.

Our previous work on La electroprecipitation indicated a surface pH increase during electroprecipitation. However, the mechanism of preconcentration, the chemistry of the deposits and their dependence on surface pH have not been studied. The goals of this work were 1) to demonstrate lanthanum preconcentration/deposition on electrodes, 2) to elucidate the mechanism of deposition, and 3) to use electrodeposition to detect lanthanum on carbon fiber microelectrodes. To measure the amount of La deposited on the surface, we used eQCM to obser the mass change (quantified as frequency change) while La precipitated on the surface of the electrode. The chemical state of the deposited film was determined using X-ray photoelectron spectrometry and Auger electron spectrometry. We hypothesized that the mechanism of preconcentration on electrode surfaces was electroprecipitation due to increased surface pH near the electrodes. We used a pH microelectrode with a tip diameter of less than 20 μm near the electrode surface to determine surface pH changes. Since we found that it is possible to electrodeposited La on carbon surface, we used carbon fiber microelectrodes with a tip diameter of less than 30 μm to electrodeposit La. Finally, we compared La electroprecipitation and its dependence on La concentration using carbon fiber microelectrodes with a commonly used mercury film microelectrode described in the literature.

Materials and Methods

Reagents.—The following chemicals were used without modification: mercury (II) nitrate monohydrate (83381-50 G, Sigma Aldrich), nitric acid (225711-475ML, Sigma Aldrich), lanthanum chloride (203521-25 G, Sigma Aldrich), lithium chloride (746460-500 G, Sigma Aldrich) and sodium chloride (BP358-1, Fisher BioReagents).

Electrochemical quartz crystal microbalance measurements.—A complete eQCM hardware/software laboratory kit was purchased from Gamry Instruments (992-00083, Gamry Instruments, Warminster, PA, USA). The eQCM wire was connected to a Gamry Interface 1000 potentiostat to control the potential of the working electrode. The eQCM electrode was then mounted and the built-in reference electrode was measured using a Keithley 6517A.

Construction of the pH and carbon fiber microelectrodes.—All-in-one pH microelectrodes were constructed following the procedures described previously. Briefly, an all-in-one needle-type pH microelectrode is fabricated bypulling a glass capillary to a tip (outer) diameter of ~20 μm and filling a liquid ion exchange (LIX) membrane to the tip. The capillary is epoxied into an outer case with the sensing tip protruding 1000-1500 μm. An agar layer (18.2 g/L with 100 M Na2SO4) is then applied to the outer case, which is used as a reference electrode for pH measurements near a polarized electrode surface. These microelectrodes were recently developed and successfully used on polarized surfaces by our group. The pH microelectrode had an 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.
The hydrolysis and solubility constants used to construct the speciation diagrams were constructed for an aqueous system of 100 mM HNO₃. The solution was then sparged for 5 minutes between experiments. Background scans were taken with a starting potential of 0.0 VAg/AgCl and a vertex potential of −2.65 VAg/AgCl. After the addition of the analytic, the solution was sparged again prior to the next experiment. This procedure allowed the formation of mercury film on carbon fiber microelectrodes.

**Carbon fiber microelectrode experiments.**—The carbon fiber microelectrode experiments were performed similarly to those of Schumacher et al. The electrochemical cell consisted of a jacketed Dr. Bob’s Cell (930-00037, Gamry Instruments). The working electrode was a glass-sheathed carbon fiber with an exposed tip, which yielded a disk geometry; this was inserted into the sealed Dr. Bob’s Cell. A Pt wire (MW-1032, Bioanalytical Systems, Inc) was used as the counter electrode, and a silver/silver chloride electrode was used as the reference electrode.

**Mercury-filmed carbon fiber microelectrode.**—A 1 mM solution of Hg₂⁺ was placed into the electrochemical cell with 0.1 M NaCl as the background electrolyte. The pH was adjusted to 3.0 with 1 M HNO₃. The solution was then sparged for 5 minutes between experiments. Background scans were taken with a starting potential of 0.0 VAg/AgCl and a vertex potential of −2.65 VAg/AgCl. After the addition of the analytic, the solution was sparged again prior to the next experiment. This procedure allowed the formation of mercury film on carbon fiber microelectrodes.

**Lanthanum speciation.**—The speciation of lanthanum was modeled using The Geochemist Workbench modeling software. Speciation diagrams were constructed for an aqueous system of 100 mM HNO₃ as the background electrolyte. The pH was adjusted to 3.0 with 1 M HNO₃. The solution was then sparged for 5 minutes between experiments. Background scans were taken with a starting potential of 0.0 VAg/AgCl and a vertex potential of −2.65 VAg/AgCl. After the addition of the analytic, the solution was sparged again prior to the next experiment. This procedure allowed the formation of mercury film on carbon fiber microelectrodes.

**SEM imaging and auger nanoprobe analysis.**—Scanning electron microscopy (SEM) and Auger electron spectroscopy (AES) analyses were carried out using an integrated Physical Electronics (PHI) 710 Scanning Auger NanoProbe (NanoAuger). Auger and SEM analyses were carried out at a primary electron beam energy of 10 keV. The SEM images and Auger/EDX scans were collected at varying fields of view. The SEM images and AES data were collected using PHI SmartSoft software and analyzed using PHI MultiPak software.

**Results and Discussion**

Our work is focused on testing the hypothesis that film formation is dependent on change in the electrode surface pH. After verifying this hypothesis, we determined the chemical composition of the film along with the chemical state of the film. Lastly, we scaled down the electroprecipitation to test whether the observed current is correlated with the bulk La concentration using a carbon fiber microelectrode (CFM) and then compared these results with results for the traditional mercury-filmed carbon fiber microelectrodes (MFCFM).

The voltammogram of a carbon-coated QCM electrode in a 1 mM La solution in 100 mM LiCl at pH 4.5 is shown in Figure 2. The voltammogram proceeds from 0 VAg/AgCl to −2.65 VAg/AgCl and then to 2 VAg/AgCl. The frequency shift was converted to a mass shift using the calibration factor (226 Hz μg⁻¹ cm⁻²) of the crystal and the Sauerbrey relation; this mass shift is plotted against the applied potential in Figure 2B. Comparing the mass response (Figure 2B) to the current response (Figure 2A) demonstrates that most of the film is attached as the polarized electrode reaches 1.4 VAg/AgCl, as indicated by the stabilization of the mass response. The onset of rapid current increase shortly after −1.40 VAg/AgCl is due to the activation of the hydrogen reduction reaction. As the electrode potential is scanned past the vertex and continues toward 2 VAg/AgCl, the mass response is observed to be constant until film detachment begins at −1.6 VAg/AgCl, which is shortly after the onset of anodic current at −1.4 VAg/AgCl. The onset of cathodic and anodic current resulted in significant surface pH changes, as shown in Figure 2C and are attributed to the hydrogen reduction reaction and the oxygen evolution reaction (OER), respectively. This is corroborated by the observation of bubble formation at large cathodic and anodic potentials.
of lanthanum saturation until shortly after the frequency shift indicated the onset of film detachment. The film is expected to be composed of La(OH)$_3$ based on the pH response and the speciation diagram for 1 mM La (Figure 3A). While the solution was sparged before the experiment, complexation of La with carbonate from dissolved carbon dioxide and its subsequent precipitation is expected to be negligible based on the speciation diagram including atmospheric carbon dioxide (Figures 3C, 3D).

While gravimetric analysis provides proof of film formation, it does not provide insight into the elemental composition or the chemical state of the film. To identify the chemistry of the film we used XPS and Auger nanoprobe analysis. The concentration of La was increased to 10 mM to obtain quick visual confirmation of precipitate on the sample surface before it was prepared for surface analysis. The speciation of 10 mM La in 100 mM NaCl at pH 3.0 was modeled (Figures 3E, 3F) to confirm that the speciation did not differ significantly from that of 1 mM La. The values used to perform the speciation modeling can be found in Table I.

**Elemental composition and chemical state of eQCM film.**—The elemental composition and chemical state of the film were determined using XPS analysis. The film was determined to contain lanthanum at a lanthanum to oxygen ratio of 1:3, even after thorough rinsing of the surface (survey scan—data not shown). A slight contamination by carbon, hydrogen, and silicon was also observed in the survey scan, so the samples were sputtered to clean the surface. A 2-keV Ar$^+$ ion sputter at a target current of 0.5 $\mu$A for 30 sec was used to remove $\sim$2 nm of material, after which a high-resolution spectrum of the La 3$d_{5/2}$ region was collected: the contaminants were no longer seen. The peaks for La 3$d_{5/2}$ were deconvoluted according to Sunding$^{22}$ and are shown in Figure 4. The multiplet splitting yielded a binding energy separation of $\sim$4 eV, which confirmed the chemical state of the lanthanum to be lanthanum hydroxide. The main peak corresponds to the contribution of the final state without charge transfer, and the two satellite peaks correspond to the final state with charge transfer from the ligand bonding and antibonding components.

SEM was used to determine that the precipitate on the electrode surface was situated in discrete clusters. An example precipitate is shown in Figure 5A with accompanying elemental maps (Figures 5B–5E) created with the use of the scanning Auger nanoprobe. La, O, and Cl atoms were shown to be colocalized on these precipitates and, to a lesser extent, directly on the Au surface as a base layer (Figures 5B–5E). The escape depth of Auger electrons depends on their kinetic energy and emission, with most of the intensity coming from the top three monolayers.$^{24}$ Therefore, the lack of an Au signal on the precipitate cluster shown in Figure 5C indicates that the cluster is at least several nanometers thick.

**Electroprecipitation of trivalent lanthanum.**—Figure 6 describes the proposed electroprecipitation mechanism of lanthanum hydroxide on a cathodically polarized electrode along with the chemical reactions given in Equations 1 and 2. The electrogeneration of hydroxyl ions induces a pH gradient near the electrode surface (as shown in Figure 2). Hydroxyl ions are generated from the hydrogen reduction reaction (Equation 1) which is activated by cathodic polarization. Meanwhile, high pH (pH $>8$) near the electrode surface results in the hydrolysis of La$^{3+}$ to La(OH)$^{3+}$, La(OH)$_2$$^+$$^2$, and finally to La(OH)$_3$. The electro-precipitation of lanthanum near the surface results in a concentration gradient, which delivers more La to the electrode surface for further precipitation.

$$2H_2O + 2e^- \rightleftharpoons H_2 + 2OH^- \quad E = -0.828V - \frac{RT}{2F} \ln ([H_2][OH^-]^2)$$

[1]

$$La(OH)_3 \rightleftharpoons La^{3+} + 3OH^- \quad K_{sp} = [La^{3+}][OH^-]^3$$

[2]
Figure 3. Geochemist Workbench speciation diagram of (A) solution and (B) precipitate species from 1 mM LaCl₃ in 0.1 M NaCl. The values for the stability constants of La hydrolysis and solubility constants are from Refs. 20 and 21 and are summarized in Table I. The figures were constructed using The Geochemist Workbench software. Speciation diagram of (D) solution and (E) precipitate species from 1 mM LaCl₃ in 0.1 M NaCl in the presence of atmospheric carbon dioxide showing that the presence of carbon dioxide does not significantly affect the speciation of La at the selected concentration. Speciation diagram of (E) solution and (F) precipitate species from 10 mM LaCl₃ in 0.1 M NaCl showing that La(OH)₃(s) is still the predominant precipitate when the La concentration is increased to 10 mM.
Table I. Values used for the speciation of La in aqueous NaCl solutions.

| Species          | Logβ or LogKs | Source | Equilibrium expression                                                                 |
|------------------|---------------|--------|----------------------------------------------------------------------------------------|
| LaOH$_2$ (aq)    | 9.06          | $I = 50$ mM (NaCl),$^{20}$ | La$_3^{3+}$(aq) + H$_2$O(l) $\rightleftharpoons$ LaOH$_{2}^{2+}$(aq) + H$_3^{+}$(aq) |
| La(OH)$_2^{2+}$(aq) | 17.14        | Logβ$_2 = 1.83 \times \log β_1 - 0.565$,$^{21}$ | LaOH$_2^{2+}$(aq) + H$_2$O(l) $\rightleftharpoons$ La(OH)$_{3}^{+}$(aq) + H$_3^{+}$(aq) |
| La(OH)$_3$(aq)   | 23.44         | Logβ$_3 = 2.464 \times \log β_2 - 1.125$,$^{21}$ | La(OH)$_2^{2+}$(aq) + H$_2$O(l) $\rightleftharpoons$ La(OH)$_{4}^{2+}$(aq) + H$_3^{+}$(aq) |
| La(OH)$_3$(s)    | 19.6          | $I = 0$ mM,$^{20}$ | La$_3^{3+}$(aq) + H$_2$O(l) $\rightleftharpoons$ La(OH)$_{3}^{2+}$(aq) + H$_3^{+}$(aq) |

Figure 4. High-resolution XPS spectrum of the La 3d$_{5/2}$ region acquired from an electroprecipitated La film on a gold-coated QCM substrate. The acquired data (markers) were background subtracted and fitted to construct the multi-peak 3d$_{5/2}$ envelope (solid line). The envelope was deconvoluted according to Sunding,$^{22}$ The peak without charge transfer from the ligand is shown at 835.6 eV (dashed-dot), and the satellite peaks with charge transfer from the ligand are shown at 839.6 eV and 837.6 eV for the bonding and antibonding components, respectively. The chemical state of La was confirmed to be La(OH)$_3$. 

Figure 5. Top: Scanning electron micrograph of a precipitate of La(OH)$_3$(s). Bottom: Elemental maps constructed from Auger electron nanoprobe spectroscopy overlaid on the micrograph above. The bright regions correspond to increasing levels of the element as labeled.

Figure 6. The proposed mechanism of the electroprecipitation of lanthanum hydroxide on a polarized electrode. The numbers in circles refer to the equations given in the text.

Concentration-dependent response of La deposition on microelectrodes.—Since La deposition on carbon electrodes required pH changes driven by cathodic current near the electrode surface, we expected a concentration-dependent response. In addition, we compared the concentration-dependent response with that of an MFCFM which was used previously in the literature.$^6$ Figures 7A and 6B show the voltammetric responses to varying concentrations of La$_3^{3+}$ of a carbon fiber microelectrode and mercury-filmed carbon fiber.
Figure 7. Voltammetric responses to varying concentrations of La$^{3+}$ of A) a carbon fiber microelectrode (CFM) and B) a mercury-filmed carbon fiber microelectrode (MFCFM). C) The concentration-dependent responses are shown in C, where the dashed line represents the background current in the absence of La ions. The electrolyte consisted of 100 mM NaCl at pH 3.0. The MFCFM was prepared in situ and required the addition of 1 mM Hg(NO$_3$)$_2$ to the solution. A triangular potential waveform with limits at 0 V$_{Ag/AgCl}$ and $-2.65$ V$_{Ag/AgCl}$ and a scan rate of 20 mV/s was applied.

Conclusions

In this study, we investigated the mechanisms of La deposition on carbon-coated electrodes using electrogravimetric analysis via eQCM. Surface pH changes were correlated to the onset of La film formation using pH microelectrodes placed near the electrode surface. The eQCM allowed us to monitor the mass deposition of La. X-ray photoelectron spectrometry, scanning electron microscopy, and Auger electron nanoprobe spectrometry were used to determine the chemistry of the La deposits. Then we verified the same mechanisms for carbon fiber microelectrodes. Finally, we compared the performance of lanthanum sensing on and mercury-filmed carbon fiber microelectrodes. We concluded that:

1. The onset of film attachment and detachment on macroelectrodes corresponded to significant surface pH changes.
2. The films formed localized precipitates. The chemical composition of the precipitates was shown to be La(OH)$_3$.
3. La and O were colocalized on these precipitates.
4. There was a concentration-dependent electrochemical response on both mercury-filmed and carbon fiber microelectrodes.

Acknowledgment

This work was funded by HDTRA-1-14-10069. The authors thank Gretchen Tibbits for providing the pH microelectrodes. A.S.M. acknowledges NIGMS training grant T32 GM008336 and the ARCS.
Foundation of Seattle. The authors acknowledge Dr. Recep Avci and Dr. Manjula Nandasiri of the Imaging and Chemical Analysis Laboratory at Montana State University for valuable discussion regarding the XPS and AES results.

ORCID
Adan Schafer Medina https://orcid.org/0000-0003-4457-7023
Cornelius F. Ivory https://orcid.org/0000-0001-8602-1176
Nathalie A. Wall https://orcid.org/0000-0001-6101-7429
Haluk Beyenal https://orcid.org/0000-0003-3931-0244

References
1. S. Cotton, in Lanthanide and Actinide Chemistry, p. 9, John Wiley & Sons, Ltd (2006).
2. P. Janoš, Electrophoresis, 24, 1982 (2003).
3. A. J. Bard, R. Parsons, and J. Jordan, Standard Potentials in Aqueous Solution, p. 834, Marcel Dekker, INC., New York, NY (1985).
4. P. D. Schumacher, N. A. Woods, J. L. Doyle, J. O. Schenk, and S. B. Clark, Analytical Chemistry, 83, 4788 (2011).
5. P. D. Schumacher, N. A. Woods, J. O. Schenk, and S. B. Clark, Analytical Chemistry, 82, 5663 (2010).
6. L. Doyle Jamie and B. Clark Sue, Radiochimica Acta, 104, 707 (2016).
7. F. C. Anson, Accounts of Chemical Research, 8, 400 (1975).
8. J. T. Babauta, A. Medina, and H. Beyenal, Journal of The Electrochemical Society, 163, H866 (2016).
9. D. Johannsmann, Physical Chemistry Chemical Physics, 10, 4516 (2008).
10. D. Salt, Hy-Q Handbook of Quartz Crystal Devices, p. 229, Van Nostrand Reinhold (UK) Co. Ltd, England (1987).
11. G. Sauertrey, Zeitschrift für Physik, 155, 206 (1959).
12. D. R. Jenke and F. E. Diebold, Water Research, 18, 855 (1984).
13. P. M. S. Monk, R. Janes, and R. D. Partridge, Journal of the Chemical Society, Faraday Transactions, 93, 3991 (1997).
14. Z. Ji-ing, Z. Yun-hong, and Y. Hanxi, Journal of Power Sources, 69, 169 (1997).
15. A. B. Yousaf, M. Imran, M. Farooq, and P. Kasak, Scientific Reports, 8, 4354 (2018).
16. Z. Lewandowski and H. Beyenal, Fundamentals of Biofilm Research, p. 672, Taylor & Francis Group, LLC, Boca Raton, FL (2014).
17. E. Atci, J. T. Babauta, and H. Beyenal, Sensors and Actuators B: Chemical, 226, 429 (2016).
18. J. T. Babauta, H. D. Nguyen, and H. Beyenal, Environmental Science & Technology, 45, 6654 (2011).
19. C. M. Bethke, Geochemical and Biogeochemical Reaction Modeling, Cambridge University Press, Cambridge (2007).
20. P. L. Brown and C. Ekberg, in Hydrolysis of Metal Ions, p. 225, Wiley-VCH Verlag GmbH & Co. KGaA (2016).
21. J. R. Haas, E. L. Shock, and D. C. Sassani, Geochim. Cosmochim. Acta, 59, 4329 (1995).
22. M. F. Sunding, K. Hadidi, S. Diplas, O. M. Letvik, T. E. Norby, and A. E. Gunnars, Journal of Electron Spectroscopy and Related Phenomena, 184, 399 (2011).
23. J. F. Moulder, J. Chastain, and R. C. King, Handbook of X-ray Photoelectron Spectroscopy: A Reference Book of Standard Spectra for Identification and Interpretation of XPS Data, Physical Electronics (1995).
24. H. F. Mathieu, in Surface Analysis – The Principal Techniques, p. 9, John Wiley & Sons, Ltd (2009).