Delivering the Full Potential of Oxygen Evolving Electrocatalyst by Conditioning Electrolytes at Near-Neutral pH

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Linear-sweep voltammograms in buffered conditions over IrO$_x$ disk electrode

![Plot of linear-sweep voltammograms](image)

**Figure S1.** Current-potential relationship for the oxygen evolution reaction (OER) over IrO$_x$. Linear-sweep voltammograms (LSVs) over the IrO$_x$ disk electrode in the rotating-disk electrode (RDE) configuration are shown, which were recorded in 0.1 mol kg$^{-1}$ Na-phosphate electrolyte solutions at pH levels from 2 to 13 (green solid line), 0.1 mol kg$^{-1}$ Na-borate electrolyte solution at pH 9.2 (black dashed line) and 0.1 mol kg$^{-1}$ Na-carbonate electrolyte solution at pH 10.3 (brown dashed-dotted line), at a disk-rotation speed of 4900 rpm, a scan rate of $-1$ mV s$^{-1}$, and a reaction temperature of 298 K. The numbers in the figure indicate the electrolyte pH in the bulk.
Potential-pH diagram for the OER over IrO\textsubscript{x} disk electrode

**Figure S2.** Potential-pH diagram for the OER over IrO\textsubscript{x} at 10 mA cm\textsuperscript{-2}. Potentials reaching +10 mA cm\textsuperscript{-2} over the IrO\textsubscript{x} RDE are plotted as a function of the pH of the electrolyte bulk. The potential was adopted from the current-potential relationship shown in **Figure S1**. The solid line labeled as $E_{eq}$ indicates the equilibrium potential for the OER.
Potential-solute molarity diagram for the OER over IrO\textsubscript{x} disk electrode

Analyzing the kinetics of the OER requires the isolation of contributions from the mass-transport, necessitating identification of the electrolyte condition that circumvents the diffusion limitation. For this reason, the OER in the phosphate solutions at a variety of molalities was examined. Figure S3 shows LSVs at pH 7 in Na-phosphate solution at 0.1, 0.5, 1.0, and 1.5 mol kg\textsuperscript{−1} over the IrO\textsubscript{x} RDE at varying disk-rotation speeds (see Figure S4 for potential-solute molarity diagram at +1 and +10 mA cm\textsuperscript{−2}, and Figure S5 for the \( j-E \) relationship at higher current densities). While the onset potential remained unchanged with varying molalities, anodic current densities depended on the disk-rotation speeds. More specifically, at the lesser molalities, the anodic current densities on the order of 10 mA cm\textsuperscript{−2} increased with the disk-rotation speed, and the variation in the anodic current densities with the disk-rotation became smaller at increasing molalities. Ultimately at molalities of 1.0 mol kg\textsuperscript{−1} or greater, \( j-E \) relationships were found to be insensitive to the disk-rotation speeds, consistent with an observation reported by Zhao et al.\textsuperscript{[S1]} These observations indicated mass-transport phenomena prevailing at the lower molalities, impeding the analysis of the kinetics at reaction rates on the order of 10 mA cm\textsuperscript{−2}, which however became absent at molalities of 1.0 mol kg\textsuperscript{−1} or greater.
Figure S3. Current-potential relationship for the OER over IrOₓ. LSVs over the IrOₓ disk electrode in the RDE configuration are shown, which was recorded in (a) 0.1, (b) 0.5, (c) 1.0, and (d) 1.5 mol kg⁻¹ Na-phosphate electrolyte solutions at pH 7, at disk-rotation speeds from 1600 to 4900 rpm, a scan rate of −1 mV s⁻¹, and a reaction temperature of 298 K.

Figure S4. Potential-solute molarity diagram for the OER over IrOₓ. Potentials reaching (a) +1 mA cm⁻² and (b) +10 mA cm⁻² over the IrOₓ RDE are plotted as a function of the solute molarity of Na-phosphate electrolyte solution at pH 7, adopted from Figure S3.
Figure S5. Current-potential relationship for the OER over IrOₓ in the current density region of ca. 100 mA cm⁻². LSVs over the IrOₓ disk electrode in the RDE configuration are shown, recorded in electrolyte solutions of (a) 0.1 mol kg⁻¹ and (b) 1.0 mol kg⁻¹ Na-phosphate at pH 7 at various disk rotation speeds from 900 to 4900 rpm, a scan rate of -1 mV s⁻¹, and a reaction temperature of 298 K. The measurement was performed from the highest to the lowest rotation speeds, followed by the highest again. The second results at 4900 rpm are denoted as 4900 rpm(2).
LSVs at various pH levels in the Na-phosphate solutions
Figure S6. Current-potential relationship for the OER over IrO$_x$ at all pH levels of 2-13. LSVs over the IrO$_x$ disk electrode in the RDE configuration are shown, recorded in electrolyte solutions of 0.1 mol kg$^{-1}$ Na-phosphate at (a) pH 2, (b) pH 3, (c) pH 4, (d) pH 5, (e) pH 6, (f) pH 8, (g) pH 9, (h) pH 10, (i) pH 11, (j) pH 12, and (k) pH 13 at various disk rotation speeds from 1600 to 4900 rpm, a scan rate of $-1$ mV s$^{-1}$, and a reaction temperature of 298 K. The measurement was performed from the lowest to the highest rotation speeds, followed by the lowest again. The second results at 1600 rpm are denoted as 1600 rpm$^{(2)}$. 

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Koutecý-Levich (K-L) plots at various pH levels in the Na-phosphate solutions
Figure S7. Koutecký-Levich (K-L) plot for the OER at various pH levels. The inverse of the current density is plotted as a function of the inverse of the square root of the rotation speed at (a) pH 2, (b) pH 3, (c) pH 4, (d) pH 5, (e) pH 6, (f) pH 8, (g) pH 9, (h) pH 10, (i) pH 11, (j) pH 12, and (k) pH 13 corresponding to the LSVs over the IrOₓ disk electrode in the RDE configuration shown in Figure S6. Open symbols correspond to 1600 rpm(2) in the LSV shown in Figure S6.
Figure S8. Tafel plots of the OER over IrO$_x$ at various pH levels. Electrode potential is compiled as a function of the kinetic current densities over the IrO$_x$ disk electrode recorded in 0.1 mol kg$^{-1}$ Na-phosphate electrolyte solutions at pH levels from 2 to 13, a scan rate of −1 mV s$^{-1}$, and a reaction temperature of 298 K.
LSVs and K-L plots in H$_2$O and D$_2$O at pH (pD) 7
Figure S9. Current-potential relationship for the OER over IrO$_x$ at pH (or pD) 7. LSVs over the IrO$_x$ disk electrode in the RDE configuration are shown, recorded in electrolyte solutions of 1.0 mol kg$^{-1}$ Na-phosphate at (a) pH 7 and (b) pD 7 at various disk rotation speeds from 1600 to 4900 rpm, a scan rate of $-1$ mV s$^{-1}$, and reaction temperature of 298 K. The measurement was performed from the lowest to the highest rotation speeds, and then the lowest rotation speed was applied again. The second results at 1600 rpm is denoted as 1600 rpm$_{(2)}$. (c)(d) Corresponding K-L plot at (a) pH 7 and (b) pD 7, respectively. The blank plot corresponds to 1600 rpm$_{(2)}$ in the LSV in (a) and (b). (e) Tafel plots using kinetic current densities over the IrO$_x$ disk electrode in the RDE configuration, obtained using K-L plots in the panel (c) and (d).
OER over IrOₓ electrode in NaOH solution

![Graph](image)

**Figure S10.** Current-potential relationship for the OER over IrOₓ in an alkaline condition. (a) LSVs over the IrOₓ disk electrode in the RDE configuration are shown, recorded in electrolyte solutions of 0.1 mol kg⁻¹ NaOH at pH 12.9 with various disk rotation speeds from 1600 to 4900 rpm, a scan rate of −1 mV s⁻¹, and reaction temperature of 298 K. The measurement was performed from the highest to the lowest rotation speeds, and then the highest rotation speed was applied again. The second results at 4900 rpm is denoted as 4900 rpm(2). (b) Corresponding K-L plot. The blank plot corresponds to 4900 rpm(2) in the LSV in (a). (c) Corresponding Tafel plots of the OER using kinetic current densities over IrOₓ disk electrode.
OER over IrO$_x$ electrode in NaOD solution

**Figure S11.** Current-potential relationship for the OER over IrO$_x$ in an alkaline condition. (a) LSVs over the IrO$_x$ disk electrode in the RDE configuration are shown, recorded in electrolyte solutions of 0.1 mol kg$^{-1}$ NaOD at pH 13 at various disk rotation speeds from 1600 to 4900 rpm, a scan rate of $-1$ mV s$^{-1}$, and a reaction temperature of 298 K. The measurement was performed from the highest to the lowest rotation speeds, and then the highest rotation speed was applied again. The second results at 4900 rpm is denoted as 4900 rpm$^{(2)}$. (b) Corresponding K-L plot. The open plot corresponds to 4900 rpm$^{(2)}$ in the LSV in (a). (c) Corresponding Tafel plots of the OER using kinetic current densities over IrO$_x$ disk electrode.
Figure S12. Current-potential relationship for the OER over IrO$_x$ at various temperatures. LSVs over the IrO$_x$ disk electrode in the RDE configuration are shown, recorded in electrolyte solutions of (a) 1.0 mol kg$^{-1}$ Na-phosphate at pH 7, (b) 1.0 mol kg$^{-1}$ Na-borate at pH 9.2, (c) 1.0 mol kg$^{-1}$ Na-carbonate at pH 10.3 and (d) 0.1 mol kg$^{-1}$ NaOH at pH 12.9, at a disk rotation speed of 3600 rpm, a scan rate of −1 mV s$^{-1}$, and a reaction temperature of 298 K, 313 K, 328 K and 343 K.
OER in 1.0 mol kg\(^{-1}\) Na-borate and Na-carbonate over IrO\(_x\) disk electrode

(a) 
(b) 
(c) 
(d) 
(e)
Figure S13. Current-potential relationship for the OER over IrO₃. LSVs over the IrO₃ disk electrode in the RDE configuration are shown, which was recorded in (a) 1.0 mol kg⁻¹ Na-borate electrolyte solution at pH 9.2 and (b) 1.0 mol kg⁻¹ Na-carbonate electrolyte solution pH 10.3, at disk-rotation speeds from 1600 to 4900 rpm, a scan rate of −1 mV s⁻¹, and a reaction temperature of 298 K. The measurement was performed from the highest to the lowest rotation speeds, and then the highest rotation speed was applied again. The second results at 4900 rpm is denoted as 4900 rpm(2). Corresponding K-L plot in (c) Na-borate and (d) Na-carbonate electrolyte solution. The blank plot corresponds to 4900 rpm(2) in the LSV in (a) and (b). (e) Corresponding Tafel plots of the OER using kinetic current densities over IrO₃ disk electrode.
Current-temperature diagram for the oxygen evolution reaction over IrO$_x$ disk electrode

**Figure S14.** Current-temperature diagram for the OER over IrO$_x$ at various overpotentials. Current densities over the IrO$_x$ disk electrode in the RDE configuration are plotted as a function of the reaction temperature, recorded in electrolyte solutions of (a) 1.0 mol kg$^{-1}$ Na-phosphate at pH 7, (b) 1.0 mol kg$^{-1}$ Na-borate at pH 9.2, (c) 1.0 mol kg$^{-1}$ Na-carbonate at pH 10.3 and (d) 0.1 mol kg$^{-1}$ NaOH at pH 12.9, which were adopted from the LSVs shown in Figure S12.
Apparent activation energy for the OER over IrO$_x$ disk electrode

**Figure S15.** Determination of the apparent activation energy for the OER over IrO$_x$. The slope values obtained in Figure S14 were plotted as a function of the overpotential, recorded in the electrolyte solutions of 1.0 mol kg$^{-1}$ Na-phosphate at pH 7, 1.0 mol kg$^{-1}$ Na-borate at pH 9.2, 1.0 mol kg$^{-1}$ Na-carbonate at pH 10.3 and 0.1 mol kg$^{-1}$ NaOH at pH 12.9, in which the intercept of y-axis corresponds to the value of apparent activation energy at zero overpotential in each condition. Overpotentials applied for this determination corresponds to the range of current density between 0.5~40 mA cm$^{-2}$.
OER measurement at high current densities using IrO₅/Ti mesh

Figure S16. OER measurement over IrOₓ at various current densities in buffered solutions. Chronopotentiometry (CP) profiles over the IrOₓ on Ti mesh are shown at 10, 20, 30, 50, and 100 mA cm⁻², which were recorded in 1.0 mol kg⁻¹ buffered solutions at a reaction temperature of 298 K without stirring. CP at 10 mA cm⁻² was conducted again at the end of each measurement in order to confirm no deterioration of the electrodes.

The CP measurement in Figure S16 was performed without stirring to define the diffusion layer thickness, which therefore is affected by the mass-transport event. As estimated, OER overpotential was smaller in phosphate solution at all reaction rates. Unexpectedly, the overpotential in the borate solution became larger than in carbonate solution, which is likely due to the lower diffusion coefficient of oxygen caused by the formation of oxygen-borate complex[S2] that can block the active site on the electrodes.
Table S1. pK\textsubscript{a} and rate constant for the OH\textsuperscript{−} generation reactions of buffering species.\textsuperscript{[S3]}

| Buffering species | pK\textsubscript{a} | \(k_{\text{OH}^-}/\text{M}^{-1}\text{s}^{-1}\) |
|-------------------|---------------------|---------------------------------|
| CO\textsubscript{3}\textsuperscript{2−}   | 10.3               | 1.2 \times 10^6                |
| PO\textsubscript{4}\textsuperscript{3−}   | 11.7               | 1.0 \times 10^6                |
| P\textsubscript{2}O\textsubscript{7}\textsuperscript{4−} | 8.45               | 1.3 \times 10^3                |
| P\textsubscript{3}O\textsubscript{10}\textsuperscript{5−} | 7.87               | 1.6 \times 10^2                |
| ATP\textsuperscript{4−}              | 6.50               | 3.8 \times 10^1                |
| C\textsubscript{6}H\textsubscript{3}O\textsuperscript{−} | 9.98               | 1.3 \times 10^6                |
| [H\textsubscript{3}C-CO-CH-CO-CH\textsubscript{3}]\textsuperscript{−} | 8.24               | 3.2 \times 10^1                |
| C\textsubscript{6}H\textsubscript{11}O\textsubscript{6}\textsuperscript{−} | 12.3               | 2.0 \times 10^6                |
| HO-(CH\textsubscript{2})\textsubscript{2}-S\textsuperscript{−} | 9.5                | 3.2 \times 10^4                |
| NH\textsubscript{3}             | 9.25               | 6.0 \times 10^5                |
| (CH\textsubscript{3})\textsubscript{3}N   | 9.79               | 1.3 \times 10^6                |
| HOOC-CH\textsubscript{2}-NH\textsubscript{2} | 9.78               | 8.4 \times 10^5                |
| Guanidine            | 12.5               | 3.2 \times 10^8                |
| Imidazole            | 6.95               | 2.2 \times 10^3                |
| Acridine            | 10.65              | 8.5 \times 10^6                |
| Piperidine          | 11.13              | 3.0 \times 10^7                |
| Uracil anion        | 9.45               | 2.8 \times 10^5                |
| Adenine anion       | 9.80               | 6.3 \times 10^5                |
| Trimethylphosphine  | 8.8                | 2.9 \times 10^2                |
| N(CH\textsubscript{2}COO\textsuperscript{−})\textsubscript{3} | 9.73               | 7.5 \times 10^2                |
| (CH\textsubscript{2})\textsubscript{2}[N(CH\textsubscript{2}VCOO\textsuperscript{−})\textsubscript{2}]\textsubscript{2} | 10.26              | 6.8 \times 10^3                |
Experimentally observed free energy of *OH and *O formation

Figure S17. Redox properties of IrO$_x$ in buffered conditions. (a) Cyclic voltammograms (CVs) highlighting redox properties over the IrO$_x$ disk electrode in a RDE configuration are shown, which were recorded in 1.0 mol kg$^{-1}$ Na-phosphate at pH 7.0, Na-borate at pH 9.2, and Na-carbonate at pH 10.3, a disk-rotation speed of 1600 rpm, a scan rate of 1 mV s$^{-1}$, and reaction temperature of 298 K. The numbers in the figure indicate the identity of redox peaks, in which the number without or with (') denote the peak recorded in the anodic and cathodic scan, respectively. (b) The free energy difference between *OH and *O adsorptions. Applying the half-coverage potential of peak 1 ($V_{\text{peak} 1}$) and peak 2 ($V_{\text{peak} 2}$) in the panel (a), the free energy of formation of *OH ($\Delta E_{*\text{OH}}$) and *O ($\Delta E_{*\text{O}}$) correspond to the $V_{\text{peak} 1}$ and $V_{\text{peak} 1} + V_{\text{peak} 2}$, respectively.\cite{54}
**Calculated overpotential for OER depending on the pK\textsubscript{a} value**

The measured exchange current density $j_0$ on the logarithmic scale and Tafel slope in buffered conditions shown in **Figure 7** was found to have a linear and a curved relationship, respectively, with the rate constants $k_{\text{OH}^-}$ and pK\textsubscript{a} values. Fitting of the results plotted in **Figure 7** yields the **Equation S1** for exchange current density $j_0$ and the **Equation S2** for Tafel slope:

$$\log(j_0) = 0.5 \cdot \log(k_{\text{OH}^-}) - 6.1,$$

**Equation S1**

$$\text{Tafel slope} = 1.1 \cdot (\log(k_{\text{OH}^-}))^2 - 0.37 \cdot \log(k_{\text{OH}^-}) + 45.$$  

**Equation S2**

In general, kinetic current density can be described by the exchange current density and the exponential term including Tafel slope value, as follows:

$$j = j_0 \exp\left(\frac{2.303 \times \eta}{\text{Tafel slope value}}\right).$$

**Equation S3**

With **Equation 29** and S1-S3, the overpotentials at given current densities were calculated as a function of the pK\textsubscript{a} value of buffering species, and are shown in **Figure S18**.
Figure S18. Calculated overpotential for the OER with respect to the pKₐ value. Overpotential for the OER over the IrOₓ disk electrode was estimated using Equation 29 and S1-S3 as a function of the pKₐ value of buffering species. The circle denotes the minimal overpotential at each current density estimated by this calculation.
Reference

[S1] Y. Zhao, N. M. Vargas-Barbosa, E. A. Hernandez-Pagan, T. E. Mallouk, *small* **2011**, 7, 2087-2093.

[S2] V. Jovancicevic, P. Zelenay, B. R. Scharifker, *Electrochim. Acta* **1987**, 32, 1553-1555.

[S3] M. Eigen, *Angew. Chem. Int. Ed.* **1964**, 3, 1-19.

[S4] D.-Y. Kuo, J. K. Kawasaki, J. N. Nelson, J. Kloppenburg, G. Hautier, K. M. Shen, D. G. Schlom, J. Suntivich, *J. Am. Chem. Soc.* **2017**, 139, 3473-3479.