Electrochemical Production of Oxalate and Formate from CO₂ by Solvated Electrons Produced Using an Atmospheric-Pressure Plasma

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In this work, we use an atmospheric-pressure plasma in argon as a cathode to electrochemically reduce carbon dioxide in aqueous solution. Using optical absorption spectroscopy, we directly show that solvated electrons reduce CO₂(aq) to form the carboxyl radical anion CO₂−, and the reaction obeys 3D bulk reaction kinetics similar to those measured in radiolysis experiments. We then use liquid ion chromatography to show that the CO₂− intermediate ultimately reacts to produce oxalate and formate. The overall faradaic efficiency of the reaction is close to 10% for a CO₂(aq) concentration of 34 mM. However, given the known reaction kinetics of solvated electrons, this efficiency should approach 100% as the concentration of CO₂(aq) is increased.

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At a rate of over 30 billion tons per year, carbon dioxide (CO₂) gas represents one of the largest sources of human waste, with most of it coming from energy and cement production.1 Natural carbon sinks do not have the capacity to absorb such a massive amount of CO₂, so much of it ends up in the atmosphere, where it acts as a greenhouse gas. While one strategy is to capture and store (or sequester) waste CO₂,2,3 much of it ends up in the atmosphere, where it acts as a greenhouse gas. Scientists have approached the challenge of CO₂ reformation with a variety of tools and techniques including catalytic reduction,4,5 photoelectrochemical reduction,6,7 and electrochemical reduction8 to produce chemicals including carbon monoxide (CO), formic acid (HCOOH), oxalic acid (C₂H₂O₄), formaldehyde (CH₂O), and methanol (CH₃OH) among others. In catalysis, large molecules or rare earth metals have sites with low electron affinity9 onto which the CO₂ adsorbs and is reduced. In photoelectrochemical reduction, a photon (usually in UV range) promotes an electron in the cathode to an excited state with enough kinetic energy to reduce the CO₂(ads). In electrochemical reduction, an applied voltage drives electrons from the metal to the CO₂(ads), thus reducing it. These three approaches are not mutually exclusive and usually overlap with one another, yielding hybrid methods such as electrocatalytic10 and photoelectrocatalytic11 reduction processes.

All of these approaches require the adsorption of CO₂ onto some substrate, where it can be reduced to form reactive intermediates that ultimately yield the final products. Hence, the adsorption processes inherently limits the overall rate of reduction. To ameliorate this, significant attempts have been made to increase the surface-to-volume ratio of the cathode substrate. For example, metallic nanoparticles have been used as substrates for electrocatalytic12 and photocatalytic13 reduction. Recent work has also attempted to incorporate catalytic molecules into metal-organic frameworks, which have an extremely large surface-to-volume ratio.14

Radiolysis is also capable of reducing CO₂(aq) in the bulk and avoids the adsorption step all together. This approach uses energetic radiation to ionize the solution, creating solvated electrons (e−(aq)) and atomic hydrogen radicals (H•), which are both powerful reducing agents, throughout the bulk of the solution.14 The solvated electron, for example, has a reduction potential of −2.98 V, so it readily reduces CO₂(aq) via

\[
e^{-}(aq) + CO_{2}(aq) \rightarrow CO_{2}^{-}(aq), \tag{1}
\]

with measured the rate constant to be \( k_i = 7.7 \times 10^{9} \text{ M}^{-1} \text{ s}^{-1}. \)
Overall, radiolysis is highly inefficient and requires the use of expensive and often impractical radiation sources. As a compromise, various researchers have used moderately energetic ultraviolet (UV) sources to produce solvated electrons via photoemission from metallic cathodes.15 Recent work by Zhu et al. has directly shown that solvated electrons can be produced by illuminating a submerged diamond substrate with UV photons.17 Subsequent work by the group has shown that these solvated electrons reduce CO₂(aq) in the bulk solution to produce CO.18

An alternative approach to ionizing radiation or submerged photoemission is to inject free electrons from the gas-phase into the liquid from a plasma or gas discharge (Fig. 1a). Plasma electrochemistry,
also called glow discharge electrolysis, is an electrochemistry technique where one (or both) of the electrodes in an electrolytic cell is replaced by a plasma. In addition to their promise for exceeding faradaic reaction rates, they have long been assumed to produce solvated electrons. In our own recent work, we used a novel optical absorption technique to show that plasma-injected electrons solvate when a direct current (DC) atmospheric-pressure plasma is used as a cathode to electrolyze an aqueous solution. Further, we showed that these plasma-injected solvated electrons react very predictably with aqueous scavengers including gaseous species that dissolve from the plasma into solution. In contrast to conventional electrochemistry, there is no adsorption step required to initiate the reduction reaction, and in contrast to conventional radiolysis, this approach does not require high-energy radiation.

In this work, we use a DC plasma electrochemical system to explore the conversion of dissolved CO₂ into other useful products. Using our optical absorption technique, we show kinetically that a single plasma-injected solvated electron reduces a single CO₂(aq) molecule, likely producing the CO₂⁻(aq) radical as an intermediate. We then use liquid ion chromatography to show that the CO₂⁻(aq) radicals either combine to produce oxalate (CO₂⁻)₂ or undergo disproportionation to yield formate (HCO₂⁻), as is commonly observed in radiolysis experiments. Further, we demonstrate that by controlling the pH of the aqueous solution, we can manipulate the relative concentration of each of these products.

Experimental

For this work, we use a DC electrolytic cell configuration with a plasma cathode as shown in Fig. 1. Our plasma is formed by a stainless steel capillary (180 μm inner diameter) suspended ~1 mm above the surface of an aqueous solution and biased negatively (~2.5 kV) relative to a submerged platinum (Pt) electrode. While a working gas could be flowed through the capillary, for the studies shown here, we operate in an inert, atmospheric pressure argon (Ar) environment in the headspace of the vessel.

In our previous work, we developed a method of total internal reflection absorption spectroscopy (TIRAS) for directly measuring solvated electrons just beneath the plasma-liquid interface. In this method, a 670 nm red laser beam passes through the liquid and is reflected off of the plasma-liquid interface and into a detector. The angle of the incidence relative to the surface is shallow enough (17°) that it is totally reflected less the small amount absorbed by the solvated electrons, as illustrated schematically in Fig. 1. Although solvated electrons have a very large extinction coefficient, ε ≈ 1.6 × 10⁵ L mol⁻¹ cm⁻¹ at 670 nm, they are so highly reactive that they only penetrate several nanometers or so into the solution before reacting away. According to the Beer-Lambert Law, the optical absorbance I/I₀ for small optical densities is

\[
\frac{I}{I_0} = \frac{2\varepsilon l}{\sin \theta} \left[ c_{(aq)} \right],
\]

where l is the average penetration depth of the solvated electrons and θ is the angle of incidence relative to the liquid surface. The average penetration depth l is only on the order of 10 nm, so the absorbance is on the order of 1–10 ppm, such that in our TIRAS system a lock-in amplification technique is used to attain a sufficient signal-to-noise ratio. In short, the plasma is driven by a 2.5 kV DC power supply (PS325, Stanford Research Systems) and the plasma current is pulsed using a home built circuit at a 20 kHz carrier frequency between high (I₂max = 10.9 ± 0.8 mA) and low (I₁max = 5.6 ± 0.4 mA) currents, which modulates the concentration and optical absorbance at 20 kHz as well. The lock-in amplifier then filters all noise outside of the 20 kHz band. Additional details regarding the TIRAS method can be found in the Supplementary Information of Ref. 21.

In this work, the same TIRAS method was used to measure the relative concentration of solvated electrons as a function of CO₂(aq) concentration. Solutions were prepared by bubbling gaseous CO₂(aq) into an inert solution of 163 mM sodium perchlorate (NaClO₄, ACS reagent, ≥98.0%, Sigma Aldrich). It is necessary to have at least 0.1 mM of salt in the solution for conductivity, or else the interface will become charged and break into mechanical oscillations. Carbon dioxide readily dissolves in water with a well-known Henry’s constant of approximately 34 mM/atm. To achieve a desired concentration of [CO₂(aq)] < 34 mM, the CO₂(g) was mixed with Ar, using two mass flow controllers (one for each gas) to control the partial pressure of CO₂(g). The gas mixture was then bubbled into the solution under one atmosphere of total pressure. To achieve a desired concentration [CO₂(aq)] > 34 mM, the solution was placed in a hyperbaric chamber, and pure CO₂(g) was bubbled at a total pressure up to three atmospheres controlled by a regulator. Schematics of both methods for controlling [CO₂(aq)] can be found in the online supplementary material for this publication.

Dissolved CO₂(aq) undergoes an equilibrium reaction to produce carbonic acid (H₂CO₃), so the concentration [CO₂(aq)] can be roughly quantified by the pH of the solution. Using pH probe measurements, we determined that the solution becomes saturated with a pH of 3.73 after 5 minutes of sparging at 1 atmosphere of CO₂ at a rate of 20 sccm. Furthermore, we found that the pH remains constant for about 15 minutes following the sparge, even with an Ar (99.999% UHP T, Airgas) purge of the headspace. It is necessary to have at least 34 mM, the CO₂(g) was mixed with Ar, using two mass flow controllers (one for each gas) to control the partial pressure of CO₂(g). The gas mixture was then bubbled into the solution under one atmosphere of total pressure. To achieve a desired concentration [CO₂(aq)] > 34 mM, the solution was placed in a hyperbaric chamber, and pure CO₂(g) was bubbled at a total pressure up to three atmospheres controlled by a regulator. Schematics of both methods for controlling [CO₂(aq)] can be found in the online supplementary material for this publication.

Results and Discussion

At low concentrations of any competing reactants or scavengers, plasma-injected solvated electrons primarily undergo 2nd order recombination

\[
2e⁻_{(aq)} + 2H₂O → 2OH⁻ + H₂, \quad [3]
\]

with a rate constant of 2k_e = 1.1 × 10⁷ M⁻¹ s⁻¹, which produces hydrogen gas and makes the solution locally more basic just beneath the plasma-liquid interface. Note that in our prior work, we have observed H₂(g) and OH⁻(aq) produced by this reaction. However, in the presence of scavengers, the optical absorption signal is quenched, as the addition of these species lowers the average lifetime of the solvated electrons. Moreover, the signal decay is inversely proportional to the scavenger concentration for a sufficiently large concentration. Because solvated electrons react vigorously with CO₂(aq) via Reaction 1, we hypothesized that dissolving various amounts of CO₂ into our solution would quench the absorbance in the same manner. Figure 2a shows the normalized optical absorbance as a function of CO₂(aq) concentration for a solution of 163 mM NaClO₄. The signal is indeed quenched by the addition of CO₂(aq), just as we have observed with other electron scavengers, indicating that the CO₂(aq) is

\[
2e⁻_{(aq)} + 2H₂O → 2OH⁻ + H₂, \quad [3]
\]
reacting with the plasma-injected electrons, lowering their lifetime and equilibrium concentration.

To understand the quenching of the signal, we perform a simple rate balance of the various reactions for the solvated electron – the reduction of CO$_2$ (Reaction 1) and 2nd order recombination (Reaction 3). Assuming the electrons are created in a uniform volume of length $l$ at a rate proportional to the current density $j$, we have

$$
\frac{j}{F} = 2k_3[e_{aq}]^2 + k_S [CO_{2aq}],
$$

where $F$ is Faraday’s constant, $i$ is the average penetration depth of the electrons (~1–10 nm), $2k_3 = 1.1 \times 10^{10}$ M$^{-1}$ s$^{-1}$ is the rate constant for Reaction 3, and $k_S = 7.7 \pm 10^9$ M$^{-1}$ s$^{-1}$ is the rate constant for Reaction 1. For large concentrations of CO$_{2aq}$, we may neglect Reaction 3 and, solving for $[e_{aq}]$, arrive at

$$
[e_{aq}] = \frac{j}{k_S F CO_{2aq}},
$$

which holds that the equilibrium concentration of solvated electrons is inversely proportional to the concentration of dissolved CO$_{2aq}$. Combining Eqs. 2 and 5, the optical absorbance is also inversely proportional to the concentration of dissolved CO$_{2aq}$

$$
I/I_0 = \left(\frac{2\sigma j}{k_S F \sin^2 \theta}\right) [CO_{2aq}]^{-1}.
$$

Plotting the absorbance as a function of $[CO_2]^{-1}$, as shown in Fig. 2a, linearizes the data at higher CO$_{2aq}$ concentrations, which is in agreement with Eq. 6.

We can further analyze this data by noting that the intensity measured by the lock-in amplifier and shown in Fig. 2a is actually the RMS amplitude of the first Fourier mode of the 20 kHz-modulated absorbance. As such, the normalized intensity in Eq. 6 can be written more formally as

$$
\frac{\Delta I}{I_0} = \frac{\sqrt{2\pi}}{\sigma F k_S F \sin^2 \theta} [CO_{2aq}]^{-1},
$$

where $I_{high}$ and $I_{low}$ are the high and low currents of pulsed plasma (10.9 ± 0.8 mA and $I_{low} = 5.6 \pm 0.4$ mA, respectively), and $\sigma_p = 400 \pm 20$ μm is the plasma radius, which was determined by imaging the plasma and applying Gaussian fits to the measured radial intensity profiles (see the supplementary information of Ref. 21 for details on the fitting technique). Applying a linear curve fit to Fig. 2b and using Eq. 7, we extrapolate a rate constant of $k_S = 7.4 \pm 2.1 \times 10^9$ M$^{-1}$ s$^{-1}$, which is in good agreement with the published value of $k_S = 7.7 \times 10^9$ M$^{-1}$ s$^{-1}$ obtained from radiolysis experiments. Overall, this observed scaling and extrapolated rate constant provide direct evidence that a single plasma-injected electron reacts with a single CO$_{2aq}$, namely Reaction 1, to produce the carboxyl radical anion CO$_2^{-aq}$.

The carboxyl radical anion CO$_2^{-aq}$ generated by Reaction 1 is commonly produced and studied via radiolysis of formate solutions.27-29 These studies have found that it quickly reacts away via recombination to form oxalate

$$
CO_2^{-aq} + CO_2^{-aq} \rightarrow (CO_2^{-})_{2aq} \quad [8]
$$

with a measured rate constant $2k = 1.4 \times 10^9$ M$^{-1}$ s$^{-1}$.27,29 Under acidic conditions, the CO$_2^{-aq}$ radical will undergo the equilibrium reaction

$$
CO_2^{-aq} + H^+ \leftrightarrow CO_2 H^{-aq} \quad [9]
$$

with a pKa value of ≈3.9 measured by Fotjik et al.27 and ≈2.3 measured by Flynn et al.28 The CO$_2$H radical is unstable, and is believed to undergo a disproportionation mechanism that ultimately yields HCO$_3^-$ and CO$_2$.28

Given the similarity between the kinetics of the solvated electrons in our plasma system and the kinetics observed in radiolysis, it is likely that the reaction kinetics of the CO$_2^{-aq}$ radical are also similar to that of radiolysis. That is, we expect to see oxalate produced under basic conditions and formate produced under acidic conditions. To determine the end products made in our system, we performed liquid ion chromatography on solutions of either 2 mM H$_2$SO$_4$ or 20 mM NaOH with 34 mM of CO$_2(aq)$ that had been treated continuously by our DC plasma for 5 min with $l \approx 9.5$ mA in a split H-cell (shown in Fig. 3a). The experiment was performed a total of five times for both types of solution.

Representative ion chromatograms from the treated solutions for both NaOH and H$_2$SO$_4$ are shown in Figs. 3b and 3c, respectively. Treating the solutions with the plasma causes a peak corresponding to oxalate to appear in both chromatograms. However, in the acidic case, a large peak corresponding to formate also appears. The formate peaks also appear in some cases for NaOH, but at far lower intensities. While we show only two solution conditions here, corresponding to pH = 2.45 and pH = 12.3, we do note that we explored a wide variety of solution conditions. In general, we found that oxalate was always formed regardless of pH, but the a significant formate peak was only observed for pH < 3. As noted above, because of Reaction 3, the solution becomes locally basic beneath the plasma-liquid interface at neutral pH conditions. For acidic conditions, the solvated reactions react directly with the excess protons via

$$
e^{-aq} + H^+ \rightarrow H_{aq}, \quad [10]$$

Figure 2. (a) The measured (normalized) optical absorbance signal as a function of the concentration of dissolved CO$_{2aq}$ for 163 mM NaClO$_4$. (b) The measured (normalized) optical absorbance signal as a function of the inverse of the concentration of dissolved CO$_{2aq}$ for 163 mM NaClO$_4$. The slope of the linear curve fit (solid line) yields an extrapolated rate constant $k_S = 7.4 \pm 2.1 \times 10^9$ M$^{-1}$ s$^{-1}$. All error bars represent the standard repeatability uncertainty at 90% confidence.
The faradaic efficiency for oxalate and formate production was then calculated using

$$\eta = \frac{zFCV}{it},$$

where $z$ is the integer charge of the product ($z=1$ for formate, $z=2$ for oxalate), $C$ is the measured concentration of the product, $V=20$ mL is the volume of treated solution, $i$ is the measured current, and $t=300$ s is the time the solution was treated.

Table 1 shows the average concentrations and faradaic efficiency for the production of both formate and oxalate. The total faradaic efficiency for both formate and oxalate is $\approx 8.9\%$ in $\text{H}_2\text{SO}_4$ and $\approx 7.9\%$ in NaOH. This low faradaic efficiency was unexpected. Some of the electrons likely undergo Reaction 3, which produces $\text{H}_2$ and $\text{OH}^-$. These cathodic reactions, driven by the plasma-solvated electrons, are balanced by oxidative water electrolysis at the anode, which we have also observed in our previous work. However, the well-known kinetics of the solvated electron suggest that only a small fraction of the electrons should undergo Reaction 3. In our previous work, we estimated that $[\text{e}^{(aq)}]\approx 1$ mM or less for the plasma current and solution composition studied here. Given that $[\text{CO}_2^{(aq)}]=34$ mM, it can be shown that Reaction 1 proceeds much faster than Reaction 3 (i.e. $k_1[\text{e}^{(aq)}][\text{CO}_2^{(aq)}]\gg 2k_3[\text{e}^{(aq)}]^3$), and over 90% if the injected electrons should reduce $\text{CO}_2^{(aq)}$. This is in sharp contrast with the $<10\%$ faradaic efficiency measured for combined oxalate and formate production. A likely explanation for the disparity is that the intermediate $\text{CO}_2^{(aq)}$ participates in other reaction pathways separate from or even following Reactions 8 and 9 yielding neutral products such as $\text{CH}_3\text{OH}, \text{CH}_2\text{O}$, or $\text{HCOOH}$, which were not detected by liquid ion chromatography. That is, it is possible other undetected products are produced by subsequent reactions, lowering the effective faradaic efficiency of oxalate and formate production.

Figures 3. (a) A schematic of the H-cell configuration used to prepare samples for ion chromatography and representative ion chromatograms for (b) 20 mM NaOH and (c) 2 mM $\text{H}_2\text{SO}_4$ for 34 mM of $\text{CO}_2^{(aq)}$ and 5 min exposure to a 10 mA DC argon plasma. A peak corresponding to oxalate is clearly seen in the $\text{H}_2\text{SO}_4$. Other peaks are due to contaminants introduced by the $\text{CO}_2(g)$ purge. 

| Concentrations and faradaic efficiencies for formate and oxalate production after 5 minutes of plasma treatment at $i \approx 9.5$ mA in solutions of 2 mM $\text{H}_2\text{SO}_4$ (pH 2.45) and 20 mM NaOH (pH 12.3). |
|-------------------------------------------------|-----------------|
| Oxalate Concentration (µM) | 47 ± 11 | 49 ± 6 |
| Oxalate faradaic Efficiency, $\eta_{ox}$ | 6.5 ± 1.5% | 6.6 ± 0.7% |
| Formate Concentration (µM) | 35 ± 16 | 18 ± 3 |
| Formate faradaic Efficiency, $\eta_f$ | 2.4 ± 1.1% | 1.3 ± 0.2% |
| Total faradaic Efficiency, $\eta_{total}$ | 8.9 ± 1.9% | 7.9 ± 0.7% |
| Current Density, $j$ (A/m²) | 7950 ± 180 | 12860 ± 250 |

The concentration of solvated electrons is approximately 0.1–1 mM. It is unlikely the local concentration of neutral OH radicals is any higher than this, because they are more reactive than solvated electrons, are not forced into solution by the electric field, and have a free energy of solvation that is an order of magnitude lower than the solvated electron. While the kinetics of solvated electrons posit that the faradaic efficiency should approach 100%, it must be noted that the thermodynamic efficiency is quite low. The plasma voltage from the cathode to the anode is measured to be approximately -200 V, so the electrons will dissipate nearly 200 eV of kinetic energy in the plasma before becoming solvated. However, much of the energy dissipated in the plasma can be used to drive gas phase reactions such as

$$\text{e}^{-} + \text{CO}_2(g) \rightarrow \text{CO}_2(g) + \text{O}_2 + \text{e}^{-},$$

which is often used in plasma reactors for $\text{CO}_2$ splitting. This reaction combined with Reaction 3 would yield syngas in addition to oxalate, which would produce two useful products from a combination of gaseous and dissolved $\text{CO}_2$ reforming. Another distinct advantage

$$e^{-}(aq) + \text{H}_2\text{O}(aq) \rightarrow \text{OH}^{-} + \text{H}_2(g).$$

Hydroxide produced via Reaction 3 or Reaction 11 will also neutralize the acid via

$$\text{OH}^{-} + \text{H}^+ \rightarrow \text{H}_2\text{O}.$$
of the plasma cathode is that it is essentially composed of argon gas, which is cheap and abundant, unlike most catalyst materials.

Summary

Using an optical absorbance measurement, we have directly shown that free electrons from an atmospheric pressure plasma can be driven into solution where they solvate and reduce CO$_2$(aq), producing the carboxyl radical anion CO$_2^-$ (aq). The kinetics of this reduction are similar to the bulk kinetics observed in radiolysis experiments. Most of the CO$_2^-$ (aq) ions typically recombine to produce oxalate in basic solutions, while some undergo a disproportionation mechanism, which yields formate. As such, we measured the production of formate to be much more pronounced under strongly acidic conditions. The total faradaic efficiency for the production of oxalate and formate was just below 10% at CO$_2$(aq) concentrations of 34 mM. In theory, this could certainly be improved by increasing the concentration of dissolved CO$_2$, but it is possible that competing side reactions that produce other products will always limit oxalate and formate products. While both the faradaic and thermodynamic efficiency of our process is low compared to electrochemical- and photocatalysis-based approaches, the plasma cathode is inexpensive and highly renewable compared to most electrode materials and catalysts.

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References

1. P. Friedlingstein, R. M. Andrew, J. Rogelj, G. P. Peters, J. G. Canadell, R. Knutti, G. Luderer, M. R. Raupach, M. Schaeffer, D. P. van Vuuren, and C. Le Quéré, Nature Geoscience, 7, 709 (2014).
2. R. S. Haszeldine, Science, 325, 1647 (2009).
3. J. Qiao, Y. Liu, F. Hong, and J. Zhang, Chem. Soc. Rev., 43, 631 (2014).
4. B. Kumar, M. Llorente, J. Froehlich, T. Dang, A. Satrum, and C. P. Kubiak, Annu. Rev. Phys. Chem., 63, 541 (2012).
5. E. E. Barton, D. M. Rampulla, and A. B. Bocarsly, J. Am. Chem. Soc., 130, 6342 (2008).
6. C. G. Vayenas, R. E. White, and M. E. Gamboa-Aldeco, Modern Aspects of Electrochemistry, Number 42, p. 89, edited by C. Vayenas et al., Springer, New York (2008).
7. J. B. Sambur, T.-Y. Chen, E. Choudhary, G. Chen, E. J. Nissen, E. M. Thomas, N. Zoa, and P. Chen, Nature, 530, 77 (2016).
8. M. Le, M. Ren, Z. Zhang, P. T. Sprunger, R. L. Kurtz, and J. C. Flake, J. Electrochem. Soc., 158, E45 (2011).
9. T. Reda, C. M. Plagge, N. J. Abram, and J. Hirst, Proc. Natl. Acad. Sci. USA, 105, 10654 (2008).
10. T. Inoue, A. Fujishima, S. Konishi, and K. Kenichi, Nature, 277, 637 (1979).
11. E. Andrews, S. Katla, C. Kumar, M. Patterson, P. Sprunger, and J. Flake, J. Electrochem. Soc., 162, F1373 (2015).
12. D. Beydoun, R. Amal, G. Low, and S. McEvoy, Journal of Nanoparticle Research, 1, 439 (1999).
13. I. Hod, M. D. Sampson, P. Deria, C. P. Kubiak, O. K. Farha, and J. T. Hupp, ACS Catal., 5, 6302 (2015).
14. G. V. Buxton, C. L. Greenstock, W. P. Helman, and A. B. Ross, J. Phys. Chem. Ref. Data, 17, 513 (1988).
15. S. Gordon, E. J. Hart, M. S. Matheson, J. Rabani, and J. K. Thomas, Discuss. Faraday Soc., 36, 193 (1963).
16. S. Kaposita and N. Hackerman, J. Electrochem. Soc., 130, 607 (1983).
17. D. Zhu, L. Zhang, R. E. Ruther, and R. J. Hamers, Nature Mater., 12, 836 (2013).
18. L. Zhang, D. Zhu, G. M. Nathanson, and J. R. Hamers, Angew. Chem., 126, 9904 (2014).
19. A. R. Denaro and A. Hickling, J. Electrochem. Soc., 155, 265 (1958).
20. J. Goodman, A. Hickling, and B. Schofield, J. Electroanal. Chem. Interfacial Electrochem., 48, 319 (1973).
21. P. Rumbach, D. M. Bartels, R. M. Sankaran, and D. B. Go, Nature Commun., 6, 7248 (2015).
22. R. Sander, Atmos. Chem. Phys., 15, 4399 (2015).
23. D. A. Mctunes and D. Belcher, J. Am. Chem. Soc., 55, 2630 (1933).
24. P. Rumbach, M. Witzke, R. M. Sankaran, and D. B. Go, J. Am. Chem. Soc., 135, 16264 (2013).
25. P. Rumbach, D. M. Bartels, R. M. Sankaran, and D. B. Go, J. Phys. D: Appl. Phys., 48, 424100 (2015).
26. M. Witzke, P. Rumbach, D. B. Go, and R. M. Sankaran, J. Phys. D: Appl. Phys., 45, 44201 (2012).
27. A. Fojtik, G. Czapski, and A. Henglein, J. Phys. Chem., 74, 3204 (1970).
28. R. Flyunt, M. N. Schuchmann, and C. von Sonntag, Chem. Eur. J., 7, 796 (2001).
29. M. Lin, Y. Katsumura, Y. Muroya, H. He, T. Miyazaki, and D. Hiroishi, Rad. Phys. Chem., 77, 1208 (2008).
30. B. Y. Locke and K.-Y. Shih, Plasma Sources Sci. Technol., 20, 034006 (2011).
31. R. Aeris, W. Somers, and A. Bogerts, ChemSusChem, 8, 702 (2015).
32. H. S. Kwak, H.-S. Uhm, Y. C. Hong, and E. H. Choi, Scientific Reports, 5 (2015).