SUPPORTING INFORMATION

Unveiling the cerium(III)/(IV) structures and charge transfer mechanism in sulfuric acid

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Section S1. Reported kinetic data for Ce$^{3+}$/Ce$^{4+}$ redox couple on various electrodes and in different acids

Table S1. Kinetics parameters for Ce$^{3+}$/Ce$^{4+}$ charge transfer for different electrodes and electrolytes, through different measurement methods. Kinetic parameters reported include standard rate constant, $k_0$, exchange current density, $i_0$, the split between reduction and oxidation peaks, $\Delta E_p$, and anodic and cathodic charge transfer coefficients, $\alpha_a$ and $\alpha_c$. In the main text we are referring to cathodic charge transfer when we report the charge transfer coefficient.

| Electrode          | Electrolyte | [Acid] (M) | [Ce$^{3+}$] (M) | [Ce$^{4+}$] (M) | Method                                                                 | Method                                                                 | Kinetic Parameters | Ref |
|--------------------|-------------|------------|-----------------|-----------------|------------------------------------------------------------------------|------------------------------------------------------------------------|--------------------|-----|
|                    | HClO$_4$    | 1          | 0.01$^{(b)}$    | 0.001–0.01$^{(b)}$ | Polarization resistance; Ce$^{4+}$ reduction                         | Polarization resistance; Ce$^{4+}$ reduction                         | $k_0 \times 10^4$ (cm s$^{-1}$) | $i_0 \times 10^2$ (mA cm$^{-2}$) | $\Delta E_p$ (mV) | $\alpha_a$ | $\alpha_c$ | |
| Au                 | H$_2$SO$_4$ | 1          | –               | 0.01$^{(b)}$    | Radiochemical & Cyclic Voltammetry (CV); Ce$^{4+}$ reduction          | Radiochemical & Cyclic Voltammetry (CV); Ce$^{4+}$ reduction         | 1.8–2.1$^{(a)}$ | –               | –               | –               | 0.33     | 1 |
|                   |             | 1          | 0.01$^{(b)}$    | 0.0001–0.01$^{(b)}$ | Polarization resistance; Ce$^{4+}$ reduction                         | Polarization resistance; Ce$^{4+}$ reduction                         | 3.8                | 9–29            | –               | 0.65±0.1 | –             | 1 |
|                   |             | 1          | –               | 0.001–0.01      | Tafel; Ce$^{4+}$ reduction                                          | Tafel; Ce$^{4+}$ reduction                                          | 39                 | –               | –               | –               | 0.16     | 3 |
|                   |             | 0.5        | 0.02            | –               | Current-Overpotential curve; Rotating Disk Electrode (RDE); Ce$^{4+}$ oxidation | Current-Overpotential curve; Rotating Disk Electrode (RDE); Ce$^{4+}$ oxidation | 0.73               | –               | –               | –               | 0.16     | 4 |
|                   |             | 0.5        | 0.0013          | 0.0013          | CV; Koutecký-Levich; Tafel                                           | CV; Koutecký-Levich; Tafel                                          | 6.2–14.2$^{(c)}$ | –               | –               | 0.12–0.13$^{(c)}$ | – | 5 |
| Boron-doped Diamond | HClO$_4$    | 0.1        | 0.01            | –               | CV; Current-Overpotential curve; Ce$^{3+}$ oxidation                 | CV; Current-Overpotential curve; Ce$^{3+}$ oxidation                 | 0.16               | 1.5             | –               | 0.29     | –             | 6 |
|                   | HNO$_3$     | 0.1        | 0.01            | –               | CV; Current-Overpotential curve; Ce$^{3+}$ oxidation                 | CV; Current-Overpotential curve; Ce$^{3+}$ oxidation                 | 0.14               | 1.4             | –               | 0.27     | –             | 6 |
|                   | H$_2$SO$_4$ | 0.1        | 0.01            | –               | CV; Current-Overpotential curve; Ce$^{3+}$ oxidation                 | CV; Current-Overpotential curve; Ce$^{3+}$ oxidation                 | 0.02               | 0.19            | –               | 0.28     | –             | 6 |
| graphite           | H$_2$SO$_4$/ MSA | 1:1    | 0.2             | 0.2             | CV; Linear Sweep Voltammetry (LSV); Current-Overpotential curve     | Current-Overpotential curve; Chronoamperometry                       | 4.17               | 810             | –               | –        | –             | 7 |
|                   | MSA         | 2          | 0.25            | 0.25            | CV; LSV; Current-Overpotential curve; Chronoamperometry             | Chronoamperometry                                                    | 4.06               | 980             | –               | –        | –             | 8 |
|                   |             | 1          | 0.05            | –               | CV                                                                     | CV                                                                     | 0.992              | –               | –               | –        | –             | 9 |
| Glassy Carbon      | HClO$_4$    | 1          | –               | 0.167           | CV                                                                     | –                                                                      | –                  | –               | 290             | –        | –             | 10|
|                   | HNO$_3$     | 1          | 0.02            | –               | CV                                                                     | –                                                                      | 20                 | –               | –               | –        | –             | 11|
|                   | H$_2$SO$_4$ | 4          | 0.02            | –               | CV; LSV; Ce$^{3+}$ oxidation                                         | –                                                                      | 0.5                | 200             | 0.91            | –        | 12            |
|                   |             | 1          | –               | 0.010           | Radiochemical & CV; Ce$^{4+}$ reduction                             | Radiochemical & CV; Ce$^{4+}$ reduction                             | 2.4–4.0$^{(a)}$     | –               | –               | –        | 0.25          | 2 |
|                   |             | 1          | 0.01            | –               | CV                                                                     | –                                                                      | –                  | 261             | –               | –        | 13            |
|                   |             | 1          | –               | 0.167           | CV                                                                     | –                                                                      | –                  | 220             | –               | –        | 10            |
|                   |             | 0.5        | 0.02            | –               | Current-Overpotential curve; RDE; Ce$^{3+}$ oxidation                | Current-Overpotential curve; RDE; Ce$^{3+}$ oxidation                | 0.87               | –               | –               | –        | 0.49          | 4 |
|                   |             | 1          | 0.012           | –               | CV                                                                     | –                                                                      | –                  | 1200            | –               | –        | 14            |

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| Glassy Carbon | MSA | 1 | 0.034 | – | CV | 35.2–36.8 \(^{a,b}\) | – | – | – | – | – | 15 |
| Glassy Carbon | MSA | 4 | 0.034 | – | CV | 58.0–85.4 \(^{a,b}\) | – | – | – | – | – | 15 |
| Glassy Carbon | MSA | 1 | – | 0.167 | CV | – | – | 290 | – | – | – | 10 |
| Ir | H\(_2\)SO\(_4\) | 1 | – | 0.010 | Radiochemical & CV; Ce\(^{4+}\) reduction | 3.2–4.3 \(^{a}\) | – | – | – | – | 0.26 | 2 |
| Pt | H\(_2\)SO\(_4\) | 0.5 | 0.019 | 0.003–0.044 | Current-Overpotential curve; Butler Volmer (BV) formulism; Ce\(^{4+}\) reduction | 0.75–1.21 | – | – | – | – | 0.12–0.13 | 16 |
| Pt | H\(_2\)SO\(_4\) | 0.5 | 0.004–0.058 | 0.007 | Current-Overpotential curve; BV formulism; Ce\(^{3+}\) oxidation | 0.35–1.01 | – | – | – | 0.59–0.87 | – | 16 |
| Pt | H\(_2\)SO\(_4\) | 1.25 | 0.2 | 0.2 | CV | 2.96 | – | – | 0.197 | 0.16 | 17 |
| Pt | H\(_2\)SO\(_4\) | 2 | 0.0013 | 0.0013 | Current-Overpotential curve; Butler Volmer (BV) formulism; Ce\(^{3+}\) oxidation | 0.35–1.01 | – | – | – | 0.59–0.87 | – | 16 |
| Pt | H\(_2\)SO\(_4\) | 0.5 | 0.016 | 0.012 | Current-Overpotential curve; Butler Volmer (BV) formulism; Ce\(^{3+}\) oxidation | 3.7 | – | – | 0.4 | 0.2 | 20 |
| Pt | H\(_2\)SO\(_4\) | 1 | – | 0.1 | Current-Overpotential curve; Butler Volmer (BV) formulism; Ce\(^{3+}\) oxidation | 3.7 | – | – | 0.4 | 0.2 | 20 |
| Pt | H\(_2\)SO\(_4\) | 1 | – | 0.1 | Current-Overpotential curve; Butler Volmer (BV) formulism; Ce\(^{3+}\) oxidation | 3.7 | – | – | 0.4 | 0.2 | 20 |
| Pt | H\(_2\)SO\(_4\) | 1 | – | 0.1 | Current-Overpotential curve; Butler Volmer (BV) formulism; Ce\(^{3+}\) oxidation | 3.7 | – | – | 0.4 | 0.2 | 20 |
| Pt | H\(_2\)SO\(_4\) | 1 | – | 0.1 | Current-Overpotential curve; Butler Volmer (BV) formulism; Ce\(^{3+}\) oxidation | – | – | 13×10\(^5\) | – | – | 0.3 | 19 |
| Pt | H\(_2\)SO\(_4\) | 0.5 | 0.02 | – | Current-Overpotential curve; Butler Volmer (BV) formulism; Ce\(^{3+}\) oxidation | 0.35 | – | – | – | 0.3 | 4 |
| Pt | H\(_2\)SO\(_4\) | 0.5 | 0.01 | – | Current-Overpotential curve; Butler Volmer (BV) formulism; Ce\(^{3+}\) oxidation | 0.35 | – | – | – | 0.3 | 4 |
| Pt | H\(_2\)SO\(_4\) | 1 | 0.0001 | 0.001 | Current-Overpotential curve; Butler Volmer (BV) formulism; Ce\(^{3+}\) oxidation | – | 13×10\(^5\) | – | – | 0.3 | 19 |
| Pt | NH\(_2\)SO\(_3\) | 2 | 0.25 | 0.25 | Current-Overpotential curve; Chronoamperometry | 0.55 | 130 | – | – | – | 8 |
| Pt | NH\(_2\)SO\(_3\) | 4 | 0.8 | – | Current-Overpotential curve; Chronoamperometry | – | – | 738 | – | – | 24 |
| Pt | NH\(_2\)SO\(_3\) | 4.5 | 0.02 | 0.2 | Current-Overpotential curve; Chronoamperometry | – | – | 37×10\(^5\) (Tafel), 24×10\(^3\) (EIS) | – | – | 25 |
| Pt | NH\(_2\)SO\(_3\) | 4.5 | 0.2 | 0.6 | Tafel method, Linear polarization, EIS | – | – | 24–67 \(^{a}\) | – | – | 26 |
| Pt | NH\(_2\)SO\(_3\) | 1 | 0.3 | 0.1 | Current-Overpotential curve; Tafel | 0.5 | 60 | – | – | – | 27 |
| SnO$_2$ on graphite felt | MSA   | 1  | 0.05 | −   | CV  | 499 | −   | 199 | −   | −   | 9   |
|--------------------------|-------|----|------|-----|-----|-----|-----|-----|-----|-----|-----|
| VCE$^{10}$ | HNO$_3$ | 1  | 0.015 | −   | CV  | 20  | −   | −   | −   | −   | 28  |

(a) A range of rate constants is provided for electrodes studied by Keikens et al. because several independent methods of calculating the rate constant were compared.

(b) Reported in Normality (N), converted to Molarity (M).

(c) In study by Sacchetto et al., the electrochemical behavior on a gold electrode was reportedly irreproducible, so kinetic parameters of the two extreme cases of behavior are reported here.

(d) A range of rate constants is provided by Devadoss et al. based on scan rate used in CV.

(e) Diethylenetriaminepentaacetic acid.

(f) Vitreous carbon electrode.

(g) In study by Nikiforidis et al., three different exchange current densities were reported because of different methods of collecting exchange current density.
Section S2. Additional EXAFS analysis of Ce³⁺ species

EXAFS standard for Ce³⁺ at Ce K-edge and L₃-edge

The fits in the k space and the magnitude component in the R space of the CeCl₃-7H₂O standard EXAFS at the Ce K-edge are shown in Fig. S1a and Fig. S1b, respectively. The fit of the CeCl₃-7H₂O standard EXAFS at the Ce L₃-edge in both the R space and the k space is included in Fig. S2. From the fits of the CeCl₃-7H₂O standard at both edges, it is evident that both Ce-O and Ce-Cl scattering paths are necessary in the fit to capture the EXAFS spectra. The fitting results for both edges are included in Table S2. Although typically the amplitude reduction factor, $S_0^2$, is not larger than 1.0, we see values greater than 1.0 for both edges here. One hypothesis for why we see $S_0^2$ values >1.0 here is that multi-electron excitation (MEE) effects were not corrected for, which are known to be prevalent for Ce samples.²⁹,³⁰ Having accurate $S_0^2$ from the CeCl₃-7H₂O is necessary to get accurate coordination numbers for our fits of the cerium ions.

Fig. S1. Ce K-edge $k^2\chi(R)$ EXAFS and fit of CeCl₃-7H₂O standard. (a) CeCl₃-7H₂O standard (orange solid line) with fit (red dashed line) in the k space. (b) CeCl₃-7H₂O standard (orange solid line) with fit (red dashed line) and Ce-O and Ce-Cl path contributions (shifted in y-axis) in the R space (magnitude).

Fig. S2. Ce L₃-edge $k^2\chi(R)$ EXAFS and fit of CeCl₃-7H₂O standard. (a) Imaginary component of Ce L₃-edge EXAFS in the R space of CeCl₃-7H₂O standard (orange solid line) with fit (red dashed line), and Ce-O and Ce-Cl path contributions (shifted in y-axis). (b) Ce L₃-edge EXAFS of CeCl₃-7H₂O standard (orange solid line) with fit (red dashed line) in the k space. (c) Magnitude component of Ce L₃-edge EXAFS in the R space of CeCl₃-7H₂O standard (orange solid line) with fit (red dashed line), and Ce-O and Ce-Cl path contributions (shifted in y-axis).
Table S2. K- and L3-edge fit parameters of CeCl3-7H2O standard. Fitting results for CeCl3-7H2O standard at the Ce L3- and K-edges from ARTEMIS, fitting with a Ce-O shell and a Ce-Cl shell. The following parameters were varied in the fit: amplitude reduction factor (S0), the shift in threshold energy (ΔE0), the shift in scattering distance ΔR, and the Debye-Waller factor (σ²). The coordination number (CN) for each shell was set as a fixed global parameter. The scattering distance R included in the Table is calculated by adding the ΔR fitted value to the expected scattering distance from the FEFF path (see Methods).

| Edge | S0² | ΔE0 (eV) | Ce-O shell R (Å) | CN (set) | Ce-Cl shell R (Å) | CN (set) | σ² (Å²) |
|------|-----|----------|------------------|---------|------------------|---------|---------|
| L3   | 1.1±0.2 | -0.58±1.59 | 2.556±0.024 | 7.7     | 2.942±0.083     | 1.3     | 0.009±0.005 |
| K    | 1.5±0.1  | -2.51±0.80 | 2.555±0.010 | 7.2     | 2.950±0.021     | 1.8     | 0.011±0.001 |

Individual and co-fits of Ce K-edge and L3-edge for Ce³⁺

The co-fit of the Ce K- and L3-edge EXAFS of Ce³⁺ in 2 M H2SO4 at the Ce K-edge with the Ce-O shell is shown in the k space and the R space (magnitude) in Fig. S3a and S3b. The results of this co-fit at the Ce-L3 edge are included in Fig. S4. In the fit, we used the edge-specific S0² and shift in threshold energy, ΔE0, from the CeCl3-7H2O standard as global fixed parameters. We varied path specific parameters (coordination number, CN, shift in scattering distance, ΔR, and the Debye-Waller factor, σ²) to obtain the best fit of the data. Fitting results are included in Table S3. It should be noted that the fit of the Ce³⁺ EXAFS at the Ce L3-edge (Fig. S4) does not visually capture the magnitude of the spectrum in the R space. We attribute this to artificial features that were not removed during the background removal and normalization procedure, as evidenced by the strong features occurring between 0 and 0.5 Å, wherein it is known that no real scattering event can be occurring. Additionally, it can be seen from the k data (Fig. S4b) that the data exhibits poor quality after ~6.0 Å⁻¹, most likely due to MEE effects as well as the interference of the L2-edge.

Fig. S3. Ce K-edge k²χ(R) EXAFS and co-fit of 0.05 M Ce³⁺ in 2 M H2SO4 with a Ce-O scattering path. (a) Ce K-edge EXAFS in the k space of 0.025 M Ce₂(CO₃)₃ in 2 M H2SO4 (blue solid line) with co-fit with L3-edge (red dashed line) using a Ce-O scattering path. (b) Magnitude component Ce K-edge EXAFS in the R space of 0.025 M Ce₂(CO₃)₃ in 2 M H2SO4 (blue solid line) with co-fit (red dashed line) using a Ce-O scattering path. Results of co-fit at Ce L3-edge are included in Fig. S4.
To confirm the trends that we observed in the co-fit shown above, we used an additional set of Ce L₃-edge Ce⁴⁺ in H₂SO₄ EXAFS data, which we collected during a different beamline run than that shown in the main text. This data set demonstrated fewer quality issues in the k space, and when normalized, exhibited fewer background features. When we co-fit these data with the Ce K-edge data, the resulting CN, ΔR, and
$\sigma^2$ were similar to those reported in Table S3, and the fit was visually in greater agreement with the EXAFS data. We could not use this set of $L_3$-edge data in the final co-fit, however, because we did not collect EXAFS of a Ce$^{3+}$ standard for that specific run. Instead, to obtain a value for $S_0^2$ for this data set, we relied on a method similar to our process from our previous work, in which we fit the Ce$^{3+}$ EXAFS with a CN set to 9 while guessing $S_0^2$. We then fixed the $S_0^2$ value to the one obtained from the previous fit and allowed CN to vary. We acknowledge that it is preferable to use a Ce$^{3+}$ standard to obtain accurate an $S_0^2$ value, and so we report the fit of the Ce$^{3+}$ EXAFS at the Ce $L_3$-edge for which we also collected EXAFS of a standard, despite the poorer quality and resulting worse visual fit.

We show the results of co-fitting the Ce K- and $L_3$-edge Ce$^{3+}$ in $H_2SO_4$ EXAFS with Ce-O and Ce-S scattering paths in Fig. S5, and the fitting parameter values for this co-fit are included in Table S3. The resulting fit was unreasonable, with the CN for the Ce-S scattering path unreasonably large with an uncertainty that is larger than the actual fitted CN ($7.3\pm7.4$ Å). Thus, we conclude that there is no conclusive evidence that Ce$^{3+}$ is complexed by a sulfate or bisulfate in the first coordination shell.

![Fig. S5. Ce K- and L3-edge k^2\chi(R) EXAFS and co-fit of Ce^{3+} in 2 M H_2SO_4 with Ce-O and Ce-S scattering paths. Ce K-edge EXAFS of 0.025 M Ce_2(CO_3)_3 in 2 M H_2SO_4 (blue solid line) with co-fit with L3-edge (red dashed line) using Ce-O and Ce-C scattering paths, in the (a) R space (imaginary), (b) k space, and (c) R space (magnitude). Ce L3-edge EXAFS of 0.05 M Ce_2(CO_3)_3 in 2 M H_2SO_4 (blue solid line) with co-fit with K-edge (red dashed line) using Ce-O and Ce-S scattering paths, in the (d) R space (imaginary), (e) k space, and (f) R space (magnitude).](#)

To further probe the influence of anions on Ce$^{3+}$ EXAFS, we compared the EXAFS of Ce$^{3+}$ at the Ce K-edge and fits with a Ce-O scattering path in three different acids: 2 M $H_2SO_4$ (Fig. S6a-c), 2 M CF_3SO_2H (TFSA, Fig. S6d-f), and 2 M CH_3SO_3H (MSA, Fig. S6g-i). The results of the fit at only the K-edge for each of these acids is included in Table S3. Although the CN obtained from the Ce-O fit for Ce$^{3+}$ in $H_2SO_4$ is lower than that obtained from the co-fit, the uncertainty ($\pm0.6$) is large enough to suggest coordination with either 8 or 9 water molecules. Our DFT and EXAFS evidence of Ce$^{3+}$ coordination with 9 water molecules from our previous work, resolves this uncertainty from the fit of the EXAFS at just the Ce K-edge. The Ce$^{3+}$-O scattering distance in $H_2SO_4$ is slightly larger than the scattering distance in either TFSA or MSA. As discussed in the main text, if Ce$^{3+}$ were complexed by sulfate or bisulfate in
H$_2$SO$_4$, the Ce$^{3+}$-O distance would be expected to be smaller than a Ce$^{3+}$-O scattering distance in which the Ce$^{3+}$ was coordinated only by water, e.g., Ce$^{3+}$ in MSA or TFSA. This supports that Ce$^{3+}$ is not complexed by sulfate (or bisulfate) in sulfuric acid.

Fig. S6. Ce K-edge $k^2 \chi(R)$ EXAFS and fits of Ce$^{3+}$ in H$_2$SO$_4$, TFSA, and MSA with Ce-O scattering path. Ce K-edge EXAFS of 0.025 M Ce$_2$(CO$_3$)$_3$ in 2 M H$_2$SO$_4$ (blue solid line) with fit (red dashed line) using a Ce-O scattering pathway in the (a) R space (imaginary), (b) k space, and (c) R space (magnitude). Ce K-edge EXAFS of 0.025 M Ce$_2$(CO$_3$)$_3$ in 2 M TFSA (green solid line) with fit (red dashed line) using a Ce-O scattering pathway in the (d) R space (imaginary), (e) k space, and (f) R space (magnitude). Ce K-edge EXAFS of 0.025 M Ce$_2$(CO$_3$)$_3$ in 2 M MSA (black solid line) with fit (red dashed line) using a Ce-O scattering path in the (g) R space (imaginary), (h) k space, and (i) R space (magnitude).

We study the influence of electrolyte concentration on Ce$^{3+}$ coordination in Fig. S7. In Fig. S7a, the Ce L$_3$-edge EXAFS peaks associated with Ce$^{3+}$-O scattering demonstrate that there is no trend in peak location or magnitude with increasing H$_2$SO$_4$ concentration. The lack of any trends in the spectra is also the case for increasing MSA concentration (Fig. S7b). The comparison of the Ce$^{3+}$ EXAFS Ce L$_3$-edge in three different acids (TFSA, MSA, and H$_2$SO$_4$) is included in Fig. S7c. Similar to the trend observed in the main text for the Ce$^{3+}$ EXAFS at the Ce K-edge, there is no shift in the peaks associated with Ce$^{3+}$-O scattering as the electrolyte is switched from acids where Ce$^{3+}$ is known to solely coordinate with water (TFSA and MSA) to H$_2$SO$_4$. As demonstrated by the Ce L$_3$-edge MD-EXAFS of Ce$^{3+}$ species (Fig. S7d), we expect there to
be a shift to the left in both peaks if Ce$^{3+}$ is complexed by sulfate. Because we do not see this shift experimentally, we conclude Ce$^{3+}$ is coordinated solely by water in sulfuric acid.

Fig. S7. Ce L$_3$-edge $k^2\chi(R)$ EXAFS for different Ce$^{3+}$ species. (a) Ce L$_3$-edge EXAFS of 0.05 M Ce$_2$(CO$_3$)$_3$ in 0.5 M H$_2$SO$_4$ (gray solid line), 1 M H$_2$SO$_4$ (red solid line), 2 M H$_2$SO$_4$ (blue solid line). (b) Ce L$_3$-edge EXAFS of 0.05 M Ce$_2$(CO$_3$)$_3$ in 0.5 M MSA (gray solid line), 1 M MSA (red solid line), 2 M MSA (blue solid line). (c) Ce L$_3$-edge EXAFS of 0.05 M Ce$_2$(CO$_3$)$_3$ in 1 M H$_2$SO$_4$ (blue solid line), 1 M MSA (black solid line), 2 M TFSA (green solid line). (d) Simulated MD-EXAFS of [Ce$^{III}$(H$_2$O)$_9$]$^{3+}$ (blue solid line) and [Ce$^{III}$(H$_2$O)$_8$(SO$_4$)]$^{3+}$ (brown solid line) for comparison to experimental data in (a)–(c). Insets are zoomed in portions of the plot with x-axis coordinates as written.
Section S3. Additional EXAFS analysis of Ce⁴⁺ species and DFT-predicted Ce⁴⁺ anion complexation bond distances and free energies

_Ce⁴⁺ EXAFS at the Ce L₃-edge_

To complement the analysis of Ce⁴⁺ EXAFS at the Ce K-edge in the main text (Fig. 2), we completed a similar analysis for Ce⁴⁺ in H₂SO₄ EXAFS at the Ce L₃-edge, as shown in Fig. S8. In Fig. S8a, we compare the Ce³⁺ EXAFS at the Ce L₃-edge to the EXAFS of Ce⁴⁺ in H₂SO₄ that we reported in our prior work 32 but renormalized here. It is the co-fit between this L₃-edge data and K edge data that is reported in the main text. In Fig. S8b, we compare additionally collected Ce L₃-edge 0.1 M Ce⁴⁺ 2 M H₂SO₄ EXAFS (collected as part of a series in which H₂SO₄ concentration was varied, labeled “Ce⁴⁺ in varied [H₂SO₄]”) to the Ce³⁺ EXAFS at the Ce L₃-edge. From both comparisons, the peaks associated with the Ce³⁺-O scattering are shifted to the left of those associated with Ce³⁺-O scattering, and there are additional scattering peaks that occur for Ce⁴⁺ between 2.5 Å and 3.25 Å that do not occur for Ce³⁺. Compared to the scattering peaks that we note for Ce⁴⁺ at the Ce K-edge, these are shifted to the right by ~0.25 Å, which is expected because the $\chi(k)$ function of the L₃- and K-edges are shifted 90° from each other, which will be translated into the R space. We see in Fig. S8c that a scattering event occurs in the same range for the Ce L₃-edge MD-EXAFS of [Ce⁴⁺(H₂O)₉(SO₄)]²⁺ that is not present for [Ce³⁺(H₂O)₉]⁺⁺ or [Ce³⁺(H₂O)₉]⁺⁴⁺. To further prove that the peaks in this 2.5 Å to 3.25 Å range are due to Ce⁴⁺-S scattering, we compare the MD-EXAFS of [Ce⁴⁺(H₂O)₉(SO₄)]²⁺ with and without sulfate scattering paths in Fig. S8d and show that peaks in the same 2.5-3.25 Å region disappear when the Ce⁴⁺-sulfate scattering path is removed. Finally, we show the results of the co-fit of the Ce⁴⁺ EXAFS at the Ce K- and L₃-edges for the case when the Ce L₃-edge Ce⁴⁺ in H₂SO₄ EXAFS data from our previous work 31 is used in Fig. S8e, and for the case when the “Ce⁴⁺ in varied [H₂SO₄]” Ce L₃-edge EXAFS data is used in the co-fit in Fig. S8f. For both co-fits, we fit the EXAFS of a CeO₂ standard collected at the Ce L₃-edge at the same time as the Ce⁴⁺ in H₂SO₄ data collection to obtain $S₀²$ and $ΔE₀$ values. In both cases, the best fit of the Ce⁴⁺ in H₂SO₄ EXAFS was achieved with Ce-O and Ce-S scattering shells, with Ce-O CN around 9 and the Ce-S CN around 3. Fitting parameter results are included farther below in Table S6.
Fig. S8. Ce L3-edge k²χ(𝑅) EXAFS and fits for different Ce³⁺ and Ce⁴⁺ species. (a) 0.05 M Ce₂(CO₃)₃ in 2 M H₂SO₄ (blue line) and 0.05 M Ce₂(CO₃)₃ oxidized to Ce⁴⁺ in 2 M H₂SO₄ (dark green solid line), (b) 0.05 M Ce₂(CO₃)₃ in 2 M H₂SO₄ (blue line) and additional 0.05 M Ce₂(CO₃)₃ oxidized to Ce⁴⁺ in 2 M H₂SO₄ (dark green solid line, “Ce⁴⁺ in varied [H₂SO₄]”), (c) simulated MD-EXAFS of [Ce³⁺(H₂O)₉]³⁺ (blue solid line), [Ce³⁺(H₂O)₈]³⁺ (gray solid line), and [Ce³⁺(H₂O)₈(SO₄)]²⁺ (dark green solid line), (d) simulated MD-EXAFS of [Ce⁴⁺(H₂O)₈(SO₄)]²⁺ (dark green solid line) and [Ce⁴⁺(H₂O)₈(SO₄)]²⁺ with pathways associated with sulfate scattering removed (light green solid line), (e) 0.05 M Ce₂(CO₃)₃ oxidized to Ce⁴⁺ in 2 M H₂SO₄ (dark green solid line) with fit (red dashed line), and Ce-O and Ce-S path contributions (shifted in y-axis), and (f) additional 0.05 M Ce₂(CO₃)₃ oxidized to Ce⁴⁺ in 2 M H₂SO₄ (dark green solid line, “Ce⁴⁺ in varied [H₂SO₄]”) with fit (red dashed line), and Ce-O and Ce-S path contributions (shifted in y-axis).
DFT-predicted Ce$^{4+}$ anion complexation bond distances

The averaged DFT-predicted Ce-O bond distances for different relevant Ce$^{3+}$ and Ce$^{4+}$ species are included in Table S4.

Table S4. Averaged DFT-predicted Ce-O bond distances for different Ce$^{3+}$ and Ce$^{4+}$ species.

| Species                                      | DFT Avg Ce-O (Å) |
|----------------------------------------------|------------------|
| $[\text{Ce}^{III}(\text{H}_2\text{O})_9]^{3+}$ | 2.574            |
| $[\text{Ce}^{III}(\text{H}_2\text{O})_8\text{SO}_4]^{4+}$ | 2.576            |
| $[\text{Ce}^{IV}(\text{H}_2\text{O})_9]^{4+}$ | 2.436            |
| $[\text{Ce}^{IV}(\text{H}_2\text{O})_8\text{SO}_4]^{2+}$ | 2.449            |
| $[\text{Ce}^{IV}(\text{H}_2\text{O})_6\text{HSO}_4]^3+$ | 2.432            |
| $[\text{Ce}^{IV}(\text{H}_2\text{O})_6(\text{HSO}_4)_3]^{3+}$ | 2.437            |

Ce$^{4+}$ EXAFS at the Ce L$_3$-edge

In Fig. S9, we show the effect of increasing H$_2$SO$_4$ concentration on Ce$^{4+}$ in H$_2$SO$_4$ EXAFS at the Ce L$_3$-edge. As demonstrated by the inset, the peaks associated with Ce$^{4+}$-S scattering demonstrate a slight increase in magnitude as the acid concentration is increased from 1 M to 2 M. This trend could indicate that the Ce$^{4+}$-S scattering becomes more prevalent with increasing H$_2$SO$_4$ concentration, aligning with our conclusion that Ce$^{4+}$ is complexed by sulfate or bisulfate in H$_2$SO$_4$.

![Fig. S9. Ce L$_3$-edge k$^2$χ(R) EXAFS of 0.1 M Ce$^{4+}$ with varied H$_2$SO$_4$ concentration.](image)

EXAFS standard for Ce$^{4+}$ at Ce K-edge and L$_3$-edge

The fit of the CeO$_2$ standard EXAFS with three paths (2 Ce-O scattering paths and 1 Ce-Ce scattering path) at the Ce K-edge and L$_3$-edge is shown in Fig. S10a-c and Fig. S10d-f, respectively. In these fits, we fixed the CN values for each path and varied the $S_0^2$ and $\Delta E_0$ parameters to obtain the best fit. All fitting parameter results are included in Table S5. We then used the edge-specific values of $S_0^2$ and $\Delta E_0$ in the co-fit of the Ce$^{4+}$ in H$_2$SO$_4$ EXAFS as global fixed parameters.

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Fig. S10. Ce K- and L₃-edge k²χ(R) EXAFS and fits of CeO² standard. (a) Imaginary component of Ce K-edge EXAFS in the R space of CeO₂ standard (dark yellow solid line) with fit (red dashed line), and two Ce-O and one Ce-Ce path contributions (shifted in y-axis), (b) Ce K-edge EXAFS of CeO₂ standard (dark yellow solid line) in the k space, and, (c) magnitude component of Ce K-edge EXAFS in the R space of CeO₂ standard (dark yellow solid line) with fit (red dashed line), and two Ce-O and one Ce-Ce path contributions (shifted in y-axis). (d) Imaginary component of Ce L₃-edge EXAFS in the R space of CeO₂ standard (dark yellow solid line) with fit (red dashed line), and two Ce-O and one Ce-Ce path contributions (shifted in y-axis), (e) Ce L₃-edge EXAFS of CeO₂ standard (dark yellow solid line) in the k space, and, (f) magnitude component of Ce L₃-edge EXAFS in the R space of CeO₂ standard (dark yellow solid line) with fit (red dashed line), and two Ce-O and one Ce-Ce path contributions (shifted in y-axis).

Table S5. K- and L₃-edge fitting parameters of CeO² standard. Fitting results for CeO₂ standard at the Ce L₃- and K-edges from ARTEMIS, fitting with two Ce-O shells and a Ce-Ce shell. The following parameters were varied in the fit: amplitude reduction factor (S₀²), the shift in threshold energy (ΔE₀), the shift in scattering distance (ΔR), and the Debye-Waller factor (σ²). The coordination number (CN) for each shell was set as a fixed global parameter. The scattering distance R included in the Table is calculated by adding the ΔR fitted value to the expected scattering distance from the FEFF path (see Methods).

| Edge | S₀² | ΔE₀ (eV) | Ce-O₁ shell | Ce-O₂ shell | Ce-Ce shell |
|------|-----|----------|-------------|-------------|-------------|
|      |     |          | R (Å) | CN (set) | σ² (Å²) | R (Å) | CN (set) | σ² (Å²) | R (Å) | CN (set) | σ² (Å²) |
| L₃   | 0.7±0.2 | 2.99±1.61 | 2.307±0.020 | 8 | 0.002±0.004 | 3.817±0.024 | 12 | 0.002±0.004 | 4.994±0.082 | 24 | 0.009±0.013 |
| K    | 1.0±0.1 | 0.82±0.90 | 2.359±0.009 | 8 | 0.006±0.001 | 3.844±0.004 | 12 | 0.004±0.001 | 4.537±0.029 | 24 | 0.007±0.003 |
**Co-fits of Ce K-edge and L_3-edge for Ce^{4+} with one Ce-O shell**

The co-fit of Ce^{4+} in H_2SO_4 EXAFS at the Ce K- and L_3-edges using only a Ce-O shell is included in Fig. S11, and the fitting parameter results are included in Table S6. The Ce-O co-fit overpredicts Ce^{4+}-O CN and does not capture the features that we have previously shown to be due to Ce^{4+}-S scattering. Because the fit of the Ce^{4+} in H_2SO_4 EXAFS with only a Ce-O scattering path results in a worse fit than the fit that includes a Ce-S scattering path, we conclude that Ce^{4+} is complexed by sulfate or bisulfate in the first coordination shell.

**Fig. S11.** Ce K- and L_3-edge k^2χ(R) EXAFS and co-fit of Ce^{4+} in 2 M H_2SO_4 with a Ce-O scattering path. Ce K-edge EXAFS of 0.025 M Ce_2(CO_3)_3 oxidized to Ce^{4+} in 2 M H_2SO_4 (green solid line) with co-fit with L_3-edge (red dashed line) using Ce-O scattering path, in the (a) R space (imaginary), (b) k space, and (c) R space (magnitude). Ce L_3-edge EXAFS of 0.05 M Ce_2(CO_3)_3 oxidized to Ce^{4+} in 2 M H_2SO_4 (green solid line) with co-fit with K-edge (red dashed line) using Ce-O scattering path, in the (d) R space (imaginary), (e) k space, and (f) R space (magnitude).
Table S6. K- and L₃-edge fitting parameters of Ce⁴⁺. Fitting results for Ce⁴⁺ in H₂SO₄ at the Ce L₃- and K-edges from ARTEMIS, fitting with either a Ce-O shell or a Ce-O shell and a Ce-S shell, and average scattering distances (with standard deviation used as uncertainty) for MD-simulated EXAFS of [Ce⁴⁺(H₂O)₆]⁴⁺ and [Ce⁴⁺(H₂O)₄(SO₄)]²⁺ species. For the fits, S₀² (amplitude reduction factor) and ΔE₀ were obtained by fitting the CeO₂ standard at the appropriate edge (see Table S4), and then were set as fixed global parameters for the fits below. Four parameters were varied in the fits for each scattering shell: the shift in scattering distance (ΔR) to obtain the scattering distance, coordination number (CN), the Debye-Waller factor (σ²), and the third cumulant (σ³). The scattering distance R included in the Table is calculated by adding the ΔR fitted value to the expected scattering distance from the FEFF path (see Methods).

| Edge     | Electrolyte                        | Ce-O shell | Ce-S shell |
|----------|------------------------------------|------------|------------|
|          |                                    | R (Å)      | σ²(Å²)/σ³(Å³) | R (Å)      | σ²(Å²)/σ³(Å³) | Ref       |
| L₃       | 0.1 M Ce⁴⁺/2 M H₂SO₄               | 2.402±0.012 | 0.007±0.002 | –          | –              | Buchanan, et al. (2020) |
| K + L₃ (Co-Fit) | K: 0.05 M Ce⁴⁺/2 M H₂SO₄, L₃: 0.1 M Ce⁴⁺/2 M H₂SO₄ | 2.395±0.010 | 9.8±1.0 | 0.008±0.001/−0.0002±0.0003 | 3.671±0.016 | 3.0±0.7 | 0.002±0.001/0.0044±0.0002 | This work |
| K + L₃ (Co-Fit) | K: 0.05 M Ce⁴⁺/2 M H₂SO₄, L₃: 0.1 M Ce⁴⁺/2 M H₂SO₄* | 2.382±0.006 | 8.6±0.5 | 0.006±0.001/−0.0005±0.0002 | 3.671±0.015 | 2.9±0.7 | 0.002±0.001/0.0044±0.0002 | This work |

| Edge     | Structure                          | Ce-O      | Ce-S      | Ref   |
|----------|------------------------------------|-----------|-----------|-------|
|          |                                    | R (Å)     | CN (set)  | R (Å) | CN (set) |          |
| MD       | [Ce⁴⁺(H₂O)₆]⁴⁺                    | 2.435±0.092 | 9 | – | – | This work |
|          | [Ce⁴⁺(H₂O)₄(SO₄)]²⁺               | 2.413±0.098 | 9 | 3.719±0.148 | 1 | This work |

*As described in the Methods section, additional 0.1 M Ce⁴⁺ 2 M H₂SO₄ EXAFS were collected as part of a series of EXAFS measurements in which H₂SO₄ concentration was varied. For the sake of completeness, this “Ce⁴⁺ in varied H₂SO₄” EXAFS sample was also used in the co-fit and showed to yield very similar results to those reported in the main text.
**DFT-predicted Ce⁴⁺ anion complexation free energies**

We consider the Gibbs free energy of Ce⁴⁺ anion complexation with sulfate or bisulfate. We find that the [Ce⁴⁺(H₂O)₆SO₄]²⁺ (Fig. S12a) and [Ce⁴⁺(H₂O)₆(HSO₄)₃]⁺ (Fig. S12b) species are comparable and most energetically favorable. As discussed in the main text, the series of ligand exchange steps from [Ce⁴⁺(H₂O)₆(HSO₄)₃]⁺ to [Ce⁴⁺(H₂O)₉]⁴⁺ is most likely quasi-equilibrated, based on the agreement of the kinetic data with the CE, E RDS rate law. Of these quasi-equilibrated steps, we expect in the reduction direction that the replacement of the last bisulfate to form [Ce⁴⁺(H₂O)₉]⁴⁺ will most likely be the slowest, based on its unfavorable free energy of 38.3 kJ/mol (Fig. S12b). For the oxidation direction, the slowest ligand exchange step would most likely be to go from [Ce⁴⁺(H₂O)₆(HSO₄)₃]⁺ to [Ce⁴⁺(H₂O)₇(HSO₄)₂]²⁺ based on the free energy of this step.

![Fig. S12. DFT-predicted free energies of different Ce⁴⁺ complexes.](image)

Free energy change for Ce⁴⁺ anion-complexation relative to Ce⁴⁺ coordination with nine water molecules as a function of (a) number of sulfates complexed, and (b) number of bisulfates complexed.
Section S4. Analysis of kinetic activity on Pt and GC RDEs

Kinetics on Pt

The averaged values of the exchange current densities obtained from the charge transfer resistance method on Pt are shown in Fig. S13a as a function of [Ce⁴⁺] and in Fig. S13b as a function of temperature. We obtained charge transfer resistances, $R_{ct}$, using Electrochemical Impedance Spectroscopy (EIS) and collected the charge transfer resistance data either immediately before or after we collected the steady state current responses to complete the Tafel analysis. The magnitudes of the exchange current densities agree within 31% of the values using the Tafel method and demonstrate similar dependence on both [Ce⁴⁺] and temperature, providing additional confidence in the reported kinetic activity of Pt.

**Fig. S13.** Exchange current densities for the Pt rotating disk electrode from charge transfer resistance ($R_{ct}$) method. Exchange current densities as a function of (a) Ce³⁺ concentration (based on titration) and (b) temperature, in 2 M H₂SO₄ solution with total cerium concentration of 0.05 M. Reported values are averaged from three runs, with error bars representing one standard deviation from the average value in both horizontal and vertical directions. An Ag/AgCl reference electrode and graphite rod counter electrode were used. The solutions were sparged with nitrogen gas for at least 15 minutes before measurements were collected and blanketing with nitrogen was continued throughout the measurement collection. All reported measurements were done at 2000 rpm of the RDE.

The kinetic trends on Pt were similar from 0.01–0.05 M but differed at high concentrations of cerium. We obtained rate constants and cathodic charge transfer coefficients at 0.01 M cerium and 0.03 M cerium (Fig. S14) that were similar to the values obtained at 0.05 M cerium, indicating that neither the cerium ion nor the electrode surface structures are changing from 0.01–0.05 M of cerium. At a total cerium concentration of 0.15 M (Fig. S15), reproducible data at intermediate concentrations of Ce⁴⁺ could not be obtained. Based on our EXAFS measurements, cerium dimers do not form in the concentration range we tested (up to 0.1 M Ce), so we hypothesize instead that the inconsistent exchange current densities collected at 0.15 M total cerium are because of the effect of cerium on oxide formation on Pt, as discussed below.
Fig. S14. Exchange current densities of Pt RDE extracted various ways at 0.01 M, 0.03 M, and 0.05 M Ce.
Exchange current densities extracted from (a) Tafel plots and (b) the charge transfer resistance ($R_{ct}$) method, as a function of Ce$^{4+}$ concentration (from titration) relative to total cerium concentration for a Pt RDE, in 2 M H$_2$SO$_4$ solution with three different total Ce concentrations: 0.01 M (gray circles), 0.03 M (red circles), and 0.05 M (blue circles). An Ag/AgCl reference electrode and graphite rod counter electrode were used. The solutions were sparged with nitrogen gas for at least 15 minutes before measurements were collected and blanketing with nitrogen was continued throughout the measurement collection. All reported measurements were collected at 2000 rpm of the RDE. The solid lines for each data set in (a) represent the predicted exchange current density for each total cerium concentration, using the Butler-Volmer rate law and the rate constant $k_0$ and cathodic charge transfer coefficient $\alpha$ reported in the main text for Pt at 0.05 M Ce.

Fig. S15. Exchange current densities of Pt RDE extracted various ways at 0.05 M and 0.15 M Ce. Exchange current densities extracted from (a) Tafel plots and (b) the charge transfer resistance method, as a function of Ce$^{3+}$ concentration (from titration) relative to total cerium concentration for a Pt RDE, in 2 M H$_2$SO$_4$ solution with two cerium concentrations: 0.05 M (blue circles) and 0.15 M (green circles). An Ag/AgCl reference electrode and graphite rod counter electrode were used. The solutions were sparged with nitrogen gas for at least 15 minutes before measurements were collected and blanketing with nitrogen was continued throughout the measurement collection. All data were collected at 2000 rpm of the RDE. The solid lines for each data set in (a) represent the predicted exchange current density for each total cerium concentration, using the Butler-Volmer rate law and the rate constant $k_0$ and cathodic charge transfer coefficient $\alpha$ reported in the main text for Pt at 0.05 M Ce.
Pt nanoparticles in sulfuric acid in the presence of Ce are significantly more oxidized than Pt in the absence of Ce at the same potential based on X-ray absorption spectroscopy (Fig. S16). We hypothesize that at higher concentrations of total Ce, the Pt is more oxidized, which decreases the activity as evidenced by the unexpectedly low exchange current densities observed for a system of 0.15 M total cerium (Fig. S15). Decreased kinetic activity on an oxidized platinum surface have been reported previously for other outer-sphere redox couples as well as the cerium redox couple. Thus, when operating at 0.15 M, more consistent pre-treatment of the Pt RDE such as the scheme suggested by Randle and Kuhn would be required to ensure that the Pt oxide that forms is consistently reproduced.

**Fig. S16. EXAFS of Pt without and with presence of cerium.** (a) Pt L$_3$-edge XANES of a Pt/C catalyst in 2 M H$_2$SO$_4$ solution, with a series of potentials (V vs RHE) applied. (b) Pt L$_3$-edge XANES of a Pt/C catalyst in a solution of 0.05 M Ce$_2$(CO$_3$)$_3$ and 2 M H$_2$SO$_4$ with a series of potentials (V vs RHE) applied. (c) Pt L$_3$-edge EXAFS of a Pt/C catalyst in 2 M H$_2$SO$_4$ solution, with two potentials (V vs RHE) applied. (d) Pt L$_3$-edge EXAFS of a Pt/C catalyst in a solution of 0.05 M Ce$_2$(CO$_3$)$_3$ and 2 M H$_2$SO$_4$, with two potentials (V vs RHE) applied. EXAFS measurements were collected in a polyacrylate electrochemical cell designed for beamline measurements. See Table S14 for XAFS normalization parameters used.
The fit of the cathodic Tafel slope data as a function of temperature using the BV rate law is included in Fig. S17. It is clear that the BV rate law is able to model an increase in cathodic Tafel slope with temperature, although the slope is not entirely captured. In the BV rate law, cathodic Tafel slopes are a function of both temperature and the charge transfer coefficient, \( \alpha \). In the BV formulism of kinetics, \( \alpha \) is assumed to be constant with temperature, thus explaining why the increase in cathodic Tafel slopes with temperature is only partially captured (through the direct dependence of Tafel slope on temperature but not through any variation of \( \alpha \) with temperature).

Fig. S17. Cathodic Tafel slopes as a function of temperature for the Pt rotating disk electrode. Cathodic Tafel slopes for the Pt RDE (blue circles) extracted from Tafel plots as a function of temperature at \( \text{Ce}^{4+} \) concentration of 0.026 M and total Ce concentration of 0.05 M and fit using the Butler-Volmer equation (blue line). Reported values are averaged from three runs, with error bars representing one standard deviation from the average value in both horizontal and vertical directions. An Ag/AgCl reference electrode and graphite rod counter electrode were used. The solutions were sparged with nitrogen gas for at least 15 minutes before measurements were collected and blanketing with nitrogen was continued throughout the measurement collection. All data were collected at 2000 rpm of the RDE. Solid line is the fit to the data from the Butler-Volmer equation. The cathodic charge transfer coefficient \( \alpha \) was obtained through minimizing the normalized mean square error of the data.

Kinetics on glassy carbon

The exchange current densities extracted from the charge transfer resistance method for the GC electrode as a function of \( [\text{Ce}^{4+}] \) and temperature are shown in Fig. S18a and Fig. S18b, respectively. The trends are similar to those observed for exchange current densities extracted from the Tafel method, i.e., exchange current densities demonstrate a maximum in value at intermediate \( [\text{Ce}^{4+}] \) and they increase with temperature. The magnitude of the exchange current densities is larger for the charge transfer resistance method than the Tafel method, although they are still lower than the kinetic activity observed for the Pt electrode. We use the exchange current densities obtained from the Tafel method in the kinetic activity analysis, given the smaller uncertainty as compared to those observed in the exchange current densities from the charge transfer resistance method.
Fig. S18. Exchange current densities for the GC RDE from charge transfer resistance method. Exchange current densities as a function of (a) Ce⁴⁺ concentration (based on titration) and (b) temperature in 2 M H₂SO₄ solution with total cerium concentration of 0.05 M. Reported values are averaged from three runs, with error bars representing one standard deviation from the average value in both horizontal and vertical directions. An Ag/AgCl reference electrode and graphite rod counter electrode were used. The solutions were sparged with nitrogen gas for at least 15 minutes before measurements were collected and blanketing with nitrogen was continued throughout the measurement collection. All data were collected at 2000 rpm of the RDE.

The cathodic Tafel slopes as a function of temperature for the GC RDE are shown in Fig. S19, along with the fit of the BV rate law to the Tafel slope data. The general trend is the cathodic Tafel slope increases with temperature, which is similar to the trend for Pt, however the average data point at 298 K is lower than those at 288 K or 293 K. The data point at 298 K has a larger uncertainty than any of the other data points, which could explain this anomaly. The BV rate law does model the increase in cathodic Tafel slope with increasing temperature using a charge transfer value of 0.23.
Fig. S19. Cathodic Tafel slope dependence on temperature for the glassy carbon rotating disk electrode. Cathodic Tafel slopes for the GC RDE (orange triangles) extracted from Tafel plots as a function temperature at Ce\(^{4+}\) concentration of 0.025 M and total Ce concentration of 0.05 M and fit using the Butler-Volmer equation (orange line). Reported values are averaged from three runs, with error bars representing one standard deviation from the average value in both horizontal and vertical directions. An Ag/AgCl reference electrode and graphite rod counter electrode were used. The solutions were sparged with nitrogen gas for at least 15 minutes before measurements were collected and blanketing with nitrogen was continued throughout the measurement collection. All data were collected at 2000 rpm of the RDE. Solid line is the fit to the data from the Butler-Volmer equation. The cathodic charge transfer coefficient \(\alpha\) was obtained through minimizing the normalized mean square error of the data.

**Table S7** compares the kinetic activity of different electrodes (either electrode material or pretreatments) for a variety of redox couples that are known to be outer-sphere, e.g., \([\text{Fe(CN)}_6]^{3-}/[\text{Fe(CN)}_6]^{4-}\). The kinetic activity for the different electrode conditions are calculated by taking the ratio of the reported standard rate constants. The ratio for the standard rate constants obtained from the fit of the BV rate law to the Ce\(^{3+}/\text{Ce}^{4+}\) kinetic data in Fig. 3 are included in **Table S7** for comparison. The factor of difference for these known outer-sphere redox couples range between 1.3−8.6, suggesting that the Ce\(^{3+}/\text{Ce}^{4+}\), which has a factor of 4.7 between Pt and GC, also behaves as if outer-sphere.

**Table S7.** Electrode effect on kinetic activity for outer-sphere redox couples, including this Ce\(^{3+}/\text{Ce}^{4+}\) work. Factor of difference refers to the ratio of the reported \(k_0\) for the electrode listed first in the Electrodes studied column to the reported \(k_0\) for the electrode listed second. Note that for simplicity, the structure of Ce\(^{4+}\) is written as [Ce\(^{IV}(\text{H}_2\text{O})_6\text{SO}_4\)]\(^{2+}\), but we show evidence that the Ce\(^{4+}\) structure could exist as either [Ce\(^{IV}(\text{H}_2\text{O})_6(\text{HSO}_4)\)]\(^{3+}\) or [Ce\(^{IV}(\text{H}_2\text{O})_6(\text{HSO}_4)\)]\(^{2}\) in sulfuric acid.

| Outer-sphere redox couple | Electrodes studied | Supporting electrolyte | Redox species | Ratio of standard rate constants at different electrodes* | Ref |
|---------------------------|---------------------|------------------------|---------------|----------------------------------------------------------|-----|
| [Ce\(^{III}(\text{H}_2\text{O})_9\)]\(^{3+}\)/[Ce\(^{IV}(\text{H}_2\text{O})_6(\text{HSO}_4)\)]\(^{3+}\) | Pt vs. GC           | 2 M H\(_2\)SO\(_4\)   | 0.05 M Ce     | 4.7                                                      | This work |
|                           | Pt, reduced vs. oxidized state | 0.5 M H\(_2\)SO\(_4\) | 0.016 M Ce\(^{3+}\)/0.012 M Ce\(^{4+}\) | ~3\(^a\) | 20 |
| [Fe(CN)\(_6\)]\(^{3-}\)/[Fe(CN)\(_6\)]\(^{4-}\)  | Pt, reduced vs. oxidized state | 1 M KCl | 0.01–0.07 M [Fe(CN)\(_6\)]\(^{3+}\)/ | 8.6 | 33 |

*Ref indicates the reference for the ratio of standard rate constants at different electrodes.
| Electrode Configuration | Solution Composition | Oxidation Potential/bar | Reference |
|-------------------------|----------------------|-------------------------|-----------|
| Pt vs. GC               | 1 M KCl, 0.002 M [Fe(CN)₆]³⁻ | 0.0005–0.01 | 36 |
| GC, polished vs. laser activation | 1 M KCl, 0.001 M [Fe(CN)₆]³⁻ | 0.002 M [Fe(CN)₆]³⁻ | 3.4 |
| [Cr(H₂O)₆]³+/[Cr(H₂O)₆]²⁺ | Pb vs. Ga, 0.5 M NaClO₄ + 0.003 M HClO₄ | 0.001–0.002 M [Cr(H₂O)₆]³⁻ | 3.8 |
| [Cr(H₂O)₆]³+/[Cr(H₂O)₆]²⁺ | Pb vs. Tl, 0.5 M NaClO₄ + 0.003 M HClO₄ | 0.001–0.002 M [Cr(H₂O)₆]³⁻ | 1.3 |
| [Cr(H₂O)₅SO₄]²-/ [Cr(H₂O)₅SO₄]⁰ | Pb vs. Ga, 0.5 M NaClO₄ + 0.003 M HClO₄ | 0.001–0.002 M [Cr(H₂O)₅SO₄]²⁻ | ~4.3 |
| [Ru(NH₃)₆]³+/[Ru(NH₃)₆]²⁺ | GC, polished vs. monolayer adsorption of AQDS, MB, BMB, and chemisorbed nitrophenyl | 1 M KCl, 0.001 M [Ru(NH₃)₆]³⁻ | ~2 |
| Ag vs. Hg²⁻ | 1 M KF, Not reported²⁻ | 2.4 |
| Pt vs. Au | 1 M KF, 0.002 M [Ru(NH₃)₆]³⁻ | 1.5 |
| [IrCl₃]²⁺/[IrCl₃]³⁻ | GC, polished vs. monolayer adsorption of AQDS, MB, BMB, and chemisorbed nitrophenyl | 1 M KCl, 5×10⁻⁴ M [IrCl₃]²⁻ | ~2 |

*a*) Ratio calculated using Ce⁴⁺ reduction data from Fig. 6 in Kuhn and Randle (1985) paper for oxide coverage of 1 relative to oxide coverage of 4.5 for the electrode labeled “Electrode 1,” which had been exposed to a longer period of phase oxide formation than other electrodes tested; 
*b*) Calculated from reported $k_{app}$ data; 
*c*) 2,6-anthraquinonedisulfonate; 
*d*) methylene blue; 
*e*) bis(4-methylstyril)benzene; 
*f*) Other metal electrodes studied as well, including Pt, Pd, Au, and Cu, with exchange current densities ranging between 97 A/cm² and 116 A/cm², while exchange current densities for Ag and Hg were 120 A/cm² and 50–79 A/cm², respectively; 
*g*) Concentrations not reported for experiments on Ag and Hg, but concentrations reported for similar experiments conducted on Pt and Au: 3.3×10⁻⁴–8.8×10⁻⁴ M [Ru(NH₃)₆]³⁻/2.8×10⁻⁴–8.3×10⁻⁴ [Ru(NH₃)₆]²⁻; 
*h*) Factor calculated using reported exchange current densities, instead of rate constants.

* Ratio is calculated by dividing the reported value of $k_0$ of the electrode listed first by that of the electrode listed second.
Section S5. Rate laws considered for cerium charge transfer

A summary of all symbols used in the derivation of the rate laws is in Table S8. Following the list of symbols, the derivation of each relevant rate law is described. The relevant rate laws are the Butler Volmer (BV) and Marcus theory (MT) rate laws, derived for a one-step charge transfer, and the rate laws derived for the CE mechanism (CE, E RDS and CE, C RDS) and the EC mechanism (EC, E RDS and EC, C RDS).

Table S8. Symbols and their definitions used in kinetic rate law derivations.

| Symbol                   | Meaning                                                                 |
|--------------------------|-------------------------------------------------------------------------|
| [Ce$$^{3+}$$]            | Concentration of bulk Ce$$^{3+}$$ species in sulfuric acid, i.e., [Ce$$^{3+}$$(H$_2$O)$_n$]$^{4+}$ |
| [Ce$$^{4+}$$]            | Concentration of bulk Ce$$^{4+}$$ species in sulfuric acid, i.e., [Ce$$^{4+}$$(H$_2$O)$_n$(HSO$_4$)$_3$]$^{4+}$ |
| n                        | Number of electrons transferred per charge transfer, assumed to be 1    |
| F                        | Faraday’s constant                                                     |
| R                        | Ideal gas law constant                                                |
| T                        | Temperature                                                           |
| U                        | Electrode potential                                                   |
| U$^\text{eq}$            | Equilibrium potential of overall charge transfer mechanism            |
| $U'_e$                   | Standard equilibrium potential of overall charge transfer mechanism    |
| $\eta$                   | Overpotential. Defined as the difference between electrode potential and standard equilibrium potential ($U - U^\text{eq}$) |

**Definitions for Butler-Volmer**

- $i_{K,BV}$: Kinetic current for Butler-Volmer (BV) derived rate law
- $k_{BV}$, $k_{-BV}$: Reduction and oxidation rate constants for $E$ step in BV derived rate law
- $A_{BV}$, $A_{-BV}$: Reduction and oxidation preexponential factors for $E$ step in BV derived rate law
- $\Delta G_{BV}^1$, $\Delta G_{-BV}^1$: Free energies of the transition state for reduction and oxidation for $E$ step in BV derived rate law
- $\Delta G_{0,BV}$: Redox transition state free energy for $E$ step in BV derived rate law when $U = U'_e$
- $\alpha$: Cathodic charge transfer coefficient
- $k_0$: Standard rate constant
- $E_a$: Apparent activation energy in finalized BV derived rate law

**Definitions for Marcus Theory**

- $i_{K,MT}$: Kinetic current for Marcus Theory (MT) derived rate law
- $k_{MT}$, $k_{-MT}$: Reduction and oxidation rate constants for $E$ step in MT derived rate law
- $K_{el}$: Electronic transmission coefficient
- $K_{p,Ce^{3+}}, K_{p,Ce^{4+}}$: Precursor equilibrium constants for the Ce$$^{3+}$$ and Ce$$^{4+}$$ species
- $v_n$: Nuclear frequency factor
- $\Delta G_{MT}^1$, $\Delta G_{-MT}^1$: Free energies of the transition state for reduction and oxidation for $E$ step in MT derived rate law
- $\lambda_{MT}$: Reorganization energy for $E$ step in MT derived rate law
- $\Delta G_{MT}$: Free energy of the $E$ step in MT derived rate law

**Definitions for CE mechanism**

- $i_{K,CE,E}$: Kinetic current for rate law for CE mechanism with $E$ RDS
- $k_1, k_{-1}$: Reduction and oxidation rate constants for $E$ step in CE mechanism
- $\Delta G_2^1, \Delta G_2^{-1}$: Free energies of the transition state for reduction and oxidation reactions for $E$ step in CE mechanism
- $\lambda_2$: Reorganization energy for $E$ step in CE mechanism
- $\Delta G_2$: Free energy of the $E$ step in CE mechanism
- $U'_e$: Standard equilibrium potential of species involved in $E$ step of CE mechanism, i.e., [Ce$$^{3+}$$(H$_2$O)$_n$]$^{4+}$ and [Ce$$^{4+}$$(H$_2$O)$_n$(HSO$_4$)$_3$]$^{4+}$
- $r_1$: Reaction rate of $C$ step in CE mechanism
- $k_1, k_{-1}$: Forward and backward rate constants for $C$ step in CE mechanism
- $K_p$: Equilibrium constant for $C$ step in CE mechanism
- $\Delta G_1$: Free energy of $C$ step in CE mechanism
- $Z_2$: Preexponential factor used in finalized rate law for CE mechanism with $E$ RDS, equal to factor of $k_1$, $K_{p,Ce^{3+}}$ or $K_{p,Ce^{4+}}$, and $v_n$
- $i_{K,CE,C}$: Kinetic current for rate law for CE mechanism with $C$ RDS
- $r_2$: Reaction rate of $E$ step in CE mechanism

**Definitions for EC mechanism**
| Symbol | Description |
|--------|-------------|
| \(i_{k,EC,E}\) | Kinetic current for rate law for EC mechanism with \(E\) RDS |
| \(k_{3,1}, k_{-3}\) | Reduction and oxidation rate constants for \(E\) step in EC mechanism |
| \(\Delta G^\circ_3, \Delta G^{-3}\) | Free energies of transition state for reduction and oxidation for \(E\) step in EC mechanism |
| \(\lambda_3\) | Reorganization energy for \(E\) step in EC mechanism |
| \(\Delta G_3\) | Free energy of the \(E\) step in EC mechanism |
| \(U_{k,3}\) | Standard equilibrium potential of species involved in \(E\) step of EC mechanism, i.e., \([\text{Ce}^4\text{V}(\text{H}_2\text{O}_6)(\text{HSO}_4)_3]^+\) and \([\text{Ce}^\text{III}(\text{H}_2\text{O}_6)(\text{HSO}_4)_3]^0\) |
| \(r_a\) | Reaction rate of \(C\) step in EC mechanism |
| \(k_{4,1}, k_{-4}\) | Forward and backward rate constants for \(C\) step in EC mechanism |
| \(K_4\) | Equilibrium constant for \(C\) step in CE mechanism |
| \(\Delta G_4\) | Free energy of \(C\) step in CE mechanism |
| \(Z_3\) | Preexponential factor used in finalized rate law for EC mechanism with \(E\) RDS, equal to factor of \(k_{el}, K_{P,CE^{++}}, \text{or } K_{P,CE^{+++}}\), and \(\nu_0\) |
| \(i_{k,EC,C}\) | Kinetic current for rate law for EC mechanism with \(C\) RDS |
| \(r_C\) | Reaction rate of \(C\) step in EC mechanism |

**BV rate law derivation**

To derive the BV rate law, the overall reaction mechanism is assumed to be the following (Eq. S1), in which the electron transfer and a chemical step occur in the same step. Including the chemical step ensures that the Ce\(^{3+}\) and Ce\(^{4+}\) are in their preferred states in sulfuric acid, i.e., \([\text{Ce}^{4+}(\text{H}_2\text{O}_6)^3]^+\) and \([\text{Ce}^\text{III}(\text{H}_2\text{O}_6)(\text{HSO}_4)_3]^\text{aq}\), respectively, satisfying Criteria 1–3 of Table 1.

\[
[\text{Ce}^\text{IV}(\text{H}_2\text{O}_6)(\text{HSO}_4)_3]^\text{aq} + 3\text{H}_2\text{O}^+ + e^- \rightleftharpoons [\text{Ce}^{\text{III}}(\text{H}_2\text{O}_6)(\text{aq})]^3^+ + 3\text{HSO}_4^- \tag{S1}
\]

For this mechanism, the kinetic current would be Eq. S2, where \([\text{Ce}^{4+}]\) and \([\text{Ce}^{3+}]\) are the bulk Ce\(^{4+}\) and Ce\(^{3+}\) species. The reduction and oxidation rate constants, \(k_{BV}\) and \(k_{-BV}\), are assumed to have an Arrhenius form\(^4\) in Eq. S3–S4, with \(A_{BV}\) and \(A_{-BV}\) as the preexponential factors, and \(\Delta G^\circ_{BV}\) and \(\Delta G^\circ_{-BV}\) as the free energies of the transition state, of the reduction and oxidation reactions, respectively.

\[
-i_{k,BV} = nF(k_{BV}[\text{Ce}^{4+}][\text{H}_2\text{O}]^3 - k_{-BV}[\text{Ce}^{3+}][\text{HSO}_4]^3) \tag{S2}
\]

\[
k_{BV} = A_{BV} \exp\left(-\frac{\Delta G^\circ_{BV}}{RT}\right) \tag{S3}
\]

\[
k_{-BV} = A_{-BV} \exp\left(-\frac{\Delta G^\circ_{-BV}}{RT}\right) \tag{S4}
\]

The transition state energies can be described using Eq. S5–S6, where \(\Delta G^\circ_{0,BV}\) is the redox transition state free energy, for the case in which the electrode potential, \(U\), is equal to the standard equilibrium potential of the redox species, \(U^\circ\), and \(\alpha\) is the charge transfer coefficient."41

\[
\Delta G^\circ_{BV} = \Delta G^\circ_{0,BV} + \alpha F(U - U^\circ) \tag{S5}
\]

\[
\Delta G^\circ_{-BV} = \Delta G^\circ_{0,BV} - (1 - \alpha) F(U - U^\circ) \tag{S6}
\]

Plugging Eq. S5–S6 into Eq. S3–S4, we obtain the following expressions for the oxidation and reduction rate constants (Eq. S7–S8).

\[
k_{BV} = A_{BV} \exp\left(-\frac{\Delta G^\circ_{0,BV}}{RT}\right) \exp\left(-\frac{\alpha F}{RT}(U - U^\circ)\right) \tag{S7}
\]
\[
    k_{-BV} = A_{-BV} \exp \left( \frac{-\Delta G_{0,BV}^{\ddagger}}{RT} \right) \exp \left( \frac{(1 - \alpha) F(U - U^e)}{RT} \right)
\] (S8)

When considering the case when the system is at equilibrium with \([\text{Ce}^{4+}] = [\text{Ce}^{3+}]\), then \(U = U^e\) and \(k_{BV}[\text{H}_2\text{O}]^3 = k_{-BV}[\text{HSO}_4]^{3}\). We then define a standard rate constant, \(k_0\), as \(k_0 \equiv A_{BV} \exp \left( \frac{-\Delta G_{0,BV}^{\ddagger}}{RT} \right) [\text{H}_2\text{O}]^3 = A_{-BV} \exp \left( \frac{-\Delta G_{0,BV}^{\ddagger}}{RT} \right) [\text{HSO}_4]^{3}\). Thus \(\text{Eq. S7–S8} \) can be simplified to

\[
    k_{BV}[\text{H}_2\text{O}]^3 = k_0 \exp \left( -\frac{\alpha F}{RT} (U - U^e) \right)
\] (S9)

\[
    k_{-BV}[\text{HSO}_4]^{3} = k_0 \exp \left( \frac{(1 - \alpha) F(U - U^e)}{RT} \right)
\] (S10)

Plugging \(\text{Eq. S9–S10}\) into the overall rate law \(\text{Eq. S2}\) and letting overpotential \(\eta = U - U_{eq}\), where \(U_{eq}\) is the equilibrium potential of the reaction and defined in \(\text{Eq. S11}\), we obtain the final rate law describing the kinetic current as a function of \(\text{Ce}^{3+}\) and \(\text{Ce}^{4+}\) bulk species, overpotential, and \(k_0\) and \(\alpha\) (\(\text{Eq. S12}\)). This is the Butler-Volmer equation and is the same as \(\text{Eq. 1}\) in the main text. The standard rate constant \(k_0\) is a function of temperature (\(\text{Eq. S13}\)) through the Arrhenius equation, where \(E_a\) is the activation energy.

\[
    U_{eq} = U^e - \frac{RT}{nF} \ln \frac{[\text{Ce}^{3+}]}{[\text{Ce}^{4+}]}
\] (S11)

\[
    -i_{K,BV} = nFk_0(T)[\text{Ce}^{3+}]^a[\text{Ce}^{4+}]^{1-a} \left( \exp \left( -\frac{\alpha F\eta}{RT} \right) - \exp \left( \frac{(1 - \alpha) F\eta}{RT} \right) \right)
\] (S12)

\[
    k_0(T) = k_0(298 \text{ K}) \exp \left( \frac{-E_a}{R} \left( \frac{1}{T} - \frac{1}{298 \text{ K}} \right) \right)
\] (S13)

\(\text{Eq. S12}\) can be used to model the exchange current density and cathodic Tafel slopes as a function of both \(\text{Ce}^{4+}\) concentration and temperature, by applying a Tafel analysis to the modeled current between the overpotential range of \(-0.250\ \text{V}\) and \(-0.118\ \text{V}\), as was done for the experimentally collected data.

**MT rate law derivation**

To derive the MT rate law, the possible overall reaction mechanisms are shown in \(\text{Eq. S14–S15}\). Note that MT does not allow for an inner-sphere structural change, failing \textit{Criterion 1} in Table 1, and meaning we must either model the \(E\) between the bisulfate-complexed (\(\text{Eq. S14}\)) or water-coordinated Ce species (\(\text{Eq. S15}\)). For the sake of simplicity, we will derive the rate law assuming \(\text{Eq. S15}\) is the appropriate reaction mechanism, but the derivation would be analogous for \(\text{Eq. S14}\).

\[
    [\text{Ce}^{IV}(\text{H}_2\text{O})_6(\text{HSO}_4)_3]^{3+}_{aq} + e^- \rightleftharpoons [\text{Ce}^{III}(\text{H}_2\text{O})_6(\text{HSO}_4)_3]^{0}_{aq}
\] (S14)

\[
    [\text{Ce}^{IV}(\text{H}_2\text{O})_9]^{4+}_{aq} + e^- \rightleftharpoons [\text{Ce}^{III}(\text{H}_2\text{O})_9]^{3+}_{aq}
\] (S15)

The kinetic current for \(\text{Eq. S15}\) would then be \(\text{Eq. S16}\), where the reduction and oxidation rate constants \(k_{MT}\) and \(k_{-MT}\) are described through \(\text{Eq. S17–S18}\), using standard Marcus theory expressions.\(^4\) In \(\text{Eq. S17–S18}\), \(\kappa_e\) is the electronic transmission coefficient, which is related to the probability of electron tunneling, \(K_{p,Ce^{4+}}\) and \(K_{p,Ce^{3+}}\) are the precursor equilibrium constants for the \(\text{Ce}^{4+}\) and \(\text{Ce}^{3+}\) species, respectively, and \(\nu_n\) is the nuclear frequency factor.\(^4\) \(\Delta G_{MT}^\ddagger\) and \(\Delta G_{-MT}^\ddagger\) are the free energies of the transition state for the reduction and oxidation rate constants defined using MT, as shown in \(\text{Eq. S19–S20}\), where \(\lambda_{MT}\) is the
reorganization energy and \( \Delta G_{MT} \) represents the free energy of the \( E \) reaction. \( \Delta G_{MT} \) is related to the electrode potential through Eq. S21.

\[
-i_{K,MT} = nF \left( k_{MT} [\text{Ce}^{IV}(\text{H}_2\text{O})_9]^{4+} - k_{-MT} [\text{Ce}^{III}(\text{H}_2\text{O})_9]^{3+} \right) \quad (S16)
\]

\[
k_{MT} = \kappa_{el} K_{p,\text{Ce}^{4+}} v_n \exp \left( \frac{-\Delta G_{MT}^1}{RT} \right) \quad (S17)
\]

\[
k_{-MT} = \kappa_{el} K_{p,\text{Ce}^{3+}} v_n \exp \left( \frac{-\Delta G_{-MT}^1}{RT} \right) \quad (S18)
\]

\[
\Delta G_{MT}^1 = \frac{\lambda_{MT}}{4} \left( 1 + \frac{\Delta G_{MT}}{\lambda_{MT}} \right)^2 \quad (S19)
\]

\[
\Delta G_{-MT}^1 = \frac{\lambda_{MT}}{4} \left( 1 - \frac{\Delta G_{MT}}{\lambda_{MT}} \right)^2 \quad (S20)
\]

\[
\Delta G_{MT} = nF(U - U_{eq}) \quad (S21)
\]

Plugging these expressions into Eq. S16, and again substituting \( \eta = U - U_{eq} \), where \( U_{eq} \) is defined in Eq. S11, and letting \( Z_{MT} = \kappa_{el} K_{p,\text{Ce}^{3+}} v_n = \kappa_{el} K_{p,\text{Ce}^{4+}} v_n \), we obtain the MT rate law (Eq. S22) that can be used to fit the exchange current densities and cathodic Tafel slopes as a function of [Ce\(^{4+}\)] and temperature using Tafel analysis in the same overpotential range as used in the experimental data collection process. Note that in the fitting process of the experimental data with the MT rate law, the concentration of the [Ce\(^{IV}(\text{H}_2\text{O})_9\)]\(^{4+}\) species in Eq. S22 was assumed to be equal to the bulk Ce\(^{4+}\) species, which we in fact know to be [Ce\(^{IV}(\text{H}_2\text{O})_9(\text{HSO}_4)_3\)]\(^{1+}\).

\[
i_{K,MT} = -nFZ_{MT} \left( [\text{Ce}^{IV}(\text{H}_2\text{O})_9]^{4+} \exp \left( \frac{-\lambda_{MT}}{4RT} \left( 1 + \frac{nF\eta}{\lambda_{MT}} \right) - \frac{RT}{\lambda_{MT}} \ln \left[ \frac{\text{Ce}^{3+}}{\text{Ce}^{4+}} \right] \right) \right) - [\text{Ce}^{III}(\text{H}_2\text{O})_9]^{3+} \exp \left( \frac{-\lambda_{MT}}{4RT} \left( 1 - \frac{nF\eta}{\lambda_{MT}} + \frac{RT}{\lambda_{MT}} \ln \left[ \frac{\text{Ce}^{3+}}{\text{Ce}^{4+}} \right] \right) \right) \quad (S22)
\]

**CE Mechanism, E RDS rate law derivation**

The kinetic current for the CE mechanism (Eq. 2a–b), assuming the E step is the RDS, is defined in Eq. S23, where the reduction and oxidation rate constants of the E step, \( k_2 \) and \( k_{-2} \), are defined using MT in Eq. S24–S25. The meanings of \( \kappa_{el}, K_{p,\text{Ce}^{3+}}, K_{p,\text{Ce}^{4+}}, \) and \( v_n \) are all the same as described previously. The free energies of the reduction and oxidation transition states for the E step, \( \Delta G_2^1 \) and \( \Delta G_{-2}^1 \), are defined using MT in Eq. S26–S27, with \( \Delta G_2 \) defined in Eq. S28 as the reaction energy of the E step, and related to the difference between the potential of the electrode, \( U \), and \( U_{E,2} \), the equilibrium electrode potential of the species involved in the E step i.e., [Ce\(^{IV}(\text{H}_2\text{O})_9\)]\(^{4+}\) and [Ce\(^{III}(\text{H}_2\text{O})_9\)]\(^{3+}\).

\[
-i_{K,C,E} = nF \left( k_2 [\text{Ce}^{IV}(\text{H}_2\text{O})_9]^{4+} - k_{-2} [\text{Ce}^{III}(\text{H}_2\text{O})_9]^{3+} \right) \quad (S23)
\]

\[
k_2 = \kappa_{el} K_{p,\text{Ce}^{4+}} v_n \exp \left( \frac{-\Delta G_2^1}{RT} \right) \quad (S24)
\]

\[
k_{-2} = \kappa_{el} K_{p,\text{Ce}^{3+}} v_n \exp \left( \frac{-\Delta G_{-2}^1}{RT} \right) \quad (S25)
\]

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\[
\Delta G_2^1 = \frac{\lambda_2}{4} \left( 1 + \frac{\Delta G_2}{\lambda_2} \right)^2 \\
\Delta G_{1-2}^1 = \frac{\lambda_2}{4} \left( 1 - \frac{\Delta G_2}{\lambda_2} \right)^2 \\
\Delta G_2 = nF(U - U_{E,2}^\circ)
\]

(S26)

(S27)

(S28)

In the kinetic current rate law, the unknown concentration of the intermediate species \([\text{Ce}^{IV}(\text{H}_2\text{O})_9]^{4+}\) must be defined in terms of known bulk species concentration, which can be done using the equilibrium constant of the \(C\) step (Eq. 2a). As mentioned in the main text, we assume that the ligand exchange occurs in one step rather than a series of \(C\) steps on the principle of choosing the simplest mechanism that fits the data. Assuming the \(C\) step is quasi-equilibrated, then the \(C\) step reaction rate, \(r_1\), would be equal to zero (Eq. S29). \(k_1\) and \(k_{-1}\) are the forward and backward rates of the \(C\) step and are related to the equilibrium constant of the \(C\) step \(K_1\) through Eq. S30. \(\Delta G_1\) in Eq. S30 is the reaction energy of the \(C\) step and is defined in Eq. S31, where \(U^*\) is the standard equilibrium electrode potential of the overall reaction, as defined earlier. Thus, in the instance that \(U = U^*\), \(\Delta G_1 = \Delta G_2\) as would be expected from Scheme 1.

\[
r_1 = 0 = k_1[[\text{Ce}^{IV}(\text{H}_2\text{O})_6(\text{HSO}_4)_3]^{4+}]_\text{aq}[[\text{H}_2\text{O}]^3

- k_{-1}[[\text{Ce}^{IV}(\text{H}_2\text{O})_9]^{4+}]_\text{aq}[[\text{HSO}_4]^3

K_1 = \frac{k_1}{k_{-1}} = \exp \left( -\frac{\Delta G_1}{RT} \right)

\Delta G_1 = -nF(U^* - U_{E,2}^\circ)
\]

(S29)

(S30)

(S31)

Using Eq. S29–S31, the concentration of \([\text{Ce}^{IV}(\text{H}_2\text{O})_9]^{4+}\) is defined as shown in Eq. S32. Plugging in Eq. S32 as well as Eq. S24–S25 into Eq. S23, the kinetic current rate law for the \(CE\) mechanisms with the \(E\) step as RDS in Eq. S33 is determined. In Eq. S33, \(Z_2 = \kappa_\text{el}K_{p,C,\text{e}^{3+}}v_n = \kappa_\text{el}K_{p,C,\text{e}^{4+}}v_n\) and \([\text{Ce}^{4+}]\) and \([\text{Ce}^{3+}]\) are the concentrations of the bulk \(\text{Ce}^{4+}\) and \(\text{Ce}^{3+}\) species.

\[
[[\text{Ce}^{IV}(\text{H}_2\text{O})_9]^{4+}]_\text{aq} = \frac{[[\text{Ce}^{IV}(\text{H}_2\text{O})_6(\text{HSO}_4)_3]^{4+}]_\text{aq}[[\text{H}_2\text{O}]^3}{[\text{HSO}_4]^3} K_1 = \frac{[[\text{Ce}^{IV}(\text{H}_2\text{O})_6]^{4+}][\text{H}_2\text{O}]^3}{[\text{HSO}_4]^3}
\]

(S32)

\[
-i_{K,CE,E} = nFZ_2 \left( \frac{[\text{Ce}^{4+}][\text{H}_2\text{O}]^3}{[\text{HSO}_4]^3} \right) K_1 \exp \left( -\frac{\lambda_2}{4RT} \left( 1 + \frac{nF(U - U_{E,2}^\circ)}{\lambda_2} \right)^2 \right)

- [\text{Ce}^{3+}] \exp \left( -\frac{\lambda_2}{4RT} \left( 1 - \frac{nF(U - U_{E,2}^\circ)}{\lambda_2} \right)^2 \right)
\]

(S33)

Eq. S33 can be further simplified by defining \(U_{E,2}^\circ\) using Eq. S34 and recognizing that \(\eta = U - U_{eq}\), to obtain the final rate law in Eq. S35 (Eq. 3 in main text). From this kinetic current expression, exchange current densities and cathodic Tafel slopes as a function of \([\text{Ce}^{4+}]\) and temperature can be modeled and compared to experimental values.

\[
U_{E,2}^\circ = U^* - \frac{RT}{nF} \ln K_1
\]

(S34)
\[ i_{K,CE,E} = -nFZ_2 \left( \frac{[Ce^{4+}][H_2O]^3}{[HSO_4]^3} K_1 \exp \left( \frac{-\lambda_2}{4RT} \left( 1 + \frac{nF\eta}{\lambda_2} - \frac{RT}{\lambda_2} \ln \frac{[Ce^{3+}]}{K_1[Ce^{4+}]} \right)^2 \right) \right. \]
\[ \left. - [Ce^{3+}] \exp \left( \frac{-\lambda_2}{4RT} \left( 1 - \frac{nF\eta}{\lambda_2} + \frac{RT}{\lambda_2} \ln \frac{[Ce^{3+}]}{K_1[Ce^{4+}]} \right)^2 \right) \right] \] (S35)

**CE Mechanism, C RDS rate law derivation**

The rate law for the case when the C step of the CE mechanism is rate-determining is defined below in Eq. S36, where again, the ligand exchange is assumed to occur in one C step instead of a series of C steps for simplicity.

\[ -i_{K,CE,C} = nF \left( k_1 \left[ [Ce^{IV}(H_2O)_6(HSO_4)_3]^{3+}_{aq} \right] [H_2O]^3 - k_{-1} \left[ [Ce^{IV}(H_2O)_9]^{4+}_{aq} \right] [HSO_4]^3 \right) \] (S36)

The concentration of the intermediate species \([Ce^{IV}(H_2O)_9]^{4+}\) is determined based on the assumption that the \(E\) step is quasi-equilibrated, and so \(r_2\), the reaction rate of the \(E\) step, is equal to zero (Eq. S37). The reduction and oxidation rate constants are defined as earlier using MT in Eq. S24–S25.

\[ r_2 = 0 = k_2 \left[ [Ce^{IV}(H_2O)_9]^{4+}_{aq} \right] - k_{-2} \left[ [Ce^{III}(H_2O)_9]^{3+}_{aq} \right] \] (S37)

Substituting Eq. S24 and S25 into Eq. S37, the concentration of the intermediate species \([Ce^{IV}(H_2O)_9]^{4+}\) is determined (Eq. S38).

\[ \left[ [Ce^{IV}(H_2O)_9]^{4+}_{aq} \right] = \left[ [Ce^{III}(H_2O)_9]^{3+}_{aq} \right] \exp \left( \frac{nF}{RT} (U - U_{E,2}^\circ) \right) \] (S38)

Plugging Eq. S38 into Eq. S36 and using the definition for \(U_{E,2}^\circ\) from Eq. S34, the definition for \(K_1\) from Eq. S30, and \(\eta = U - U_{eq}\), the final rate law for the CE mechanism with the C step RDS is found in Eq. S39. Exchange current densities and Tafel slopes can be derived from this rate law to compare to experimental values.

\[ i_{K,CE,C} = -nFk_1 \left( [Ce^{4+}][H_2O]^3 - [Ce^{4+}][HSO_4]^3 \exp \left( \frac{nF\eta}{RT} \right) \right) \] (S39)

Briefly, Eq. S39 cannot capture the maximum in exchange current density with \([Ce^{4+}]\) or the cathodic Tafel slopes observed experimentally, so is not a correct rate law.

**EC Mechanism, E RDS rate law derivation**

For the EC mechanism, the \(Ce^{4+}\)-anion complex \([Ce^{IV}(H_2O)_6(HSO_4)_3]^+\) undergoes an endothermic \(E\) to form the higher energy \(Ce^{3+}\) species \([Ce^{III}(H_2O)_6(HSO_4)_3]^{0}\) (Eq. S40a), which then undergoes a favorable ligand exchange C step with water to form the \([Ce^{III}(H_2O)_6]^3\) species (Eq. S40b). Like the CE mechanism, the ligand exchange in the EC mechanism is assumed to occur in one C step instead of a series of C steps.

\[ [Ce^{IV}(H_2O)_6(HSO_4)_3]^{3+}_{aq} + e^- \rightleftharpoons [Ce^{III}(H_2O)_6(HSO_4)_3]^{0}_{aq} \] (S40a)

\[ [Ce^{III}(H_2O)_6(HSO_4)_3]^{0}_{aq} + 3H_2O_{aq} \rightleftharpoons [Ce^{III}(H_2O)_6]^{3+}_{aq} + 3HSO_4^{-}_{aq} \] (S40b)

Assuming a rate-determining step exists, the proposed mechanism in Eq. S40 has two possible rate laws. Considering the case when the \(E\) step is the RDS, the kinetic current would be described as in Eq. S41 using MT. The reduction and oxidation rate constants of the \(E\) step are defined in Eq. S42–S43, where \(K_{el}, K_{p,el}, K_{el}, K_{p,el}, \) and \(u_n\) are all the same as described previously. \(\Delta G_{\delta}^0\) and \(\Delta G_{\delta,3}\) are the free energies of the reduction and oxidation transition states of the \(E\) step, respectively, and are also defined in terms of MT.
in Eq. S44–S45, where \( \lambda_3 \) is the reorganization energy of the \( E \) step and \( \Delta G_3 \) is the reaction energy of the \( E \) step, which is related to electrode potential through Eq. S46. In Eq. S46, \( U_{E,3} \) is the standard equilibrium potential of the species involved in the \( E \) step, i.e., \( [\text{Ce}^{4+} \text{(H}_2\text{O)}_b\text{(HSO}_4)_3]^0 \) and \( [\text{Ce}^{3+} \text{(H}_2\text{O)}_b\text{(HSO}_4)_3]^0 \).

\[
-i_{K,EC,E} = nF \left( \frac{k_3}{k_{-3}} \left[ [\text{Ce}^{4+} \text{(H}_2\text{O)}_6\text{(HSO}_4)_3]^0_{\text{aq}} \right] + \frac{k_{-3}}{k_3} \left[ [\text{Ce}^{3+} \text{(H}_2\text{O)}_6\text{(HSO}_4)_3]^0_{\text{aq}} \right] \right)
\]  

(S41)

\[
k_3 = \kappa_e K_{p,C,\text{Ce}^{4+}} n_{\text{aq}} \exp \left( \frac{-\Delta G_3^1}{RT} \right)
\]  

(S42)

\[
k_{-3} = \kappa_e K_{p,C,\text{Ce}^{3+}} n_{\text{aq}} \exp \left( \frac{-\Delta G_{-3}^1}{RT} \right)
\]  

(S43)

\[
\Delta G_{f,3} = \frac{\lambda_3}{4} \left( 1 + \frac{\Delta G_3}{\lambda_3} \right)^2
\]  

(S44)

\[
\Delta G_{b,3} = \frac{\lambda_3}{4} \left( 1 - \frac{\Delta G_3}{\lambda_3} \right)^2
\]  

(S45)

\[
\Delta G_3 = nF (U - U_{E,3}^r)
\]  

(S46)

The unknown concentration of the intermediate \([\text{Ce}^{3+} \text{(H}_2\text{O)}_b\text{(HSO}_4)_3]^0\) in Eq. S41 can be defined in terms of the known concentration of the bulk \( \text{Ce}^{3+} \) species, \([\text{Ce}^{3+} \text{(H}_2\text{O)}_b]^3^+\), and the equilibrium constant of the \( C \) step. Assuming the \( C \) step is quasi-equilibrated, then the reaction rate of the \( C \) step, \( r_4 \), is equal to zero (Eq. S47). In Eq. S47, the forward and backward rates of the \( C \) step, \( k_4 \) and \( k_{-4} \), are related to the equilibrium constant \( K_4 \), as shown in Eq. S48. \( K_4 \) can also be related to the free energy of the \( C \) step, \( \Delta G_4 \), as shown in Eq. S48. \( \Delta G_4 \) is related to the electrode potential through Eq. S49, where, as defined earlier, \( U^r \) is the standard equilibrium potential. When \( U = U^r \), \( \Delta G_3 = \Delta G_4 \).

\[
r_4 = 0 = k_4 \left[ [\text{Ce}^{3+} \text{(H}_2\text{O)}_6\text{(HSO}_4)_3]^0_{\text{aq}} \right] [\text{H}_2\text{O}]^3 - k_{-4} \left[ [\text{Ce}^{3+} \text{(H}_2\text{O)}_6\text{(HSO}_4)_3]^0_{\text{aq}} \right] [\text{H}_2\text{O}]^3
\]  

(S47)

\[
K_4 = \frac{k_4}{k_{-4}} = \exp \left( \frac{\Delta G_4}{RT} \right)
\]  

(S48)

\[
\Delta G_4 = -nF (U^r - U_{E,3}^r)
\]  

(S49)

Solving Eq. S47–S49 for the concentration of \([\text{Ce}^{3+} \text{(H}_2\text{O)}_b\text{(HSO}_4)_3]^0\) results in Eq. S50, where \([\text{Ce}^{3+}]\) is the concentration of the bulk \( \text{Ce}^{3+} \) species. Plugging Eq. S50 into the kinetic current rate law (Eq. S41), Eq. S51 is obtained. In Eq. S51, \( Z_3 = \kappa_e K_{p,\text{Ce}^{3+}} n_{\text{aq}} = \kappa_e K_{p,\text{Ce}^{4+}} n_{\text{aq}} \) and \([\text{Ce}^{4+}]\) is the concentration of the bulk \( \text{Ce}^{4+} \) species.

\[
\left[ [\text{Ce}^{3+} \text{(H}_2\text{O)}_6\text{(HSO}_4)_3]^0_{\text{aq}} \right] = \left[ [\text{Ce}^{3+} \text{(H}_2\text{O)}_6\text{(HSO}_4)_3]^3_{\text{aq}} \right] [\text{H}_2\text{O}]^3 / K_4 [\text{H}_2\text{O}]^3
\]  

(S50)

\[
-i_{K,EC,E} = nF Z_3 \left( \frac{[\text{Ce}^{4+}]}{[\text{Ce}^{3+}][\text{HSO}_4]^3} K_4 [\text{H}_2\text{O}]^3 \right) \exp \left( \frac{-\lambda_3}{4RT} \left( 1 + \frac{nF (U - U_{E,3}^r)}{\lambda_3} \right)^2 \right)
\]  

(S51)
$E_{E,3}$ is defined in Eq. S52, which, along with $\eta = U - U_{eq}$, can be used to simplify the kinetic current rate law for the EC mechanism with the $E$ step as the RDS further into Eq. S53. This kinetic current can then be used to derive expressions for exchange current density and cathodic Tafel slopes as a function of [Ce$^{4+}$] and temperature.

$$U^*_{E,3} = U^* - \frac{RT}{nF}\ln K_4$$

(S52)

$$i_{K,EC,E} = -nFZ_3\left(\frac{[\text{Ce}^{4+}] \exp \left(\frac{-\lambda_3}{4RT} \left(1 + \frac{nF\eta}{\lambda_3} - \frac{RT}{\lambda_3} \ln \frac{[\text{Ce}^{3+}]}{K_4[\text{Ce}^{4+}]}\right)^2\right)}{K_4[H_2O]^3 \exp \left(\frac{-\lambda_3}{4RT} \left(1 - \frac{nF\eta}{\lambda_3} + \frac{RT}{\lambda_3} \ln \frac{[\text{Ce}^{3+}]}{K_4[\text{Ce}^{4+}]}\right)^2\right)}\right)$$

(S53)

Briefly, although Eq. S53 does capture the experimentally observed behavior, the parameters from fitting are physically unrealistic as discussed below.

**EC Mechanism, C RDS rate law derivation**

The rate law for the EC mechanism when the $C$ step is the RDS is shown in Eq. S54. The ligand exchange is assumed to occur as one $C$ step.

$$-i_{K,EC,C} = nF(k_4[[\text{Ce}^{III}(H_2O)6(\text{HSO}_4)3]_{aq}^0][H_2O]^3 - k_{-4}[[\text{Ce}^{III}(H_2O)9]_{aq}^3][\text{SO}_4^{2-}]^3)$$

(S54)

The concentration of the unknown intermediate species, $[[\text{Ce}^{III}(H_2O)9(\text{HSO}_4)3]_{aq}^0]$, can be calculated assuming the $E$ step is quasi-equilibrated, meaning the $E$ step reaction rate, $r_3$, is equal to zero, as shown in Eq. S55. In Eq. S55, the reduction and oxidation rate constants of the $E$ step are defined using MT, as shown previously in Eq. S42–S43.

$$r_3 = 0 = k_3[[\text{Ce}^{IV}(H_2O)6(\text{HSO}_4)3]^+_aq] - k_{-3}[[\text{Ce}^{III}(H_2O)6(\text{HSO}_4)3]_{aq}^0]$$

(S55)

Plugging these expressions for $k_3$ and $k_{-3}$ into Eq. S55, the concentration of $[[\text{Ce}^{III}(H_2O)6(\text{HSO}_4)3]_{aq}^0$ is calculated, as shown in Eq. S56.

$$[[\text{Ce}^{III}(H_2O)6(\text{HSO}_4)3]_{aq}^0] = [[\text{Ce}^{IV}(H_2O)6(\text{HSO}_4)3]^+_aq] \exp \left(\frac{-nF}{RT} (U - U^*_{E,3})\right)$$

(S56)

Substituting Eq. S56 in Eq. S54 and using the definition for $E^*_{E,3}$ from Eq. S52, the definition for $K_4 = k_4/k_{-4}$, and $\eta = U - U_{eq}$, the kinetic current can be simplified further into Eq. S57. This rate law can be used to model exchange current densities and cathodic Tafel slopes as a function of [Ce$^{4+}$] and temperature.

$$-i_{K,EC,C} = nFk_{-4}[[\text{Ce}^{3+}][H_2O]^3 \exp \left(-\frac{nF\eta}{RT}\right) - [\text{Ce}^{3+}][\text{HSO}_4^{3-}]^3$$

(S57)

Briefly, Eq. S57 cannot capture the maximum in exchange current density with [Ce$^{4+}$] observed experimentally, and so it is not a correct rate law.

**Kinetic fitting results**

Table S9 includes the optimal fitting parameters used in the fit of each rate law to the Pt and GC data. Fitting parameters were obtained by minimizing the normalized mean square error between the observed and modeled exchange current density and cathodic Tafel slope values. As discussed in the main text, the
CE, E RDS rate law was the only rate law that satisfactorily met all nine criteria (Table 1) and had reasonable results.

Table S9. Fitted parameters for all considered rate laws. The values of the parameters used in each of the rate law fits to the Pt and GC data are included. The rate laws considered are the BV and MT rate laws, as well as the CE, E RDS, CE, C RDS, EC, E RDS, and the EC, E RDS rate laws. The corresponding rate law equations are included for reference. For comparison, the DFT-predicted equilibrium constant $K_1$ and reorganization energy are included. The rate law most consistent with the experimental data is the CE mechanism with an E RDS.

| Rate Law Fitting Results | BV (Eq. 1) | | MT (Eq. S22) | | CE mechanism, E RDS (Eq. 3) | | CE mechanism, C RDS (Eq. S39) | | EC mechanism, E RDS (Eq. S53) | | EC mechanism, C RDS (Eq. S57) | From density functional theory modeling |
|--------------------------|------------|---------------|--------------------------|-----------------------------|--------------------------|--------------------------|--------------------------|--------------------------|--------------------------|--------------------------|
| $E_a$ (kJ mol$^{-1}$)    | $\alpha$  | $k_0$ (cm s$^{-1}$) | NMSE | $\lambda_{MT}$ (kJ mol$^{-1}$) | $Z_{MT}$ (cm s$^{-1}$) | NMSE | $\lambda_2$ (kJ mol$^{-1}$) | $K_1$ | $Z_2$ (cm s$^{-1}$) | NMSE | $\lambda_3$ (kJ mol$^{-1}$) | $K_4$ | $Z_3$ (cm s$^{-1}$) | NMSE | $k_{-4}$ (cm s$^{-1}$) | NMSE | $\lambda$ (kJ mol$^{-1}$) | $K_1$ |
| Pt RDE                  | 48.3       | 0.23          | 1.43×10$^{-4}$ | 0.050 | 29.7 | 1.43×10$^{-3}$ | 0.097 | 663.4 | 6.6×10$^{-6}$ | 8.22×10$^2$ | 0.051 | 60.0 | 2.4×10$^{-3}$ | 4.19×10$^{-4}$ | 0.074 | 1.37×10$^{-4}$ | 1.514 | 2.80×10$^{-3}$ | 1.562 |
| GC RDE                  | 41.2       | 0.23          | 2.99×10$^{-5}$ | 0.079 | 29.8 | 2.89×10$^{-4}$ | 0.084 | | | | | | | | | |

*Note, the DFT-predicted $\lambda$ value is for the [Ce$^{3+}$]/[Ce$^{4+}$] CT, and the DFT-predicted $K_1$ value is for the ligand exchange energy from [Ce$^{4+}$([H$_2$O)$_6$])$^{4+}$] to [Ce$^{4+}$([H$_2$O)$_6$HSO$_4$])$^{4+}$.

Fig. S20 shows the fit of the Pt and GC kinetic data to the MT rate law, with fitting parameters $\lambda_{MT}$ and $Z_{MT}$ optimized to minimize the mean squared error between the experimental and modeled values. As discussed in the main text, the MT rate law is unable to capture the asymmetry of the observed data points, with the maximum in exchange current density predicted to occur at 50% [Ce$^{4+}$] instead of the observed ~70% [Ce$^{4+}$], as shown in Fig. S20a for Pt and Fig. S20c for GC. The modeled cathodic Tafel slope behavior as a function of [Ce$^{4+}$] for both Pt and GC (Fig. S20c, Fig. S20g) also does not agree with the observed behavior due to the forced symmetry of the MT rate law. The increase in exchange current density and cathodic Tafel slope as a function of temperature is only partially captured for both Pt and GC, most likely due to the low fitted reorganization energy values for both Pt and GC that are approximately equal at 30 kJ/mol (Fig. S20b,d for Pt and Fig. S20f,h for GC).
**Fig. S20. Fit of Pt and GC data to MT rate law.** Fit of the MT rate law to the experimental data for Pt (a) exchange current densities as a function of [Ce⁴⁺], (b) exchange current densities as a function of temperature, (c) cathodic Tafel slopes as a function of [Ce⁴⁺], and (d) cathodic Tafel slopes as a function of temperature. Data in (a) and (c) collected at room temperature in 2 M H₂SO₄ at total cerium concentration of 0.05 M. Data in (b) and (d) collected at a total cerium concentration of 0.05 M with a Ce⁴⁺ concentration of 0.026 M. Solid blue lines are the fit to the data from the MT rate law. The reorganization energy $\lambda_M$ and preexponential factor $Z_M$ in (a)-(d) were obtained through minimizing the NMSE of the Pt data (NMSE = 0.097). Fit of the MT rate law to the experimental data for GC (e) exchange current densities as a function of [Ce⁴⁺], (f) exchange current densities as a function of temperature, (g) cathodic Tafel slopes as a function of [Ce⁴⁺], and (h) cathodic Tafel slopes as a function of temperature. Data in (e) and (g) collected at room temperature in 2 M H₂SO₄ at total cerium concentration of 0.05 M. Data in (f) and (h) collected at a total cerium concentration of 0.05 M with a Ce⁴⁺ concentration of 0.025 M. Solid orange lines are the fit to the data from the MT rate law. The reorganization energy $\lambda_M$ and preexponential factor $Z_M$ in (e)-(h) were obtained through minimizing the NMSE of the GC data (NMSE = 0.084). Reported values are averaged from three runs, with error bars representing one standard deviation from the average value in both horizontal and vertical directions. An Ag/AgCl reference electrode and graphite rod counter electrode were used for all measurements. All measurements were collected at 2000 rpm of the RDE where mass transport is not limiting.
The fit of the CE, E RDS derived rate law to the cathodic Tafel slope as a function of temperature is shown in Fig. S21. The model successfully predicts an increase in cathodic Tafel slope with increasing temperature, although the slope is not completely captured. This is most likely due to the value of the reorganization energy of the E step, $\lambda_2$, being lower than what would be required to achieve a faster increase in cathodic Tafel slope with temperature. The fitted value of $\lambda_2$ is obtained through the fit of not only the data shown in Figure S21, but also the data in Figure 4b–d shown in the main text. The best fit was found for a value of $\lambda_2$ of 100.2 kJ/mol to satisfactorily fit the rest of the data in addition to the Tafel slope data.

![Graph showing fit of Pt cathodic Tafel slope as a function of temperature with CE, E RDS rate law.](image)

**Figure S21.** Fit of Pt cathodic Tafel slope as a function of temperature with CE, E RDS rate law. Tafel slopes for the Pt RDE (blue circles) extracted from Tafel plots as a function temperature at Ce$^{4+}$ concentration of 0.026 M and total Ce concentration of 0.05 M and fit using the CE, E RDS rate law (blue line). Reported values are averaged from three runs, with error bars representing one standard deviation from the average value in both horizontal and vertical directions. An Ag/AgCl reference electrode and graphite rod counter electrode were used. The solutions were sparged with nitrogen gas for at least 15 minutes before measurements were collected and blanketing with nitrogen was continued throughout the measurement collection. All data were collected at 2000 rpm of the RDE. The reorganization energy $\lambda_2$ and equilibrium constant $K_1$ were obtained through minimizing the NMSE of the Pt data (NMSE = 0.049).

The fit of the GC data to the CE, E RDS rate law is shown in Fig. S22. Similar to the fit of the Pt data (Fig. 4b–d), the CE, E RDS rate law successfully predicts a maximum in exchange current density as a function of [Ce$^{4+}$] at ~70% [Ce$^{4+}$] (Fig. S22a), an increase in exchange current density with temperature (Fig. S22b), a decrease in cathodic Tafel slope with increasing [Ce$^{4+}$] (Fig. S22c) and an increase in Tafel slope with temperature (Fig. S22d). The optimal fitting parameters for the fit of the GC data to the CE, E RDS rate law are $K_1 = 6.5 \times 10^{-5}$, $\lambda_2 = 71.8$ kJ/mol, and $Z_2 = 8.64$. The differences between the fitted values for GC and Pt are discussed in the main text.
Fig. S22. Fit of GC data to CE, E RDS rate law. Fit of the CE, E RDS rate law to the experimental data for GC (a) exchange current densities as a function of [Ce⁴⁺], (b) exchange current densities as a function of temperature, (c) cathodic Tafel slopes as a function of [Ce⁴⁺], and (d) cathodic Tafel slopes as a function of temperature. Data in (a) and (c) collected at room temperature in 2 M H₂SO₄ at total cerium concentration of 0.05 M. Data in (b) and (d) collected at a total cerium concentration of 0.05 M with a Ce⁴⁺ concentration of 0.025 M. Solid orange lines are the fit to the data from the CE, E RDS rate law. The reorganization energy 𝜆₂ and equilibrium constant 𝐾₁ were obtained through minimizing the NMSE of the GC data (NMSE = 0.065). Reported values are averaged from three runs, with error bars representing one standard deviation from the average value in both horizontal and vertical directions. An Ag/AgCl reference electrode and graphite rod counter electrode were used for all measurements. All measurements were collected at 2000 rpm of the RDE where mass transport is not limiting.

The fits of the CE, C RDS rate law to the Pt and GC data are shown in Fig. S23. Although the rate law satisfies Criterion 6, which asserts that the exchange current density will increase with temperature, as shown in Fig. S23b for Pt and Fig. S23f for GC, it fails to capture the maximum in exchange current density at ~70% Ce⁴⁺ concentration (Criterion 5, Fig. S23a for Pt and Fig. S23e for GC). This is because the anodic and cathodic branches of the current expression (Eq. S36) are only dependent on either [Ce⁵⁺] or [Ce⁴⁺], and never are a factor of both. From Eq. S39, the anodic current increases exponentially with positive overpotential, and the cathodic branch current is essentially constant with overpotential. As a result, Tafel slopes are unrealistically large at magnitudes of greater than 18,000 mV/decade, which is why they do not appear in Fig. S23c–d for Pt or Fig. S23g–h for GC (Criteria 7–9).
Fig. S23. Fit of Pt and GC data to CE, C RDS rate law. Fit of the CE, C RDS rate law to the experimental data for Pt (a) exchange current densities as a function of [Ce^4+], (b) exchange current densities as a function of temperature, (c) cathodic Tafel slopes as a function of [Ce^4+], and (d) cathodic Tafel slopes as a function of temperature. Data in (a) and (c) collected at room temperature in 2 M H_2SO_4 at total cerium concentration of 0.05 M. Data in (b) and (d) collected at a total cerium concentration of 0.05 M with a Ce^4+ concentration of 0.026 M. Solid blue lines are the fit to the data from the CE, C RDS rate law. The C step forward rate constant k_1 in (a)-(d) was obtained through minimizing the NMSE of the Pt data (NMSE = 46.6). Fit of the CE, C RDS rate law to the experimental data for GC (e) exchange current densities as a function of [Ce^4+], (f) exchange current densities as a function of temperature, (g) cathodic Tafel slopes as a function of [Ce^4+], and (h) cathodic Tafel slopes as a function of temperature. Data in (e) and (g) collected at room temperature in 2 M H_2SO_4 at total cerium concentration of 0.05 M. Data in (f) and (h) collected at a total cerium concentration of 0.05 M with a Ce^4+ concentration of 0.025 M. Solid orange lines are the fit to the data from the CE, C RDS rate law. The C step forward rate constant k_1 in (e)-(h) was obtained through minimizing the NMSE of the GC data (NMSE = 49.4). Reported values are averaged from three runs, with error bars representing one standard deviation from the average value in both horizontal and vertical directions. An Ag/AgCl reference electrode and graphite rod counter electrode were used for all measurements. All measurements were collected at 2000 rpm of the RDE where mass transport is not limiting.
Fig. S24 shows the fits of the EC, C RDS rate law to the Pt and GC data. Similar to the CE, C RDS rate law discussed above, the kinetic current rate law (Eq. S57) predicts a linear dependence of exchange current density with [Ce⁴⁺], as shown in Fig. S24a for Pt and Fig. S24e for GC. The behavior of the Tafel slopes is not appropriately captured in the case of the EC, C RDS rate law (Fig. S24c–d for Pt, and Fig. S24g–h for GC) because the cathodic current is predicted to increase exponentially with negative overpotential, making Tafel slopes too small compared to experimentally reported Tafel slopes (failing Criterion 7) and essentially constant with changes in [Ce⁴⁺] or temperature (failing Criteria 8-9).
Figure S24. Fit of Pt and GC data to EC, C RDS rate law. Fit of the EC, C RDS rate law to the experimental data for Pt (a) exchange current densities as a function of [Ce⁴⁺], (b) exchange current densities as a function of temperature, (c) cathodic Tafel slopes as a function of [Ce⁴⁺], and (d) cathodic Tafel slopes as a function of temperature. Data in (a) and (c) collected at room temperature in 2 M H₂SO₄ at total cerium concentration of 0.05 M. Data in (b) and (d) collected at a total cerium concentration of 0.05 M with a Ce⁴⁺ concentration of 0.026 M. Solid blue lines are the fit to the data from the EC, C RDS rate law. The C step backward rate constant \( k_{-4} \) in (a)-(d) was obtained through minimizing the NMSE of the Pt data (NMSE = 1.51). Fit of the EC, C RDS rate law to the experimental data for GC (e) exchange current densities as a function of [Ce⁴⁺], (f) exchange current densities as a function of temperature, (g) cathodic Tafel slopes as a function of [Ce⁴⁺], and (h) cathodic Tafel slopes as a function of temperature. Data in (e) and (g) collected at room temperature in 2 M H₂SO₄ at total cerium concentration of 0.05 M. Data in (f) and (h) collected at a total cerium concentration of 0.05 M with a Ce⁴⁺ concentration of 0.025 M. Solid orange lines are the fit to the data from the EC, C RDS rate law. The C step backward rate constant \( k_{-4} \) in (e)-(h) was obtained through minimizing the NMSE of the GC data (NMSE = 1.56). Reported values are averaged from three runs, with error bars representing one standard deviation from the average value in both horizontal and vertical directions. An Ag/AgCl reference electrode and graphite rod counter electrode were used for all measurements. All measurements were collected at 2000 rpm of the RDE where mass transport is not limiting.
The fit of the $EC, E$ RDS rate law to the Pt and GC data is included in Fig. S25. While all kinetic behavior (Criteria 5–9) is technically met through the fit, some of the optimized fitting parameters for Pt were unreasonable, i.e., the reorganization energy was unreasonably large at 663 kJ/mol, and for both Pt and GC, the predicted equilibrium constant of the $C$ step suggested that Ce$^{3+}$ was preferentially complexed by sulfate, not coordinated by water. As discussed in the main text, our EXAFS results and DFT-predicted free energy of Ce$^{3+}$ water coordination contradict this finding, and thus we can reject the $EC, E$ RDS rate law. It can also be argued that while the cathodic Tafel slopes do decrease slightly with the increase in [Ce$^{4+}$] for Pt (Fig. S25c), the slope of the predicted behavior is not steep enough, possibly due to the unreasonably large, predicted, reorganization energy value.
Fig. S25. Fit of Pt and GC data to $EC, E$ RDS rate law. Fit of the $EC, E$ RDS rate law to the experimental data for Pt (a) exchange current densities as a function of $[Ce^{4+}]$, (b) exchange current densities as a function of temperature, (c) cathodic Tafel slopes as a function of $[Ce^{4+}]$, and (d) cathodic Tafel slopes as a function of temperature. Data in (a) and (c) collected at room temperature in 2 M $H_2SO_4$ at total cerium concentration of 0.05 M. Data in (b) and (d) collected at a total cerium concentration of 0.05 M with a $Ce^{4+}$ concentration of 0.026 M. Solid blue lines are the fit to the data from the $CE, E$ RDS rate law. The reorganization energy $\lambda_3$, equilibrium constant $K_4$, and preexponential constant $Z_3$ were obtained through minimizing the NMSE of the Pt data (NMSE = 0.051). Fit of the $EC, E$ RDS rate law to the experimental data for GC (e) exchange current densities as a function of $[Ce^{4+}]$, (f) exchange current densities as a function of temperature, (g) cathodic Tafel slopes as a function of $[Ce^{4+}]$, and (h) cathodic Tafel slopes as a function of temperature. Data in (e) and (g) collected at room temperature in 2 M $H_2SO_4$ at total cerium concentration of 0.05 M. Data in (f) and (h) collected at a total cerium concentration of 0.05 M with a $Ce^{4+}$ concentration of 0.025 M. Solid orange lines are the fit to the data from the $CE, E$ RDS rate law. The reorganization energy $\lambda_3$, equilibrium constant $K_4$, and preexponential constant $Z_3$ were obtained through minimizing the NMSE of the GC data (NMSE = 0.074). Reported values are averaged from three runs, with error bars representing one standard deviation from the average value in both horizontal and vertical directions. An Ag/AgCl reference electrode and graphite rod counter electrode were used for all measurements. All measurements were collected at 2000 rpm of the RDE where mass transport is not limiting.
Section S6. DFT-predicted reorganization energies

The computed reorganization energies relevant to the cerium redox reaction in sulfuric acid, i.e., the water-coordinated Ce³⁺/Ce⁴⁺ species, are included in Table S10. Reorganization energies were calculated as described in the Methods section. Considering the CE mechanism from which \( \lambda_2 \) is determined by fitting experimental kinetic data of the Ce³⁺/Ce⁴⁺ redox reaction, the relevant Ce³⁺/Ce⁴⁺ species are \([\text{Ce}^{III}(\text{H}_2\text{O})_9]^{3+}/[\text{Ce}^{IV}(\text{H}_2\text{O})_9]^{4+}\). The calculated \( \lambda \) value for the \([\text{Ce}^{III}(\text{H}_2\text{O})_9]^{3+}/[\text{Ce}^{IV}(\text{H}_2\text{O})_9]^{4+}\) species (87.2 kJ/mol) is lower than the fitted \( \lambda_2 \) value for Pt (100.2 kJ/mol) but higher than the value for GC (71.8 kJ/mol).

Table S10. The inner- (\( \lambda_i \)) and outer-sphere (\( \lambda_o \)) reorganization energies and the total reorganization energy (\( \lambda \)) from DFT. \( \lambda_i \) is calculated by averaging \( E_{ox}(R^{red}) - E_{ox}(R^{ox}) \) and \( E_{red}(R^{ox}) - E_{red}(R^{red}) \), where \( E \) is the energy of the oxidized or reduced state with COSMO implicit solvation and \( R \) is the geometry. \( \lambda_o \) is calculated by averaging \( G_{ox}^{\text{eq}} - G_{ox}^{\text{eq}} \) and \( G_{red}^{\text{eq}} - G_{red}^{\text{eq}} \), where \( G \) is the free energy of the oxidized or reduced state, defined at either equilibrium or non-equilibrium conditions.

| Ce species involved in \( E \) | \( E_{ox}(R^{red}) - E_{ox}(R^{ox}) \) (kJ mol\(^{-1}\)) | \( E_{red}(R^{ox}) - E_{red}(R^{red}) \) (kJ mol\(^{-1}\)) | \( \lambda_i \) (kJ mol\(^{-1}\)) | \( G_{ox}^{\text{eq}} - G_{ox}^{\text{eq}} \) (kJ mol\(^{-1}\)) | \( G_{red}^{\text{eq}} - G_{red}^{\text{eq}} \) (kJ mol\(^{-1}\)) | \( \lambda_o \) (kJ mol\(^{-1}\)) | \( \lambda \) (kJ mol\(^{-1}\)) |
|-----------------------------|-------------------------------------------------|-------------------------------------------------|---------------------------------|---------------------------------|---------------------------------|---------------------------------|---------------------------------|
| \([\text{Ce}^{III}(\text{H}_2\text{O})_9]^{3+}/[\text{Ce}^{IV}(\text{H}_2\text{O})_9]^{4+}\) | 61.7 | 19.1 | 40.4 | 46.7 | 46.8 | 46.8 | 87.2 |

Although the computed reorganization energies in the oxidation and reduction direction are not perfectly symmetric, they are not sufficiently different to explain the large asymmetry in the charge transfer. The \( \lambda_2 \) value that we obtain from fitting the Pt and GC data assumes that the reorganization energy of the oxidation step is equal to the reorganization energy of the reduction step, i.e., the reorganization energies are symmetric. We see from the calculations (Table S10), however, that for the \([\text{Ce}^{III}(\text{H}_2\text{O})_9]^{3+}/[\text{Ce}^{IV}(\text{H}_2\text{O})_9]^{4+}\) species, the reorganization energy associated with the reduction (\( E_{ox}(R^{red}) - E_{ox}(R^{ox}) + G_{ox}^{\text{eq}} - G_{ox}^{\text{eq}} = 108.4 \text{ kJ/mol} \)) is not equal to the oxidation reorganization energy (\( E_{red}(R^{ox}) - E_{red}(R^{red}) + G_{red}^{\text{eq}} - G_{red}^{\text{eq}} = 65.9 \text{ kJ/mol} \)), and as is convention, we instead report the average of these two values. While this analysis suggests that we may have an asymmetric Marcus theory electron transfer, we find that a factor of two difference between oxidation and reduction reorganization energies does not capture the extreme asymmetry observed in our kinetics. To demonstrate this, we show the free energy curves for a system with symmetric reorganization energies in Fig. S26a, for a system where the oxidation and reduction reorganization energies differ by a factor of two in Fig. S26b, and for a system where the reorganizations energies differ by a factor of nine in Fig. S26c. In the symmetric case, the intersection of the parabolas occurs at a reaction coordinate of 0.5, corresponding to a symmetric charge transfer coefficient of 0.5. In the asymmetric case where the reorganization energies differ by a factor of two, the intersection of the Marcus theory parabolas are only slightly shifted from the value of 0.5. For the intersection to shift to a reaction coordinate value of 0.25, which would align with our observed value of \( \alpha \), the reorganization energies would have to differ by a factor of nine (Fig. S26c), which is unrealistic. This finding agrees with a previous report that the cerium redox reaction’s unusual asymmetry cannot be described with an asymmetric model of Marcus theory alone.³
Fig. 26. Free energy parabolas using Marcus theory for two species, with the reorganization energy of the reduction, $\lambda_{ox}$, fixed to 100 kJ/mol, and the oxidation reorganization energy, $\lambda_{red}$, set to (a) 100 kJ/mol, representing a symmetric system, (b) 200 kJ/mol, and (c) 900 kJ/mol.

From our predicted rate law for a CE, E RDS mechanism, in acids other than H$_2$SO$_4$, the Ce$^{3+}$/Ce$^{4+}$ kinetics would depend on the complexation energy of Ce$^{4+}$, i.e., $K_1$. The rate law for this mechanism in Eq. S35 (Eq. 3 in main text) is dependent on the preexponential factor, $Z_2$, ligand exchange equilibrium constant, and reorganization energy. If other acids follow the CE mechanism, the reorganization energy would be the same in all acids, since the species in the $E$ step would still be [Ce$^{III}$$(H_2O)_9$]$^{3+}$ and [Ce$^{IV}$$(H_2O)_9$]$^{4+}$. The ligand exchange equilibrium constant values in different acids from our DFT-predicted anion complexation energies$^{31}$ follow the experimental trend in redox potential shift from non-complexing HClO$_4$ to other acids. The preexponential factor may differ depending on the acid, but assuming these changes are minor compared to the effect of $K_1$, the rate would primarily depend on the value of $K_1$, with a higher $K_1$ (weaker anion complexation) resulting in faster kinetics. The order in DFT-predicted $K_1$ is HClO$_4$ > CH$_3$SO$_3$H > HNO$_3$ > CF$_3$SO$_3$H > H$_2$SO$_4$ > HCl, so the Ce$^{3+}$/Ce$^{4+}$ kinetic rate activity is expected to follow this order as well if the CE mechanism is dominant in these acids. As shown in Table S1, there is a large range in the values of standard rate constants reported for the Ce$^{3+}$/Ce$^{4+}$ redox couple as a function of both electrode and electrolyte. While trends on Au and Pt specifically are inconclusive because of the large variation reported in Ce$^{3+}$/Ce$^{4+}$ kinetic activity in H$_2$SO$_4$, kinetic trends on BDD and GC do appear to follow the expected trend, with kinetic activity following the order HClO$_4$ > HNO$_3$ > H$_2$SO$_4$ on BDD and HNO$_3$ > H$_2$SO$_4$ on GC. The expected trend is not followed on graphite, however, on which a mixture of MSA and H$_2$SO$_4$ has faster kinetics than MSA. However, it is entirely possible an EC mechanism may dominate in other electrolytes, in which case the reorganization energy and ligand exchange equilibrium constant would both be different in each acid. While further analysis of the effect of acid on cerium redox kinetics is beyond the scope of this work, this simple analysis demonstrates the utility of the rate laws developed for the CE and EC mechanisms to understand trends in kinetic performance.
Section S7. Experimental methods

S7.1 EXAFS spectra comparing cerium(III) carbonate and cerium(III) trifluoromethanesulfonate precursors

To confirm our previous UV-Vis spectroscopy findings that the coordination of Ce$^{3+}$ does not change in 2 M TFSA (CF$_3$SO$_3$H) as the precursor salt is changed, here we compare the Ce K-edge EXAFS of a 0.05 M Ce$^{3+}$ solution prepared from 0.025 M Ce$_2$(CO$_3$)$_3$ to the EXAFS of a 0.05 M Ce(CF$_3$SO$_3$)$_3$ in 2 M TFSA solution in Fig. S27a-c. The spectra do not change significantly with precursor salt. For reference, the Ce K-edge EXAFS of 0.025 Ce$_2$(CO$_3$)$_3$ in 2 M H$_2$SO$_4$, 2 M TFSA, and 2 M MSA are compared in Fig. S27d-f. The differences in EXAFS spectra in Fig. S27a-c are less significant than those observed in Fig. S27d-f, for which we have already concluded that there exist no differences in Ce$^{3+}$ coordination (Fig. S6). Thus, this EXAFS comparison presents additional evidence that the use of Ce$_2$(CO$_3$)$_3$ as a precursor salt does not result in appreciable Ce$^{3+}$-carbonate complexation in acidic media following sparging with nitrogen.

Fig. S27. Ce K-edge $k^2\chi(R)$ EXAFS of Ce$^{3+}$ in TFSA, H$_2$SO$_4$, and MSA. Ce K-edge EXAFS of 0.025 M Ce$_2$(CO$_3$)$_3$ in 2 M TFSA (green solid line) and 0.05 M Ce(CF$_3$SO$_3$)$_3$ in 2 M TFSA (dark blue solid line) in the (a) R space (imaginary), (b) k space, and (e) R space (magnitude). Ce K-edge EXAFS of 0.025 M Ce$_2$(CO$_3$)$_3$ in 2 M H$_2$SO$_4$ (blue solid line), 2 M TFSA (green solid line), and 2 M MSA (black solid line) in the (d) R space (imaginary), (e) k space, and (f) R space (magnitude).

S7.2 EXAFS spectra comparing cerium(III) carbonate and cerium(IV) sulfate precursors

To confirm that the carbonate from the Ce$_2$(CO$_3$)$_3$ precursor was not remaining in solution to complex with the Ce ions during kinetic measurements, we compared the Ce$^{3+}$/Ce$^{4+}$ kinetic activity on the Pt RDE for two different Ce solutions: 0.025 M Ce$_2$(CO$_3$)$_3$ in 2 M H$_2$SO$_4$ and 0.05 M Ce(SO$_4$)$_2$ in 2 M H$_2$SO$_4$. Fig. S28a shows the exchange current density for the two solutions as a function of Ce$^{4+}$ concentration and Fig. S28b shows the cathodic Tafel slopes as a function of Ce$^{4+}$ concentration. To obtain the different concentrations of Ce$^{4+}$ versus Ce$^{3+}$ for the Ce(SO$_4$)$_2$ solution, the solution was electrochemically reduced as needed. There is no significant difference in either the exchange current densities or Tafel slopes of the Ce$_2$(CO$_3$)$_3$ solution compared to the Ce(SO$_4$)$_2$, indicating that the Ce$^{3+}$ and Ce$^{4+}$ ions are behaving the same in each of these
solutions. Thus, we conclude that there is no appreciable complexation of either Ce\(^{3+}\) or Ce\(^{4+}\) with carbonate at the experimental conditions we tested.

Fig. S28. Kinetic activity for Ce solutions prepared from Ce\(_2\)(CO\(_3\))\(_3\) and Ce(SO\(_4\))\(_2\) on the Pt RDE from Tafel method. (a) Exchange current densities and (b) cathodic Tafel slopes as a function of Ce\(^{4+}\) concentration (based on titration) in 2 M H\(_2\)SO\(_4\) solution with total cerium concentration of 0.05 M, with cerium ions prepared from either 0.025 M Ce\(_2\)(CO\(_3\))\(_3\) (orange points) or 0.05 M Ce(SO\(_4\))\(_2\) (blue points). An Ag/AgCl reference electrode and graphite rod counter electrode were used. The solutions were sparged with nitrogen gas for at least 15 minutes before measurements were collected and blanketing with nitrogen was continued throughout the measurement collection. All data were collected at 2000 rpm of the RDE.

S7.3 Crossover measurements

Crossover of cerium ions through the ion exchange membrane can occur throughout the electrochemical oxidation procedure and kinetic measurements, resulting in a decrease in the total amount of cerium ions present in solution at the time of titration. To ensure the total cerium ion concentrations were consistent for each kinetic measurement, a sample of the solution in both the working and counter electrode compartments of the electrochemical cell was collected and UV-Vis measurements of these samples were collected. The UV-Vis spectra of the samples were compared to ascertain how much cerium was present in the counter electrode compartment. Fig. S29 shows an example of this comparison, with Fig. S29a showing the spectra of cerium solutions that had been oxidized in the working electrode compartment of the electrochemical cell to different amounts of Ce\(^{4+}\) over the course of an experimental run that lasted for a total of 48 hours. Throughout the oxidation process, the peaks shift from those expected for pure Ce\(^{3+}\) solutions (between 190 nm and 290 nm) to those expected for Ce\(^{4+}\) in H\(_2\)SO\(_4\) (centered at 320 nm). Fig. S29b shows the spectra of the corresponding counter electrode solutions for each oxidation, along with the initial Ce\(^{3+}\) solution spectrum from the working electrode compartment for comparison. The solution in the counter electrode after Oxidation 1 is shown in the inset in Fig. S29b, from which there is a negligible amount of cerium present after the first oxidation. From Fig. S29b, after 48 hours (Oxidation 3), the amount of Ce\(^{3+}\) present in the counter electrode was approximately 8% of the total cerium added to the working electrode compartment initially, based on the intensity of the peaks at 255 nm. The amount of Ce\(^{3+}\) present would account for all the Ce ions present in the solution, because the counter electrode compartment would be undergoing a reduction reaction to counter the oxidation reaction occurring in the working electrode compartment. Based on this analysis, no kinetic measurements were collected using solutions that had been in the electrochemical cell for more than 48 hours.
Fig. S29. UV-Vis spectra of solutions with different Ce$^{3+}$/Ce$^{4+}$ concentration ratios in 2 M H$_2$SO$_4$. UV-Vis spectra of (a) cerium solutions from the working electrode compartment of the electrochemical cell; initial solution (yellow solid line) was 0.025 M Ce$_2$(CO$_3$)$_3$ in 2 M H$_2$SO$_4$, and then solutions were electrochemically oxidized to have different amounts of Ce$^{4+}$, as determined through titration; Oxidation 1 (blue solid line) was collected 20 minutes after solution was added to the electrochemical cell; Oxidation 2 (orange solid line) was collected 3 hours after solution was added to the electrochemical cell; and Oxidation 3 (brown solid line) was collected 48 hours after solution was added to the electrochemical cell; (b) cerium solutions from the counter electrode compartment of the electrochemical cell that corresponded to the first oxidation (blue solid line, in inset, which represents zoomed in area of y-axis), second oxidation (orange solid line), and third oxidation (brown solid line), with UV-Vis spectrum of initial solution collected from working electrode compartment (yellow solid line) for comparison.

S7.4 XAFS methods

We compare the XANES of the Ce$^{4+}$ in H$_2$SO$_4$ solutions that had been shipped overnight in dry ice and stored in a refrigerator to CeO$_2$ standard XANES at both the Ce K- and L$_3$-edges to confirm a 100% Ce$^{4+}$ oxidation state. As demonstrated in Fig. S30, the Ce$^{4+}$ XANES does not shift to the left of the CeO$_2$ standard XANES significantly for either edge, which would be expected if Ce$^{4+}$ had reduced back to Ce$^{3+}$. Thus, we conclude that our samples were appropriately managed to maintain 100% Ce$^{4+}$ oxidation state.
Fig. S30. Ce L₃- and K-edge Ce⁴⁺ and CeO₂ XANES. (a) Ce K-edge XANES of 0.025 M Ce₂(CO₃)₃ oxidized to Ce⁴⁺ in 2 M H₂SO₄ (dark green solid line) and CeO₂ standard (dark yellow solid line), and (b) Ce L₃-edge XANES of 0.05 M Ce₂(CO₃)₃ oxidized to Ce⁴⁺ in 2 M H₂SO₄ (dark green solid line), 0.025 M Ce₂(CO₃)₃ oxidized to Ce⁴⁺ in 2 M H₂SO₄ (light orange solid line), and CeO₂ standard (dark yellow solid line).

The masses of CeCl₃ and CeO₂ mixed with BN in the preparation of the Ce³⁺ and Ce⁴⁺ standard pellets, respectively, are included in Table S11. We varied the mass of CeCl₃, CeO₂, and BN to optimize absorption lengths and edge step of the samples. Although the Ce³⁺ standard was CeCl₃·7H₂O, it was purchased as CeCl₃, but mixed in air and the CeCl₃ hydrolyzed.

Table S11. CeCl₃-7H₂O/BN and CeO₂/BN ratios for new Ce L₃- and K-edge measurements. Specified ratios were used to achieve necessary number of absorption lengths and edge step.

| Standard   | Edge | Mass of CeCl₃ added (mg) | Mass of CeO₂ added (g) | Mass of BN added (mg) |
|------------|------|--------------------------|------------------------|-----------------------|
| CeCl₃-7H₂O | Ce L₃| 3.3                      | NA                     | 166                   |
|            | Ce K | 50                       | NA                     | 250                   |
| CeO₂       | New Ce L₃| NA                     | 4.78                   | 139                   |
|            | Ce K | NA                       | 50                     | 250                   |

The XAFS normalization parameters used for all Ce samples studied are included in Table S12. The EXAFS fitting parameters used for all Ce samples are included in Table S13. Whenever possible, the normalization parameters were kept consistent for all Ce³⁺ and all Ce⁴⁺ samples, and only varied when necessary to obtain appropriate normalization of the spectra.
### Table S12. Normalization parameters for each L₃- and K-edge measurement.

| Sample            | Edge | $E_0$ (eV) | Pre-edge range       | Normalization range       | Spline k range       |
|-------------------|------|------------|----------------------|--------------------------|----------------------|
| CeCl₃·7H₂O        | Ce K | 40430      | −150 eV to −91.31 eV | 45.531 eV to 871.14 eV   | 0 Å⁻¹ to 18.021 Å⁻¹  |
|                   | Ce L₃ | 5724.55   | −143.61 eV to −9 eV  | 21 eV to 201 eV         | 0 Å⁻¹ to 10.461 Å⁻¹  |
| Ce³⁺ ion          | Ce K | 40430      | −150 eV to −91.31 eV | 45.531 eV to 871.14 eV   | 0 Å⁻¹ to 18.021 Å⁻¹  |
|                   | Ce L₃ | 5724.55   | −143.61 eV to −9 eV  | 22 eV to 201 eV         | 0 Å⁻¹ to 10.461 Å⁻¹  |
| CeO₂              | Ce K | 40431      | −172.298 eV to −91.63 eV | 61.995 eV to 1137.247 eV | 0 Å⁻¹ to 17.977 Å⁻¹  |
|                   | Ce L₃ | 5727.14   | −143.61 eV to −23.12 eV | 32 eV to 335 eV        | 0 Å⁻¹ to 10.449 Å⁻¹  |
|                   | New Ce L₃ | 5727.14 | −143.61 eV to −19 eV | 33 eV to 330 eV        | 0 Å⁻¹ to 10.449 Å⁻¹  |
| Ce⁴⁺ ion          | Ce K | 40431      | −150 eV to −91.31 eV | 58.16 eV to 871.14 eV   | 0 Å⁻¹ to 15.965 Å⁻¹  |
|                   | Ce L₃ | 5727.14   | −143.61 eV to −23.12 eV | 32 eV to 330 eV        | 0 Å⁻¹ to 10.449 Å⁻¹  |
|                   | New Ce L₃ | 5727.14 | −143.61 eV to −9 eV | 33 eV to 251 eV        | 0 Å⁻¹ to 10.449 Å⁻¹  |
| 0.05 M CeL₃ (used in Fig. 2f) | | | | | |
| New Ce L₃ | 5727.14 | −143.61 eV to −9 eV | 33 eV to 201 eV        | 0 Å⁻¹ to 10.449 Å⁻¹  |

### Table S13. Fitting parameters for each L₃- and K-edge measurement.

| Sample            | Edge | $R_b$ (Å) | $E_0$ (eV) | Pre-edge range       | Normalization range       | Spline k range       |
|-------------------|------|-----------|------------|----------------------|--------------------------|----------------------|
| CeCl₃·7H₂O        | Ce K | 1.4 Å to 3.0 Å | 40430      | −150 eV to −91.31 eV | 45.531 eV to 871.14 eV   | 0 Å⁻¹ to 18.021 Å⁻¹  |
|                   | Ce L₃ | 1.2 Å to 3.0 Å | 5724.55   | −143.61 eV to −9 eV  | 21 eV to 201 eV         | 0 Å⁻¹ to 10.461 Å⁻¹  |
| Ce³⁺ ion          | Ce K | 1.4 Å to 3.0 Å | 40430      | −150 eV to −91.31 eV | 45.531 eV to 871.14 eV   | 0 Å⁻¹ to 18.021 Å⁻¹  |
|                   | Ce L₃ | 1.2 Å to 3.0 Å | 5724.55   | −143.61 eV to −9 eV  | 22 eV to 201 eV         | 0 Å⁻¹ to 10.461 Å⁻¹  |
| CeO₂              | Ce K | 1.4 Å to 4.6 Å | 40431      | −150 eV to −91.31 eV | 58.16 eV to 871.14 eV   | 0 Å⁻¹ to 15.965 Å⁻¹  |
|                   | Ce L₃ | 1.4 Å to 4.6 Å | 5727.14   | −143.61 eV to −9 eV  | 33 eV to 330 eV        | 0 Å⁻¹ to 10.449 Å⁻¹  |
| Ce⁴⁺ ion          | Ce K | 1.4 Å to 4.6 Å | 40431      | −150 eV to −91.31 eV | 58.16 eV to 871.14 eV   | 0 Å⁻¹ to 15.965 Å⁻¹  |
|                   | Ce L₃ | 1.4 Å to 4.6 Å | 5727.14   | −143.61 eV to −9 eV  | 33 eV to 251 eV        | 0 Å⁻¹ to 10.449 Å⁻¹  |

The normalization parameters for the Pt L₃-edge measurements included in Fig. S16 are included in Table S14.

### Table S14. Normalization parameters for Pt L₃-edge measurements.

| Sample    | Edge | $E_0$ (eV) | $R_b$ kg (Å) | Pre-edge range       | Normalization range       | Spline k range       |
|-----------|------|------------|--------------|----------------------|--------------------------|----------------------|
| Pt XANES  | Pt L₃| 11562.17   | 1.0          | −99.30 eV to −50 eV  | 24 eV to 1165.95 eV      | 0 Å⁻¹ to 9.023 Å⁻¹   |
| Pt EXAFS  | Pt L₃| 11562.17   | 1.0          | −99.30 eV to −50 eV  | 24 eV to 290.20 eV       | 0 Å⁻¹ to 9.023 Å⁻¹   |
S7.5 Kinetic measurements

The exchange current densities from the Tafel method were measured as a function of rotation rate for several Ce\(^{4+}\) concentrations (with total Ce ion concentration fixed at 0.05 M) for the Pt and GC RDEs, as shown in Fig. S31a and Fig. S31b, respectively. For all [Ce\(^{4+}\)] tested for both Pt and GC, the magnitude of the exchange current density is not dependent on rotation rate once 2000 rpm is reached. Thus, we concluded that 2000 rpm was an appropriate rotation rate to use for all kinetic measurements to ensure mass transfer was non-limiting.

In addition to plotting the exchange current density as a function of rotation rate to identify any significant mass transport effects, a Koutecký-Levich analysis was conducted for the Pt RDE for a solution of 0.02 M Ce\(^{4+}\)/2 M H\(_2\)SO\(_4\) (total Ce ion concentration was 0.05 M) to confirm measured currents are independent of mass transport. In this analysis, steady state currents were collected at a broad range of potentials at the following rotation rates \(\omega\): 100, 500, 1000, 2000, and 3000 rpm. The inverse of the observed steady state current density was then plotted as a function of rotation rate \(-1/2\) (converted to rad/s), so that the kinetic-limited current can be extracted from the y-intercept, according to the Koutecký-Levich equation, Eq. S58, where \(i_m\) is the measured steady state current density, \(i_K\) is the kinetically-limited current density, \(B_L\) is the Levich constant, and \(\omega\) is rotation rate, in rad/s.

\[
\frac{1}{i_m} = \frac{1}{i_K} + \frac{1}{B_L \omega^{1/2}} \tag{S58}
\]

Fig. S32a is the Koutecký-Levich plot for the Pt RDE in a 2 M H\(_2\)SO\(_4\) solution, with a total cerium concentration of 0.05 M and a Ce\(^{4+}\) concentration of 0.02 M, and Figs S32b and S32c are the Tafel plots used to identify exchange current density from the kinetically limited current densities and the measured steady state current densities, respectively. It should be noted that the current densities in Fig. S32 were extracted from a Tafel plot by fitting a linear trendline in an overpotential range of \(-0.250\) V to \(-0.050\) V and extrapolating to \(\eta = 0\) to obtain \(i_0\). This larger overpotential range was used to ensure that there were at least three data points for the linear trendline fitting. As can be seen from Fig. S32, the exchange current density determined from the Tafel plot that uses the measured steady state current densities is 0.372 mA/cm\(^2\), while the exchange current density determined from the Tafel plot that uses the kinetically limited current densities extracted from the Koutecký-Levich plot is 0.375 mA/cm\(^2\), representing a less than 1%
difference. Thus, it can be concluded that the activity of the Pt RDE in 2 M H₂SO₄ with 0.05 M total cerium ions is not mass-transport limited.

![Fig. S32. Koutecký-Levich analysis of Ce³⁺/Ce⁴⁺ kinetics on Pt RDE. (a) Koutecký-Levich plot for Pt RDE in 2 M H₂SO₄/0.05 M Ce solution (0.02 M Ce⁴⁺), (b) Tafel plot for Pt RDE in 2 M H₂SO₄/0.05 M Ce solution (0.02 M Ce⁴⁺) using kinetically limited current densities, extracted from the Koutecký-Levich plot in (a), and (c) Tafel plot for Pt RDE in 2 M H₂SO₄/0.05 M Ce solution (0.02 M Ce⁴⁺) using measured steady state current densities.](image)

Another method to confirm that there are no mass transfer limitations is to measure kinetics in different reactors with different mass transport conditions. To confirm our kinetic activities are independent of electrochemical reactor design, exchange current densities (Tafel method) of the Pt RDE (2000 rpm) were compared to those of a Pt wire for a 0.05 M Ce/2 M H₂SO₄ solution with stir bar rotation at several Ce⁴⁺ concentrations. For the platinum wire electrode, a magnetic stir plate was used to operate outside of the mass transfer limited regime, as confirmed by the unchanging exchange current density with increased stirring speeds. As can be seen from Fig. S33, similar exchange current densities were obtained with the Pt RDE as were obtained with the Pt wire as a function of Ce⁴⁺ concentration, confirming that both mass transfer and surface area effects were successfully controlled.
Fig. S33. Exchange current densities for Pt RDE and Pt wire. Comparison of exchange current densities determined from the Tafel plot method for the Pt RDE and Pt wire as a function of Ce$^{4+}$ concentration. Data collected at room temperature in 2 M H$_2$SO$_4$. An Ag/AgCl reference electrode and graphite rod counter electrode were used for all measurements, and $i_0$ were normalized by the electrochemically active surface area determined from hydrogen underpotential deposition.
Section S8. Computational methods

In Fig. S34 we show the modeled Ce$^{3+}$ and Ce$^{4+}$ species that were used as starting configurations to generate the MD-EXAFS. The MD-EXAFS was calculated using an 8 Å periodic box after confirming that the spectra did not change significantly compared to a 10 Å periodic box for the [Ce$^{IV}$(H$_2$O)$_9$]$^{4+}$ species (Fig. S35).

![Modeled species for the Ce$^{3+}$/Ce$^{4+}$ MD-EXAFS.](image)

**Fig. S34.** Modeled species for the Ce$^{3+}$/Ce$^{4+}$ MD-EXAFS. Atom color legend: hydrogen = white; oxygen = red; cerium = beige; chlorine = green; sulfate = yellow; carbon = gray; nitrogen = blue.

![MD-EXAFS for [Ce(H$_2$O)$_9$]$^{4+}$](image)

**Fig. S35.** MD-EXAFS for [Ce(H$_2$O)$_9$]$^{4+}$ in an 8 Å periodic box with 15 solvent waters and in a 10 Å periodic box with 32 waters at the (a) K edge and (b) L$_3$-edge.
We determined that the reorganization energies for the \([\text{Ce}^{\text{III}}(\text{H}_2\text{O})_9]^3+/[\text{Ce}^{\text{IV}}(\text{H}_2\text{O})_9]^4+\) redox reaction converged with the Stuttgart RSC 1997 ECP basis set for the cerium ion and the 6-31+G* basis set, as seen in Fig. S36 for the outer-sphere reorganization energies. The inner-sphere reorganization energies were found to similarly converge in a series of calculations without using COnductor-like Screening MOdel (COSMO). Although the final inner-sphere reorganization energies reported in Table S10 were calculated using COSMO, we expect that the inner-sphere reorganization energies calculated from each basis set would experience a near constant shift (by the energy of the implicit solvent), and so we conclude that the inner-sphere reorganization energies converge with the Stuttgart RSC 1997 ECP and 6-31+G* basis sets as well.

Figure S36. Outer-sphere reorganization energy converges with increasing basis set size for \([\text{Ce}(\text{H}_2\text{O})_9]^3+\rightleftharpoons[\text{Ce}(\text{H}_2\text{O})_9]^4+ + e^-\) redox couple. Mixed basis sets utilize the first basis set and its associated ECP on the cerium atom, and the 6-31+G* basis set on all non-cerium atoms.
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