

Cooling water to near freezing breaks the activity–stability trade-off of water oxidation electrocatalysis

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Supplementary Note

Supplementary Note 1. Temperature-dependent standard equilibrium potential of water oxidation

According to Salvi and de Bethune^{1,2}, the standard electrode potential of OER at a measured temperature (E_T^0) can be calculated using:

$$E_T^0 (\text{O}_{2(\text{g})}, \text{H}^+/\text{H}_2\text{O}_{(\text{liq.})}) = E_{298}^0 + (T - 298.15) \times \left(\frac{dE^0}{dT} \right)_{298} + 0.5(T - 298.15)^2 \times \left(\frac{d^2E^0}{dT^2} \right)_{298} \quad (\text{Eq. 1})$$

where E_{298}^0 , $(dE^0/dT)_{298}$, and $(d^2E^0/dT^2)_{298}$ are the standard electrode potential (1.23 V vs NHE), first temperature coefficient (-8.46×10^{-4} V/K), and second temperature coefficient (5.52×10^{-7} V/K²) of the half reaction of water oxidation at 25 °C and pH = 0, respectively. The temperature-dependent potentials are shown in Supplementary Fig. 6a and Supplementary Table 2.

Finally, the OER overpotential at different temperatures was calculated as follows:

$$\eta_{\text{OER}} = E_{\text{OER}} (\text{V vs RHE}) - E_T^0 (\text{O}_{2(\text{g})}, \text{H}^+/\text{H}_2\text{O}_{(\text{liq.})}) \quad (\text{Eq. 2})$$

Supplementary Note 2. Temperature-dependent equilibrium potential of the Ag/AgCl reference electrode

iR -compensated applied potential was calculated using the following equation:

$$E_{\text{iR}} (\text{V vs Ag/AgCl}) = E (\text{V vs Ag/AgCl}) - (i \times R_{\text{solution}}(T)) \quad (\text{Eq. 3})$$

where E (V vs Ag/AgCl), i , and $R_{\text{solution}}(T)$ are the applied potential (V vs Ag/AgCl), current (A), and measured temperature-dependent resistance of the electrolyte solution (Ω), respectively.

Further, E_{OER} (V vs RHE) was calculated as follows:

$$E_{\text{OER}} (\text{V vs RHE}) = E_{\text{iR}} (\text{V vs Ag/AgCl}) + E_T (\text{Ag/AgCl}) + \frac{2.303RT}{F} \text{pH} \quad (\text{Eq. 4})$$

where E_T (Ag/AgCl) is the equilibrium potential of Ag/AgCl reference electrode with saturated KCl (V vs. SHE) at a measured temperature (Supplementary Fig. 4 and 5).

The Ag/AgCl reference electrode was calibrated in the same electrolyte used for the electrocatalytic measurements. A platinum wire placed in the same compartment served as the hydrogen electrode, and the potential difference relative to Ag/AgCl was recorded at 80, 60, 40, 25, 20, 0, -4, -8, and -12 °C. During each measurement, the electrolyte was continuously

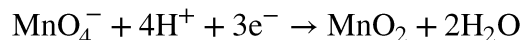
saturated with H₂ gas to establish the reversible H₂/H⁺ equilibrium on the Pt surface. The potential was monitored under open-circuit conditions until stabilization was achieved (see Supplementary Fig. 4).

The measured potentials inherently include the temperature-dependent activity of chloride ions in the saturated KCl reference, reflecting the equilibrium potential of the Ag/AgCl electrode at each temperature. The reference junction remained liquid throughout the tests because the freezing point of saturated KCl (~−14 °C) is lower than the lowest experimental temperature in this study, as reported in a recent molecular simulation and thermodynamic study³. Supplementary Fig. 5 and Supplementary Table 1 summarize the experimentally determined E_T (Ag/AgCl) values at each temperature. Potentials from literature^{4,5} are also shown for comparison. The measured potentials closely followed the reported values above 0 °C and remained consistent down to the subzero temperatures.

After the reference electrode was re-calibrated, we note that the maximum potential drift was 8 mV (Supplementary Table 1), that is too small to significantly affect the end-of-life measurement by chronopotentiometry (Figure 3a, Supplementary Figure 15).

Supplementary Note 3. Temperature-dependent equilibrium potential of MnO₄[−] formation and the UV-vis measurement

The equilibrium potential of the Mn(IV)/Mn(VII) redox couple was expressed in the reduction convention as⁶:



with the standard potential of $E_{298\text{ K}}^0 = 1.70\text{ V}$ vs SHE at 25 °C.

Accordingly, the Nernst equation is written as

$$E_T (\text{Mn}^{\text{IV}}/\text{Mn}^{\text{VII}}) = E_{298\text{ K}}^0 (\text{Mn}^{\text{IV}}/\text{Mn}^{\text{VII}}) - \frac{RT}{nF} \ln Q \quad (\text{Eq. 5})$$

$$E_T (\text{Mn}^{\text{IV}}/\text{Mn}^{\text{VII}}) = E_{298\text{ K}}^0 (\text{Mn}^{\text{IV}}/\text{Mn}^{\text{VII}}) - \frac{RT}{nF} \ln \left(\frac{a(\text{MnO}_2) a(\text{H}_2\text{O})}{a(\text{MnO}_4^-) a(\text{H}^+)^4} \right) \quad (\text{Eq. 6})$$

where R is the gas constant, T temperature, F the Faraday constant, $n = 3$ the number of electrons transferred, and Q the reaction quotient. Because MnO₂(s) and H₂O(l) are pure phases with constant activity ($a \approx 1$), Eq. 6 simplifies to

$$E_T (\text{Mn}^{\text{IV}}/\text{Mn}^{\text{VII}}) = E_{298}^0 (\text{Mn}^{\text{IV}}/\text{Mn}^{\text{VII}}) + \frac{RT}{3F} \ln [a(\text{MnO}_4^-) a(\text{H}^+)^4] \quad (\text{Eq. 7})$$

At pH 0, $a(\text{H}^+) = 1$, and the equation further reduces to

$$E_T (\text{Mn}^{\text{IV}}/\text{Mn}^{\text{VII}}) = E_{298}^0 (\text{Mn}^{\text{IV}}/\text{Mn}^{\text{VII}}) + \frac{RT}{3F} \ln a(\text{MnO}_4^-) \quad (\text{Eq. 8})$$

Since the concentration of MnO_4^- was in several $\mu\text{M/h}$ range and the supporting electrolyte concentration (1 M H_2SO_4 + 0.5 M Na_2SO_4) was much higher, the activity coefficient ($\gamma_{\text{MnO}_4^-}$) was approximated as unity, yielding

$$E_T (\text{Mn}^{\text{IV}}/\text{Mn}^{\text{VII}}) = E_{298}^0 (\text{Mn}^{\text{IV}}/\text{Mn}^{\text{VII}}) + \frac{RT}{3F} \ln (\gamma_{\text{MnO}_4^-} C_{\text{MnO}_4^-}) \quad (\text{Eq. 9})$$

The temperature dependence of the standard potential $E_T^0 (\text{Mn}^{\text{IV}}/\text{Mn}^{\text{VII}})$ is not well established because thermochemical data for aqueous MnO_4^- and solid MnO_2 are limited. Therefore, $E_T^0 (\text{Mn}^{\text{IV}}/\text{Mn}^{\text{VII}})$ was assumed to be constant at 1.70 V vs SHE across the temperature range, although, in principle, it varies slightly with temperature through the reaction entropy (ΔS^0). From the tabulated S^0 values⁷ for $\text{MnO}_2(\text{s})$ and $\text{MnO}_4^-(\text{l})$, The estimated drift is -22 ± 2 mV between 80 and -12 °C, which is negligible relative to the kinetic overpotentials considered. Under these approximations, the calculated equilibrium potential of the Mn(IV)/Mn(VII) couple lies between 1.56 and 1.60 V vs SHE (Supplementary Fig. 6b), providing the thermodynamic reference for evaluating the overpotential associated with MnO_4^- generation.

Next, the equilibrium potential of the $\text{O}_2/\text{H}_2\text{O}$ was expressed as

$$E_T (\text{O}_2/\text{H}_2\text{O}) = E_T^0 (\text{O}_2/\text{H}_2\text{O}) + \frac{RT}{4F} \ln a(\text{O}_2) \quad (\text{Eq. 10})$$

Because the bulk O_2 partial pressure during OER was near 1 bar and the electrolyte in the anode compartment was saturated during OER, $a(\text{O}_2) \approx 1$, giving

$$E_T (\text{O}_2/\text{H}_2\text{O}) = E_T^0 (\text{O}_2/\text{H}_2\text{O}) \quad (\text{Eq. 11})$$

Finally, the overpotential of MnO_4^- generation ($\eta_{\text{MnO}_4^-}$) was obtained by referencing the applied anodic bias to both equilibrium potentials as

$$\eta_{\text{MnO}_4^-} = \eta_{\text{OER}} - [E_T (\text{Mn}^{\text{IV}}/\text{Mn}^{\text{VII}}) - E_T (\text{O}_2/\text{H}_2\text{O})] \quad (\text{Eq. 12})$$

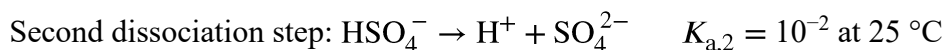
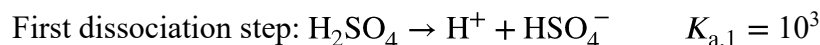
here $E_T (\text{Mn}^{\text{IV}}/\text{Mn}^{\text{VII}})$ and $E_T (\text{O}_2/\text{H}_2\text{O})$ are the temperature-dependent equilibrium potentials for MnO_4^- formation and OER, respectively. The bracketed term represents the thermodynamic bias required for the oxidation of Mn(IV) to Mn(VII) relative to the OER at a given temperature.

Before the UV-vis measurement, the electrolyte was intentionally agitated during syringe sampling to promote homogenization. Consequently, the measured absorbance reflects the bulk-average MnO_4^- concentration rather than the local concentration near the electrode surface^{8,9}. The

absorbance was converted to concentration using a calibration curve (Supplementary Fig. 13) prepared with 5, 10, 50, 100, and 150 μM KMnO_4 (Fujifilm Wako Pure Chemical). Each MnO_4^- dissolution data point (solid circle) shown in Fig. 2 and Supplementary Fig. 14 was obtained from an independent experiment to evaluate potential-dependent trends of MnO_4^- dissolution at different temperatures.

Supplementary Note 4. Temperature-dependent pH of the electrolyte

The pH of the electrolyte varies with temperature because the dissociation constants of H_2SO_4 are temperature-dependent. The first dissociation constant ($K_{a,1}$) of H_2SO_4 is sufficiently large ($K_{a,1} = 10^3$), so we assumed that 1 M H_2SO_4 almost completely dissociates into ~ 1 M of proton across the temperature range examined here. However, the second dissociation constant ($K_{a,2}$) is significantly lower than $K_{a,1}$, resulting in an incomplete second dissociation step, and the value is sensitive to temperature.



As reported by Marshall et al.¹⁰, $K_{a,2}$ increases noticeably as the temperature decreases to 25°C (Supplementary Fig. 19a, red open circles), leading to an increase in proton concentration and a corresponding decrease in pH. Therefore, the pH of the electrolyte in this study must be calculated rather than assumed constant.

The Raman spectra of the electrolyte (Supplementary Fig. 16a) showed characteristic peaks of SO_4^{2-} and HSO_4^- at 982.2 and 1052.2 cm^{-1} , respectively^{11–13}. The extent of the second dissociation constant was evaluated by the $\text{SO}_4^{2-}/\text{HSO}_4^-$ peak ratio (Supplementary Fig. 16b). From these ratios, the relative $K_{a,2}$ values of the electrolyte at different temperatures were estimated (Supplementary Fig. 19a). The resulting pH change was only ~ 0.01 upon cooling from 80 to -15°C (Supplementary Fig. 19b) when the temperature decreased from 80 to -8°C , corresponding to voltage shift of $\sim 0.6\text{ mV}$. Therefore, $\text{pH} = 0$ was used to calculate the potential of OER (V vs RHE) (Eq. 4).

At -8°C , no visible ice formation was detected (Supplementary Fig. 21e, k), and no ice-related features were observed in the OH-stretch Raman spectrum (Supplementary Fig. 17a, b), confirming that the electrolyte remained liquid below its equilibrium freezing point. When the cell was shaken without applied potential, however, ice crystallization occurred immediately (Supplementary Fig. 21j, l–o), verifying that the electrolyte was in a supercooled state at -8°C .

Supplementary Note 5. Temperature-dependent solubility of the salt component

Although H_2SO_4 is completely miscible with water over a wide temperature range¹⁴, the solubility of Na_2SO_4 decreases markedly upon cooling. In pure water, the solubility limit of Na_2SO_4 is 0.52 m (0.50 M) at 7 °C and 0.29 m (0.28 M) at -1.2 °C, according to Krumgalz¹⁵. This thermodynamic trend persists at subzero temperatures^{15,16}. In the present mixed electrolyte (1 M H_2SO_4 and 0.5 M Na_2SO_4), the actual solubility limit of Na_2SO_4 is expected to deviate from these values because of protonation equilibria and common-ion effects¹⁷, although the overall temperature-dependent trend should remain similar. Nevertheless, in most runs no visible precipitation occurred between 0 and -12 °C, suggesting that the electrolyte remained supersaturated.

Supplementary Note 6. Physicochemical and transport properties

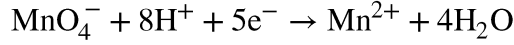
- Viscosity

Kinematic viscosity (ν) increases as temperature decreases (Supplementary Figure 34a), which indicates that the electrolyte becomes more resistant to flow at low temperature¹⁸. The density, ρ , changes only slightly with temperature. Namely, ρ remains around 1.09–1.12 g cm⁻³ across the measured range, higher than pure water because of the high salt concentration¹⁹ (Supplementary Figure 34b). These results yielded an increase in the dynamic viscosity of the electrolyte upon cooling (Supplementary Figure 34c). For example, η increased from approximately 0.6 mPa s at 60 °C to approximately 1.4 mPa s at 20 °C, approximately 2.5 mPa s at 0 °C, and nearly 3.5 mPa s near -10 °C. This indicates that mass transport becomes slower at lower temperature and may contribute to the apparent temperature dependence of the electrochemical response, although it does not explain the opposite temperature trends observed for OER and MnO_4^- dissolution.

- Diffusion coefficient of MnO_4^-

To address the possible influence of diffusion on our results, we have estimated the diffusion coefficient of MnO_4^- , $D_{\text{MnO}_4^-}(T)$, in the electrolyte using rotating disk electrode (RDE) measurements over the temperature range from 55 °C to -6 °C. The raw voltammograms show that the cathodic current increases systematically with rotation rate at each temperature (Supplementary Figure 35a–f). In particular, higher rotation speeds gave larger cathodic limiting currents, consistent with enhanced hydrodynamic mass transport of MnO_4^- onto the Pt disk electrode. This rotation-rate dependence confirms that the selected potential region contains a diffusion-limited contribution and supports the use of Levich analysis to estimate $D_{\text{MnO}_4^-}(T)$.

The cathodic limiting current for MnO_4^- reduction increased at higher rotation rates (Supplementary Figure 36a), consistent with mass-transport-controlled behavior. The diffusion coefficient was extracted using the Levich equation. The number of electrons was assumed to be $n = 5$, corresponding to the reduction of Mn(VII) to Mn(II) in acidic media:



This assignment is supported by Desideri²⁰, who reported that permanganate is reduced irreversibly to Mn(II) on platinum in mineral acid media.

The obtained MnO_4^- diffusion coefficient decreased upon cooling (Supplementary Figure 36b), also consistent with the increase in electrolyte viscosity. These data show that MnO_4^- transport is slower at lower temperature and therefore cannot explain the enhanced MnO_4^- dissolution observed below 0 °C. Furthermore, as long as n is constant across all temperatures, this analysis gives essentially same conclusion that diffusion is not the origin of the anti-Arrhenius behavior of MnO_4^- dissolution. We also note that deviations were observed from the Stokes–Einstein equation, which is reasonable considering that concentrated acidic electrolytes contain non-ideal ion–ion and ion–solvent interactions²¹.

- Diffusion coefficient of protons

Proton diffusion was not directly measured in the present electrolyte. Literature reports show that proton mobility is temperature-dependent but remains high in aqueous media because of structural diffusion via proton transfer^{22,23}. In the present system, proton depletion at the anode is unlikely because the electrolyte contains 1 M H_2SO_4 and both OER and MnO_4^- formation generate, rather than consume, protons. However, transport of excess protons from the electrode to the bulk electrolyte may affect local proton activity, especially at low temperature where viscosity increases and diffusion slows. Such local acidification may contribute to shifts in local overpotential and to the apparent activation parameters. Nevertheless, because the bulk electrolyte is already strongly acidic and proton mobility is relatively high, proton transport is unlikely to be the sole origin of the large activation-energy divergence between OER and MnO_4^- dissolution. As a qualitative reference, the reported limiting diffusion coefficient of excess protons at infinite dilution is on the order of $D_{\text{H}^+} = \sim 6 \times 10^{-5} \text{ cm}^2 \text{ s}^{-1}$ at 0 °C²³, compared with $D_{\text{MnO}_4^-} = \sim 6 \times 10^{-6} \text{ cm}^2 \text{ s}^{-1}$ measured in the present electrolyte (Supplementary Figure 36b).

- Ion conductivity

Because the cell geometry was fixed, the ionic conductivity is inversely proportional to the measured solution resistance according to:

$$\kappa(T) \propto \frac{K_{\text{cell}}}{R_{\text{solution}}(T)} \quad (\text{Eq. 13})$$

where K_{cell} is the cell constant. Thus, the increase in $R_{\text{solution}}(T)$ upon cooling indicates a decrease in conductivity at lower temperature²⁴.

- Dielectric constant

According to Owen et al.²⁵, the dielectric constant of water is approximately 87.9 at 0 °C, 80.2 at 20 °C, and 60.8 at 80 °C. This reflects the reduced ability of water dipoles to orient in response to

an electric field at higher temperature. We note that the values are for pure water, whereas the present electrolyte is highly concentrated. Therefore, the calculation should be regarded as an estimate rather than an exact description of the interfacial dielectric environment.

- Classical Debye length

The temperature dependence of the classical Debye length was estimated using Debye–Hückel expression, the temperature-dependent dielectric constant of water²⁵ and the ionic strength of the electrolyte:

$$\lambda_D(T) \propto \sqrt{\frac{\epsilon_r(T)\epsilon_0 k_B T}{2N_A e^2 (1000I)}} \quad (\text{Eq. 14})$$

where I is the ionic strength (mol L^{-1}). For the present concentrated electrolyte, 1 M H_2SO_4 + 0.5 M Na_2SO_4 , I is on the order of several molar (3–4 M). The estimated λ_D is extremely short and changes only weakly from 80 to 0 °C (Supplementary Table 16), because the decrease in T upon cooling is partly compensated by the increase in $\epsilon_r(T)$. Therefore, the activation energy divergence is unlikely to originate mainly from changes in classical electrostatic screening. Instead, it is more likely to reflect changes in other interfacial factors, such as compact-layer structure, specific ion interactions, interfacial solvation, water structure, or reaction-pathway differences. This calculation provides an approximate because classical Debye–Hückel theory is not quantitatively valid in such a concentrated electrolyte.

- O_2 solubility

Previous studies have shown that O_2 solubility depends on temperature and sulfuric acid concentration²⁶. Changes in local O_2 supersaturation could influence bubble nucleation, bubble removal, and temporary blockage of the electrode surface. These effects cannot be excluded completely in the present study. To elucidate their possible influences, the solution resistance was re-measured after consecutive LSV scans under unstirred conditions to maximize the accumulation of residual O_2 bubbles (Supplementary Figure 28a, Supplementary Table 15). As a result, apparent activation energy for OER above 0 °C remained essentially unchanged even when iR correction was performed using post-LSV solution resistances (Supplementary Figure 28b).

In addition, the catalytic lifetime decreased upon lowering the temperature from 4 to –4 °C, even when the applied current density was reduced from 100 to 50 (Supplementary Fig. 15a, d) and further 25 mA cm^{-2} (Supplementary Fig. 15b, e). These results indicate that neither Joule heating nor O_2 bubble accumulation can account for the shortened catalyst lifetime under subzero conditions.

These physicochemical and transport properties are summarized in Supplementary Table 17.

Supplementary Note 7. Freezing point depression of the electrolyte

The freezing point depression (FPD) was calculated using the following equation:

$$\Delta T_f = i \cdot K_f \cdot m \quad (\text{Eq. 15})$$

where i is the van't Hoff factor (number of dissociated ion particles), K_f is the cryoscopic constant of water ($1.86 \text{ K kg mol}^{-1}$), and m is the molality of the solute^{27–29} ($m_{\text{H}_2\text{SO}_4} = 1.04 \text{ m}$ and $m_{\text{Na}_2\text{SO}_4} = 0.52 \text{ m}$). FPD is a colligative property that is dependent on the total number of dissolved ion particles. This relation assumes ideal behavior, that is, complete or partial dissociation, accurate concentration, and negligible ion pairing.

In the first dissociation step, H_2SO_4 is assumed to be completely dissociated into 1 H^+ and 1 HSO_4^{2-} . The second dissociation step was neglected because $K_{a,2}$ considerably lower than $K_{a,1}$. Na_2SO_4 was assumed to dissociate completely into 2 Na^+ and 1 SO_4^{2-} . The presence of excess SO_4^{2-} from Na_2SO_4 introduces a common ion effect that suppresses the second dissociation of H_2SO_4 . Therefore, $i_{\text{H}_2\text{SO}_4} = 2$ and $i_{\text{Na}_2\text{SO}_4} = 3$ were used.

The freezing-point depression of the mixed electrolyte can be expressed as:

$$\Delta T_f = K_f (i_{\text{H}_2\text{SO}_4} m_{\text{H}_2\text{SO}_4} + i_{\text{Na}_2\text{SO}_4} m_{\text{Na}_2\text{SO}_4}) \quad (\text{Eq. 16})$$

Thus, the calculated freezing point of the electrolyte is $-6.88 \text{ }^\circ\text{C}$.

Supplementary Note 8. Possible influence of heterogeneity of ice formation

During the measurements, no macroscopic ice formation was observed, and the electrolyte remained visually liquid around the $\gamma\text{-MnO}_2$ working electrode over the temperature range from 0 to $-8 \text{ }^\circ\text{C}$. The electrochemical cell was immersed in a temperature-controlled incubator, and the electrolyte temperature was monitored in the anodic compartment close to the working electrode after thermal equilibration (Supplementary Figure 2). However, microscopic heterogeneity, interfacial freeze-concentration, or local temperature/concentration gradients cannot be fully excluded under sub-zero conditions.

Supplementary Note 9. Fitting the MnO_4^- dissolution data

We have fitted the dissolution data using a single exponential curve:

$$v = \Gamma k^0 \exp \frac{\alpha F \eta}{RT} \quad (\text{Eq. 17})$$

where Γ is the active site density, k^0 is the standard heterogeneous rate constant, α is the electron transfer coefficient, and F, R, T are the Faraday coefficient, gas constant, and temperature. There are two free variables, Γk^0 and α , which were fitted using two methods:

1. Directly fitting the exponential curve to the permanganate formation rate
2. Fitting a straight line to the logarithm of the formation rate (Tafel plot format)

Both methods were tested and the one with smaller residual error was chosen as the optimal fit for each temperature. The optimization was performed using a standard Python package (scipy.optimize.curve_fit).

Supplementary Note 10. Arrhenius analysis

The temperature dependence of the OER and MnO_4^- dissolution reactions was analyzed using an Arrhenius-type relationship for the experimentally observed reaction rate, v :

$$v = Ae^{-E_a/RT} \quad (\text{Eq. 18})$$

where A is the pre-exponential factor, E_a is the apparent activation energy, R is the ideal gas constant, and T is the absolute temperature. Taking the natural logarithm gives the expression shown in Fig. 1 of the main manuscript:

$$\ln v = -\frac{E_a}{R} \left(\frac{1}{T} \right) + \ln A \quad (\text{Eq. 19})$$

To compare the two electrochemical reactions on a common scale, their reaction rates were expressed as equivalent current densities according to Faraday's law:

$$j = nFv \quad (\text{Eq. 20})$$

where j is the current density, n is the number of electrons transferred during the reaction and F is the Faraday constant. Accordingly, the Arrhenius-type relationship can be expressed in terms of current density as:

$$j = A \exp \left(\frac{-E_a}{RT} \right) \quad (\text{Eq. 21})$$

Please note that, in this case, nF from Eq. 20 is absorbed into A . Taking the natural logarithm gives the expression shown in Eq. 3 of the main manuscript:

$$\ln j = \ln A - \frac{E_a}{RT} \quad (\text{Eq. 22})$$

Thus, E_a was determined from the slope of the linear relationship between $\ln j$ and $1/T$, where the slope is $-E_a/R$. Next, the Bell–Evans–Polanyi (BEP)-type relationship was used to express E_a with the applied overpotential (η) as follows:

$$E_a = E_a^0 + \alpha \Delta G \quad (\text{Eq. 23})$$

$$E_a = E_a^0 - \alpha n F \eta \quad (\text{Eq. 24})$$

where E_a^0 is the apparent activation energy at zero overpotential, α is the effective transfer coefficient and η is the reaction overpotential. Substitution into Eq. 21 gives:

$$j = A \exp \left[-\frac{E_a^0 - \alpha n F \eta}{RT} \right] \quad (\text{Eq. 25})$$

or

$$\ln j = \ln A + \left(-\frac{E_a^0}{R} + \frac{\alpha n F \eta}{R} \right) \frac{1}{T} \quad (\text{Eq. 26})$$

Therefore,

$$\text{slope} = -\frac{E_a^0 - \alpha n F \eta}{R} = -\frac{E_a}{R} \quad (\text{Eq. 27})$$

Supplementary Note 11. Eyring analysis

The standard form of the equation is:

$$k = \kappa \frac{k_B T}{h} \exp \left(-\frac{\Delta G^\ddagger}{RT} \right) \quad (\text{Eq. 28})$$

where κ is the transmission coefficient, k_B is Boltzmann's constant, h is Planck's constant, $\Delta G^\ddagger$ is the activation Gibbs free energy. By definition,

$$\Delta G^\ddagger = \Delta H^\ddagger - T \Delta S^\ddagger \quad (\text{Eq. 29})$$

where $\Delta H^\ddagger$ is the activation enthalpy, and $\Delta S^\ddagger$ is the activation entropy. Thus, the rate constant can be expanded to:

$$k = \kappa \frac{k_B T}{h} \exp \left(\frac{\Delta S^\ddagger}{R} \right) \exp \left(-\frac{\Delta H^\ddagger}{RT} \right) \quad (\text{Eq. 30})$$

In heterogeneous electrocatalytic reactions, the reactant and electrode are in close proximity, and thus we assume the transmission coefficient (κ) to be unity. For heterogeneous electrocatalytic

reactions, the catalytic current is given by the product of the reaction rate and active site concentration³⁰:

$$j = nF\theta_0 a_R \times k \quad (\text{Eq. 31})$$

Solutions are assumed to be diluted with respect to the solvent. This assumption implies that the solvent can be approximated with pure liquid; thus, a_R has a value of 1. Combined with Eq. 30, current density can be expressed as follows:

$$j = nF\theta_0 a_R \kappa \frac{k_B T}{h} \exp\left(\frac{\Delta S^\ddagger}{R}\right) \exp\left(\frac{-\Delta H^\ddagger}{RT}\right) \quad (\text{Eq. 32})$$

Assuming a linear dependence of $\Delta H^\ddagger$ on the applied overpotential, consistent with a BEP-type treatment, $\Delta H^\ddagger$ can be expressed as:

$$\Delta H^\ddagger = \Delta H_0^\ddagger - \alpha n F \eta \quad (\text{Eq. 33})$$

Therefore,

$$j = nF\theta_0 a_R \kappa \frac{k_B T}{h} \exp\left(\frac{\Delta S^\ddagger}{R}\right) \exp\left(\frac{-\Delta H_0^\ddagger + \alpha n F \eta}{RT}\right) \quad (\text{Eq. 34})$$

and

$$j = nF\theta_0 a_R \kappa \frac{k_B T}{h} \exp\left(\frac{\Delta S^\ddagger}{R}\right) \exp\left(-\frac{\Delta H^\ddagger}{RT}\right) \exp\left(\frac{\alpha n F \eta}{RT}\right) \quad (\text{Eq. 35})$$

Taking the logarithm of both sides gives the expression shown in Eq. 4 of the main manuscript:

$$\ln\left(\frac{j}{T}\right) = \left\{ \ln\left(nF\theta_0 a_R \kappa \frac{k_B}{h}\right) + \frac{\Delta S^\ddagger}{R} \right\} - \left(\frac{\Delta H_0^\ddagger}{R} - \frac{\alpha n F \eta}{R} \right) \frac{1}{T} \quad (\text{Eq. 36})$$

The thermodynamic parameters can be determined from kinetic data obtained from plots of $\ln j/T$ and $1/T$ (Supplementary Fig. 29). The equation generates a straight line with a negative slope and y-intercept, which contain the values of $\Delta H^\ddagger$ and $\Delta S^\ddagger$, respectively.

$$\text{slope} = -\frac{\Delta H_0^\ddagger - \alpha n F \eta}{R} = -\frac{\Delta H^\ddagger}{R} \quad (\text{Eq. 37})$$

$$y \text{ intercept} = \ln \left(nF\theta_0 a_R \kappa \frac{k_B}{h} \right) + \frac{\Delta S^\ddagger}{R} \quad (\text{Eq. 38})$$

A set of parallel lines across a range of temperatures is expected from the Eyring equation, with each line accounting for the effect of overpotential (η).

Supplementary Note 12. Estimating active site concentrations of γ -MnO₂

To estimate apparent $\Delta S^\ddagger$ for the OER and MnO₄⁻ dissolution, the coverage of electrochemically active sites (θ_0) on γ -MnO₂ was required. In this study, the relative surface area, determined from the double-layer capacitance, was used as a practical approximation of the active site concentration. The same θ_0 value was applied for both OER and MnO₄⁻ dissolution, representing the initial surface population of oxidizable Mn–O sites.

The capacitance was obtained by measuring the non-Faradaic capacitive current associated with double-layer charging, derived from the scan-rate dependence of cycle voltammograms (CVs). CVs were recorded in a capacitive region of γ -MnO₂ (1.09–1.19 V vs Ag/AgCl) at scan rates of 5–400 mV s⁻¹ at room temperature (Supplementary Figure 30). The anodic and cathodic charging currents measured at 1.14 V vs Ag/AgCl were plotted as a function of scan rate. The double-layer capacitance (C_{DL}) was taken as the average of the absolute value of the slope of the linear fits. Relative surface area was calculated as follows:

$$\text{Relative Surface Area} = \frac{C_{DL}}{C_s} \quad (\text{Eq. 39})$$

where C_s is the specific capacitance of the sample ($C_s = 0.035 \text{ mF cm}^{-2}$ in 1 M H₂SO₄)³¹. The resulting relative surface area was 37.14 cm², giving a roughness factor (RF) of 18.6 relative to the 2 cm² geometric area. We note that both C_{DL} and C_s are temperature-dependent³², thus the value of C_{DL} at room temperature was used as a relative descriptor. This is to minimize differences in surface area among independently prepared electrodes. Assuming a surface atomic site density of 5 nm⁻² for γ -MnO₂, a representative value for metal oxides^{33–35}, the surface site density was estimated to be $1.86 \times 10^{16} \text{ cm}^{-2}$. This corresponds to an effective active site concentration of $2.99 \times 10^{-8} \text{ mol cm}^{-2}$, accounting for 1.4% of the total Mn deposited on FTO ($2.18 \times 10^{-6} \text{ mol cm}^{-2}$). This estimate agrees with our previous report indicating only ~1% of the Mn atoms deposited on the electrode act as electrochemically active sites³⁶.

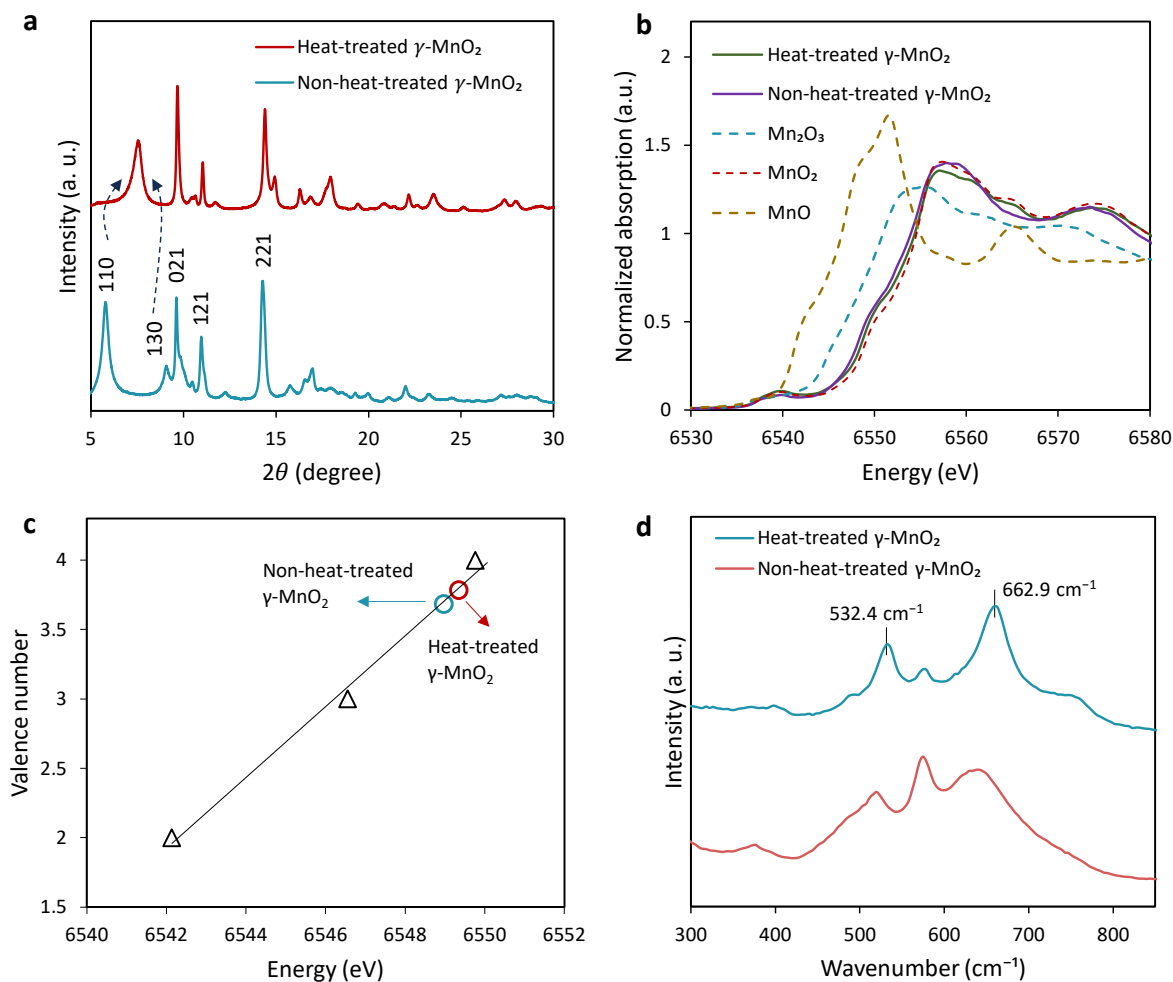
We have also recalculated the assumed C_{DL} variation over a 100-fold range, from 13 to 0.13 mF cm⁻², corresponding to 2.99×10^{-7} and $2.99 \times 10^{-9} \text{ mol cm}^{-2}$. This range is orders of magnitude larger than the temperature-induced variation in C_{DL} reported for polycrystalline Pt in 0.1 M HClO₄, where the C_{DL} decreased from 43 to 35 $\mu\text{F cm}^{-2}$ between 20 and 60 °C³⁷. Although the absolute

values of $\Delta S^\ddagger$ and $\Delta G^\ddagger$ varied with the assumed C_{DL} , the compensating relationship between $\Delta H^\ddagger$ and $\Delta S^\ddagger$ interpretation remained unchanged (Supplementary Figure 33).

Supplementary Note 13. Scan-rate dependence and chronopotentiometry measurement of OER

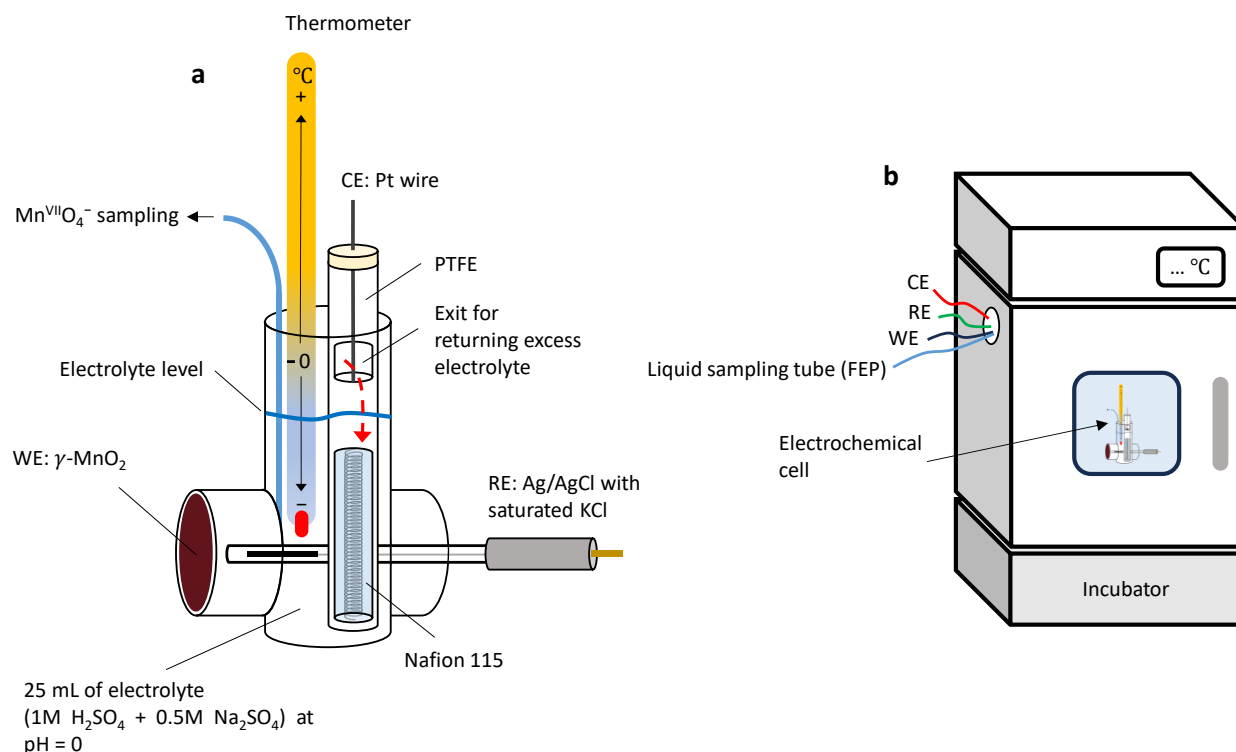
Additional linear sweep voltammetry (LSV) measurements over scan from 1 mV s⁻¹ to 10 mV s⁻¹ were conducted together with chronopotentiometric measurements at all temperatures. As shown in the Supplementary Fig. 10a–g, no mass-transport-limited plateau was observed, except at –12 °C, where partial ice formation limited OER at high overpotentials (Supplementary Fig. 10h). The apparent activation energies derived from scan rates in the temperature range between 80 °C and 0 °C differed by less than approximately 13.4 % at $\eta_{OER} = 0.65$ V (Supplementary Table 7). In addition, the apparent activation energy obtained by chronopotentiometry agreed well with those obtained from LSV. These results demonstrate that the selected potential window is under kinetic control and that the extracted apparent activation parameters are not significantly influenced by temperature-dependent mass-transport effects.

Supplementary Figure



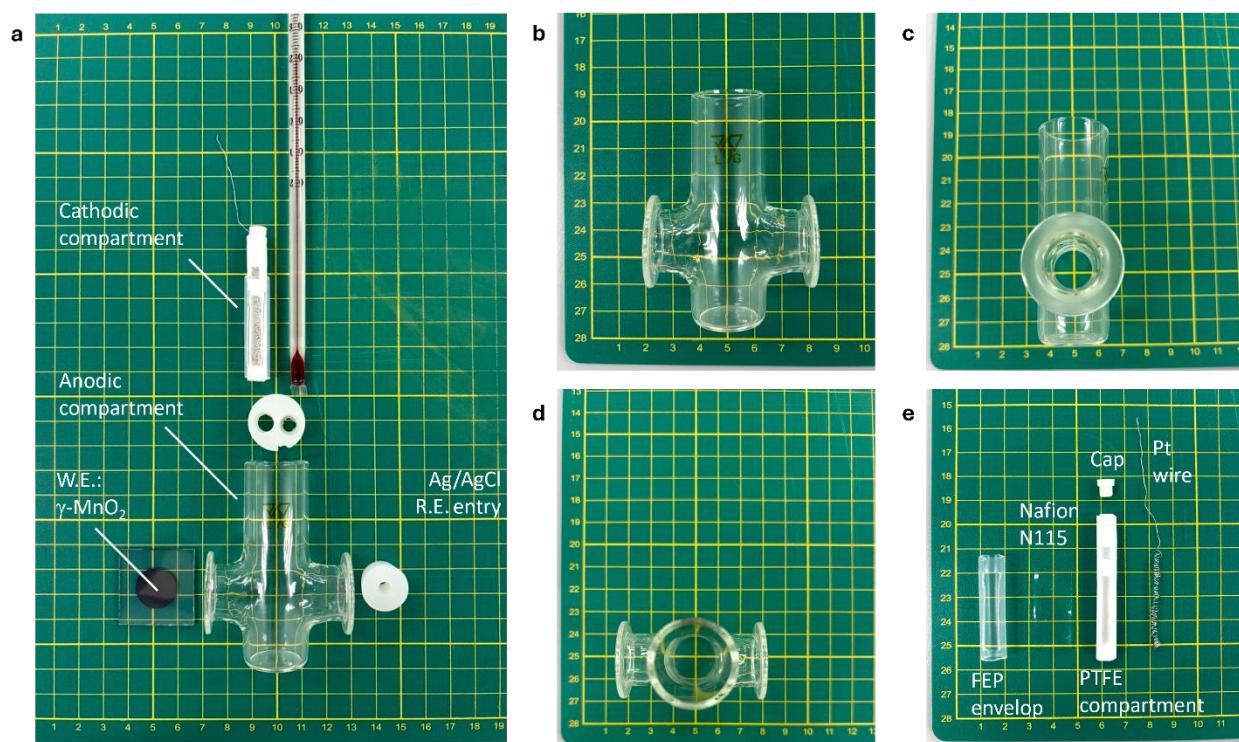
Supplementary Figure 1. Characterization of freshly prepared γ -MnO₂.

(a) Synchrotron radiation powder X-ray diffraction (SR-PXRD) patterns, (b) Mn K-edge X-ray absorption near edge structure (XANES) spectra, (c) edge position (defined as the energy at which the normalized absorption was 0.5 of the XANES spectra plotted against Mn oxidation states), and (d) Raman spectra of heat-treated and non-heat-treated γ -MnO₂. MnO, Mn₂O₃, and MnO₂ were characterized as reference samples.



Supplementary Figure 2. Schematic of the electrochemical setup for the temperature-controlled measurements.

(a) Three-electrode cell configuration with a γ -MnO₂/FTO working electrode, Pt counter electrode, and Ag/AgCl reference electrode. The anodic and cathodic compartments were separated by a Nafion membrane (115), which is stable down to $-12\text{ }^{\circ}\text{C}$ ³⁸. The PTFE cathode compartment was designed to return the excess water from the catholyte to the anolyte, thereby preventing premature shutdown caused by ice formation in the cathode compartment. A bar thermometer was inserted to monitor electrolyte temperature during operation. (b) The electrochemical cell was placed inside an incubator for precise temperature control during linear sweep voltammetry (LSV) and chronopotentiometry (CP) measurements. Electrolyte containing dissolved MnO₄⁻ was drawn through an FEP tube using glass syringe for UV-vis analysis.

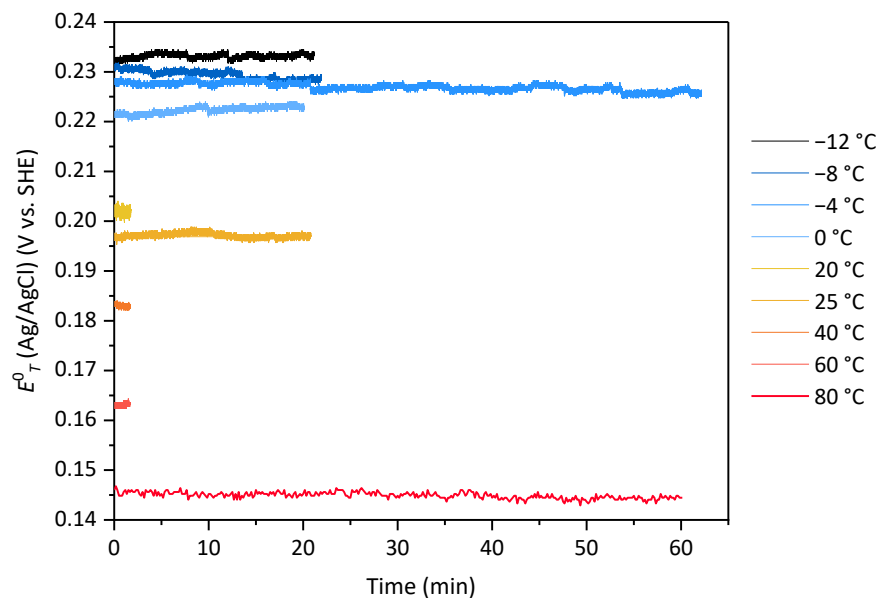


Supplementary Figure 3. The configuration of the electrochemical cell configuration used for temperature-dependent OER and MnO_4^- dissolution measurements.

(a) Photograph of the electrochemical cell components showing the anodic compartment containing the $\gamma\text{-MnO}_2$ working electrode, thermometer bar, Ag/AgCl reference-electrode (KCl sat.) entry, and the Nafion-separated cathodic compartment. (b–d) Photographs of the electrochemical cell from different angles. (e) Individual components of the cathode compartment, including the custom-fabricated FEP envelope and PTFE compartment, Nafion N115 membrane, septum cap, and Pt wire counter electrode. The PTFE compartment was fabricated from a PTFE bar and contained two openings: one for ionic transport through the Nafion membrane and one for H_2 gas release. The Nafion-covered PTFE compartment was sealed with the FEP envelope, whose inner diameter matched the outer diameter of the PTFE compartment. No leakage was observed after assembly. In addition, because Nafion is a cation-exchange membrane, crossover of anionic MnO_4^- is expected to be minimal³⁹. The thermometer was positioned in the anodic electrolyte to monitor the electrolyte temperature inside the cell.

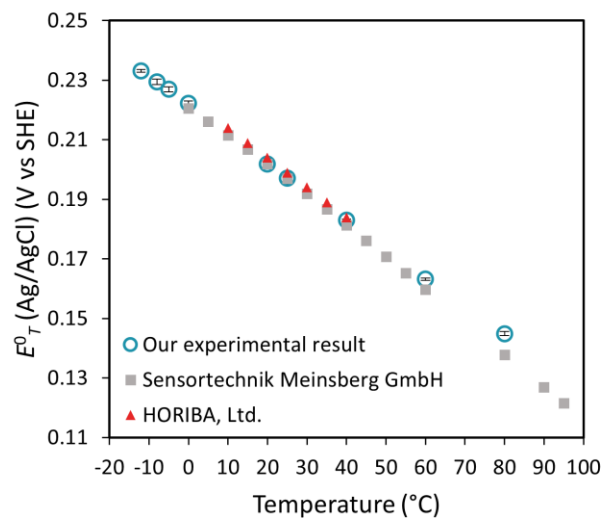
During the measurements, no macroscopic ice formation was observed, and the electrolyte remained visually liquid around the $\gamma\text{-MnO}_2$ working electrode over the temperature range from 0 to -8°C . The electrochemical cell was immersed in a temperature-controlled bath, and the electrolyte temperature was monitored in the anodic compartment close to the working electrode after thermal equilibration (Supplementary Fig. 2). Therefore, large macroscopic thermal gradients or bulk freezing are unlikely to be the dominant origin of the MnO_4^- dissolution anomaly. However,

microscopic heterogeneity, interfacial freeze-concentration, or local temperature/concentration gradients cannot be fully excluded under sub-zero conditions.



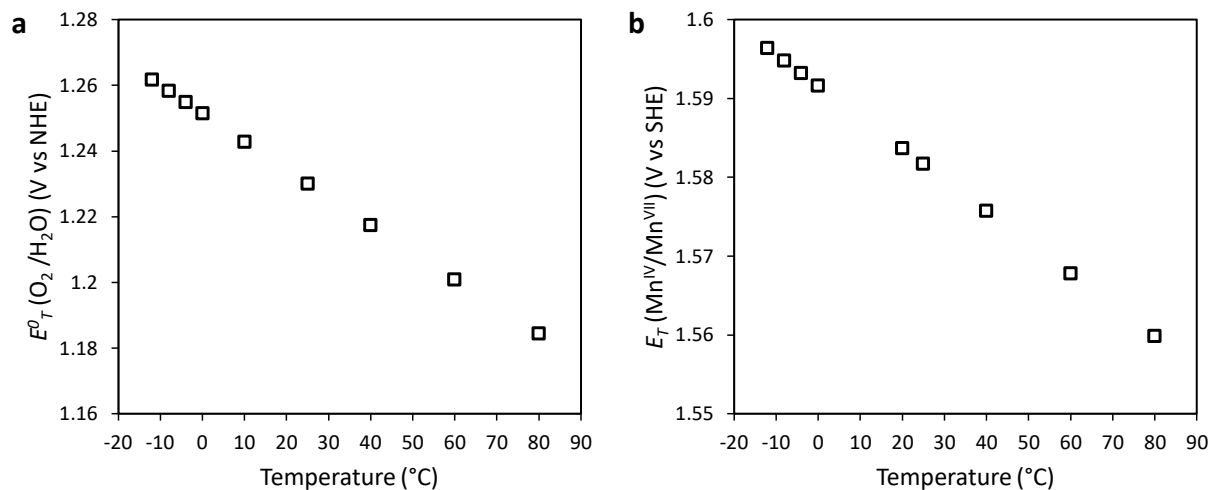
Supplementary Figure 4. Potential stability of the Ag/AgCl reference electrode over the temperature range of -12 to 80 °C.

The potential was monitored as a function of time under different temperature conditions, showing minimal drift within the time range. It was also monitored until stabilization was achieved to determine the temperature-dependent equilibrium potential of Ag/AgCl as shown in Supplementary Figure 5.



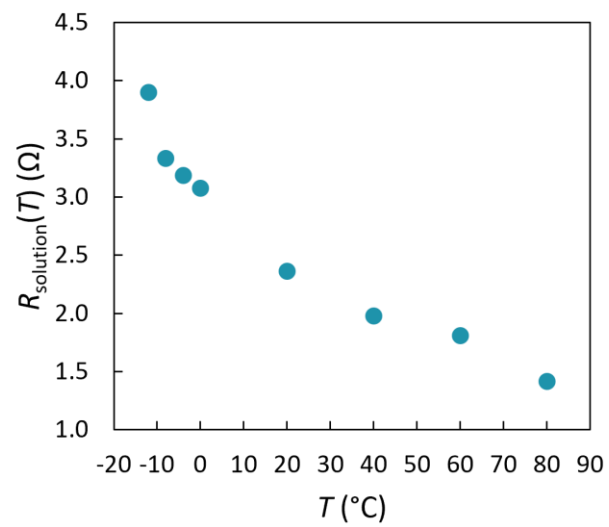
Supplementary Figure 5. Temperature dependence of the Ag/AgCl reference electrode from -12 to 80 °C, compared with reported values.

Each data point shows the average potential at a given temperature obtained from Supplementary Figure 3. Potential instability during the calibrations is shown in the vertical bars. The value can also be seen in Supplementary Table 1.

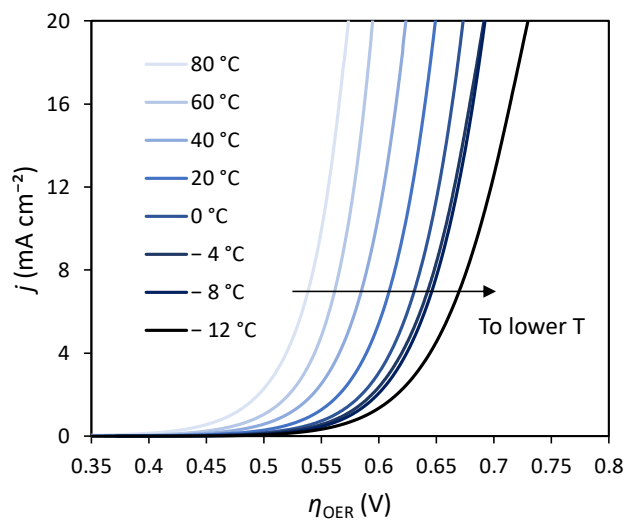


Supplementary Figure 6. Equilibrium potential of water oxidation (a) and MnO_4^- (b) within the temperature range between -12 and 80 $^\circ\text{C}$.

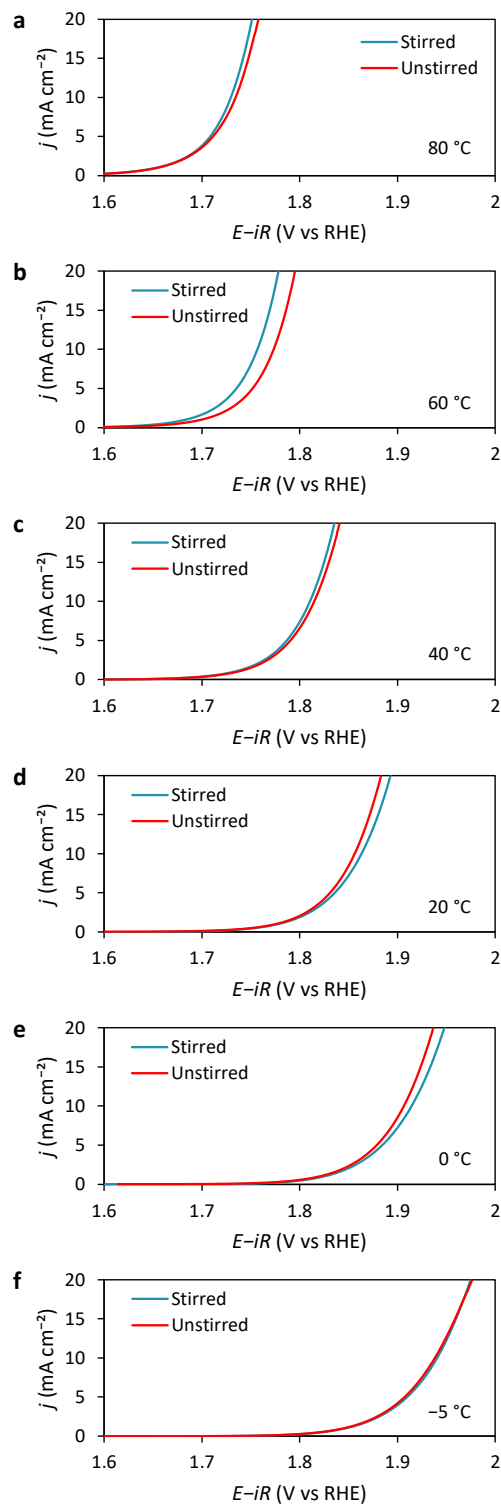
The value at each temperature can be seen in Supplementary Table 2.



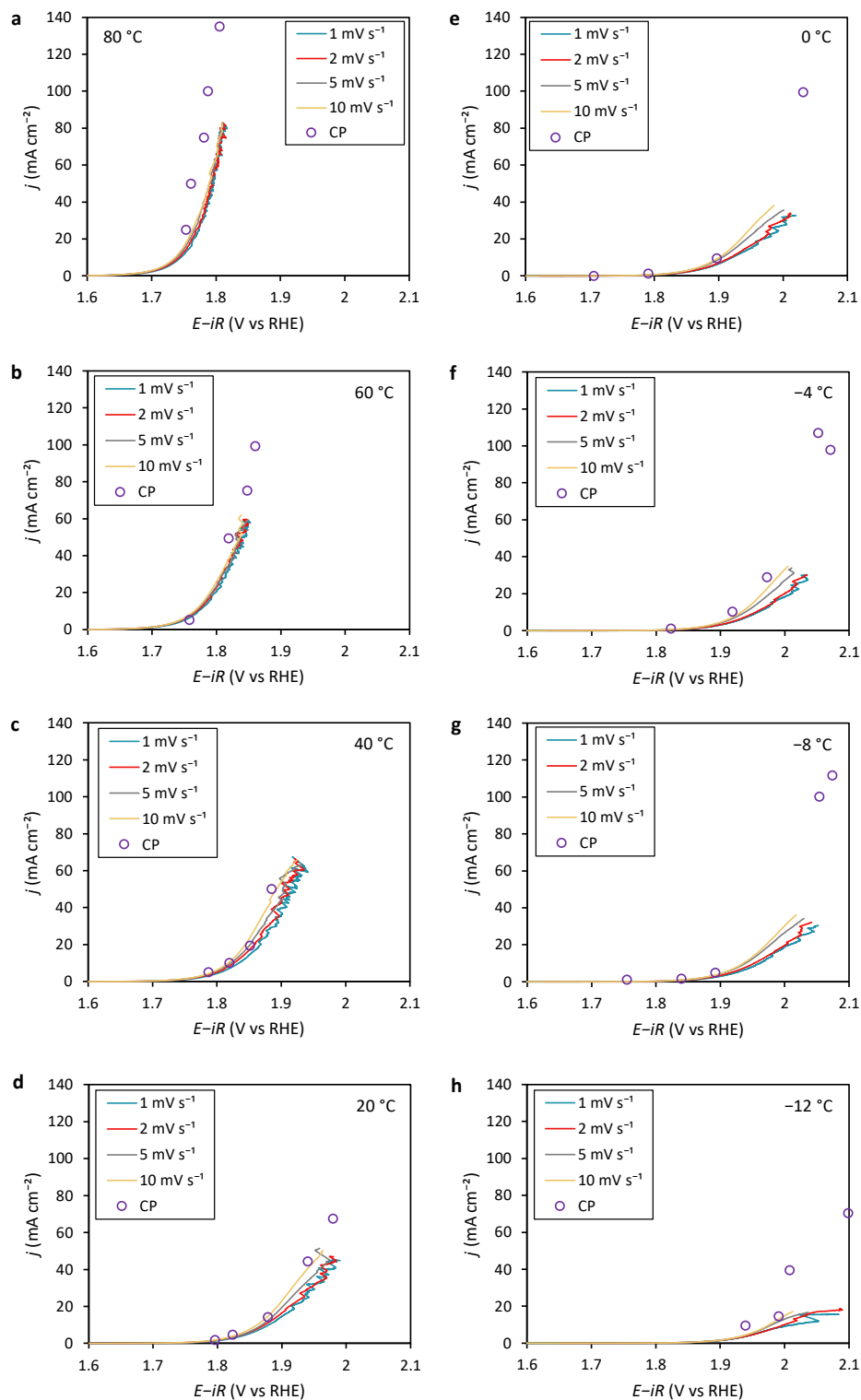
Supplementary Figure 7. Temperature-dependent solution resistance, $R_{\text{solution}}(T)$, of 1 M H_2SO_4 + 0.5 M Na_2SO_4 measured using EIS at 1.2 V and 1000 Hz.



Supplementary Figure 8. Potential dependence curves of OER on γ -MnO₂ from 80 °C to -12 °C. The arrow shows that the curves shifted to higher overpotentials (η_{OER}) as the temperature decreased. All the potential dependences curves were obtained at a scan rate of 5 mV s⁻¹.

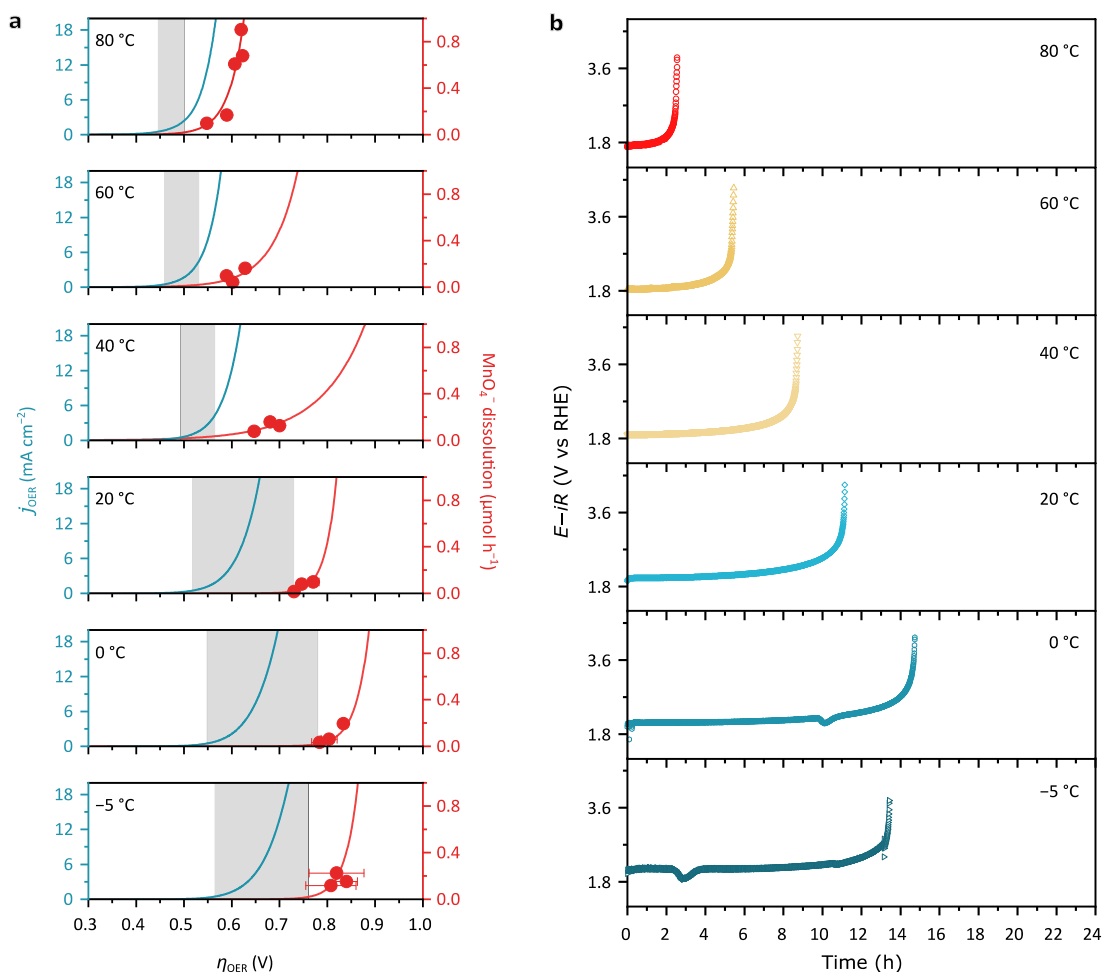


Supplementary Figure 9. Potential dependence curves of OER on $\gamma\text{-MnO}_2$ from 80 °C to -5 °C in stirred (using a magnetic bar, 1580–1700 rpm) and unstirred electrolyte (a–f).



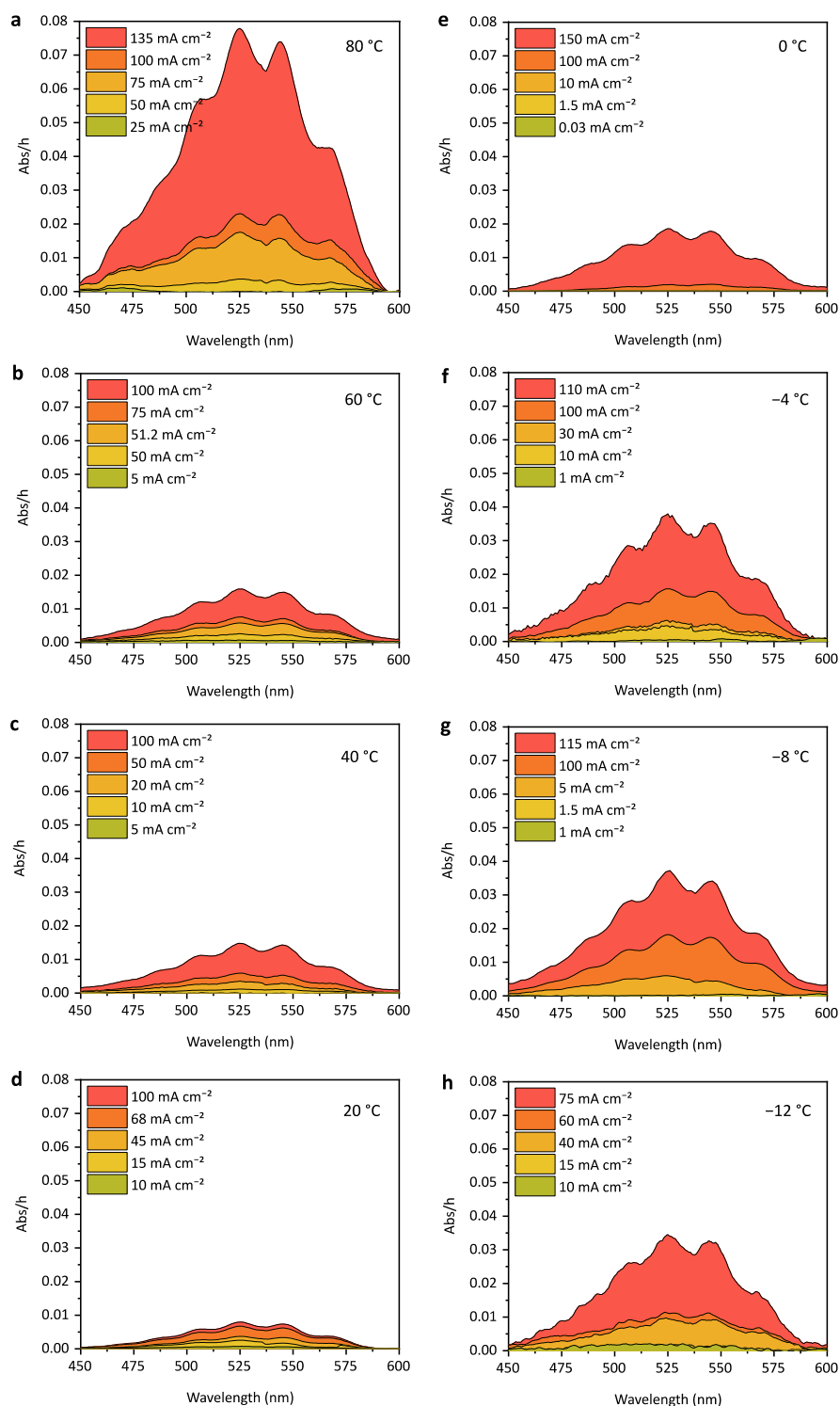
Supplementary Figure 10. Scan-rate dependence and chronopotentiometry measurement of OER polarization curves over the temperature range from 80 to -12 °C under unstirred conditions.

LSV curves of γ -MnO₂ measured in 1 M H₂SO₄ + 0.5 M Na₂SO₄ at scan rates of 1, 2, 5, and 10 mV s⁻¹ at (a) 80, (b) 60, (c) 40, (d) 20, (e) 0, (f) -4, (g) -8, and (h) -12 °C. Purple open circles show current–potential points obtained from chronopotentiometric measurements that was conducted at fixed current densities selected to give overpotentials within $\eta_{\text{OER}} = 0.65 \pm 0.02$ V, depending on temperature. Each measurement was held for at least 60 s, and the reported overpotential represents the average of the collected potential values.

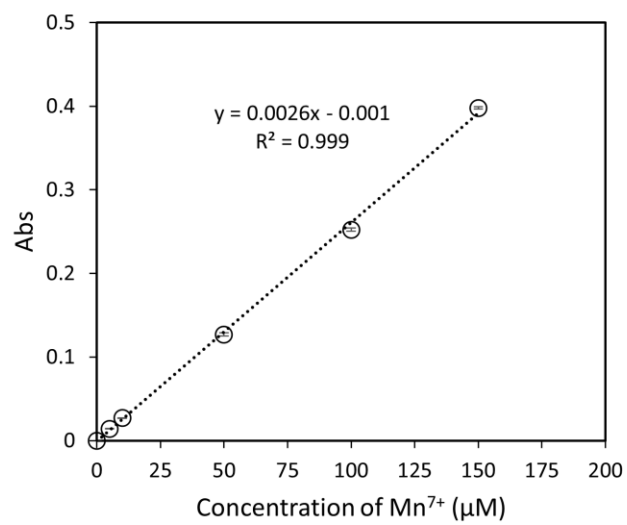


Supplementary Figure 11. Activity and stability of γ -MnO₂/FTO under stirring conditions (using a magnetic stirrer bar, 1580–1700 rpm) at temperatures from 80 to -5 °C.

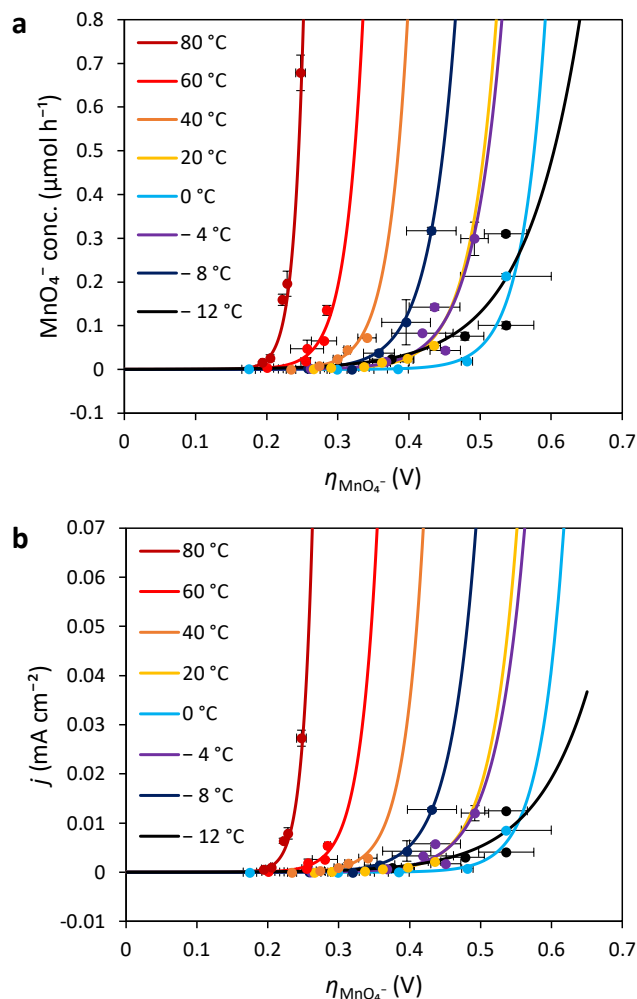
(a) Potential dependence of the OER (blue-green) and MnO₄⁻ dissolution (red) from γ -MnO₂ under stirred conditions. (b) Chronopotentiometric curves recorded for γ -MnO₂ at 100 mA cm⁻². All other conditions are the same as in Figs. 2 and 3 of the main text. Each potential-dependent MnO₄⁻ data point was obtained from an independent water electrolysis experiment. Horizontal bars indicate potential fluctuations during chronopotentiometry measurements, not statistical errors.



Supplementary Figure 12. MnO_4^- dissolution measured by UV-vis spectroscopy at various applied current densities and temperatures between -12 and 80 °C.

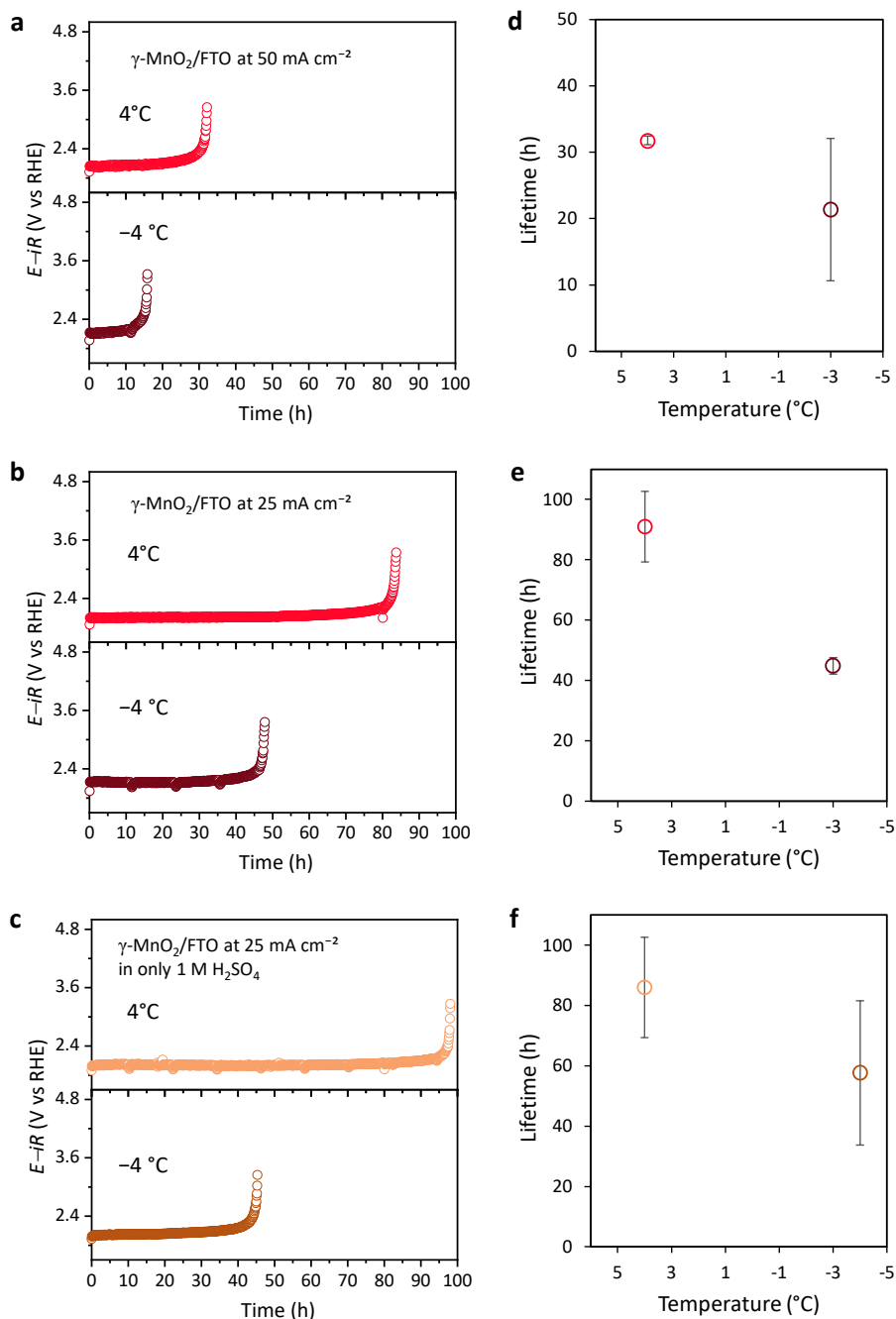


Supplementary Figure 13. Calibration curve for calculating MnO_4^- produced during OER.



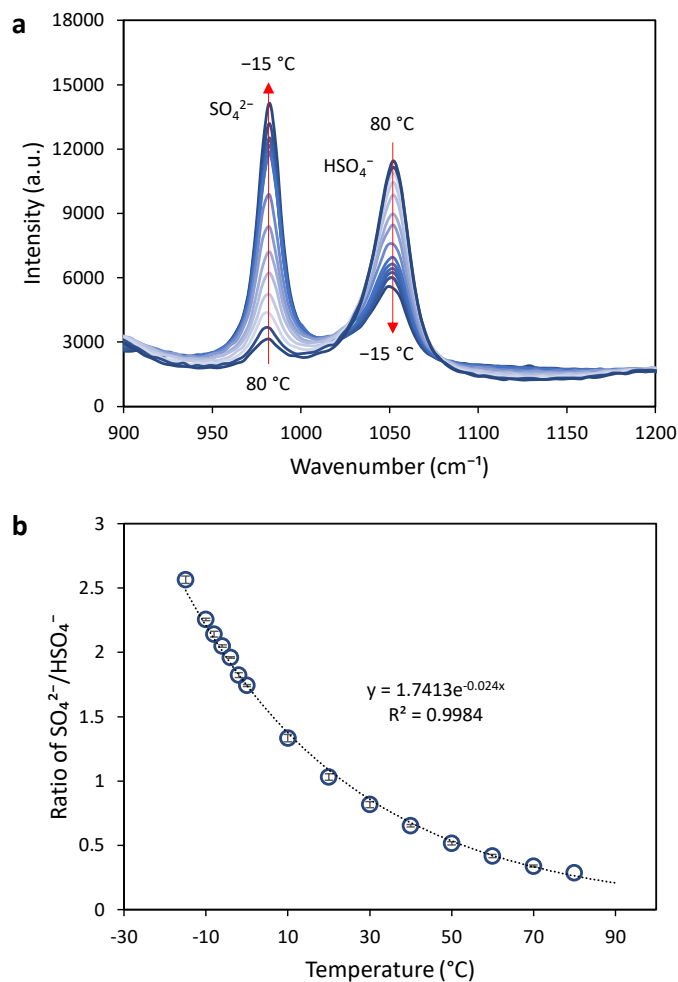
Supplementary Figure 14. Potential-dependent MnO_4^- dissolution from 80 °C to -12 °C.

Each circle denotes MnO_4^- dissolution determined by UV-vis spectroscopy under positive bias potentials. MnO_4^- dissolution was firstly measured in Abs and converted into amounts ($\mu\text{mol h}^{-1}$) (a) and current density (j , mA cm^{-2}) (b), while lines show fits at each temperature. Each potential-dependent MnO_4^- data point was obtained from an independent water electrolysis experiment. Horizontal bars indicate potential deviations during chronopotentiometry, not statistical errors. Vertical values are means of UV-vis measurements ($n = 3$) from three electrolyte samples collected from the same water electrolysis experiment, with error bars showing $\pm$ s.d., to assess the uniformity of MnO_4^- concentration at different temperatures.



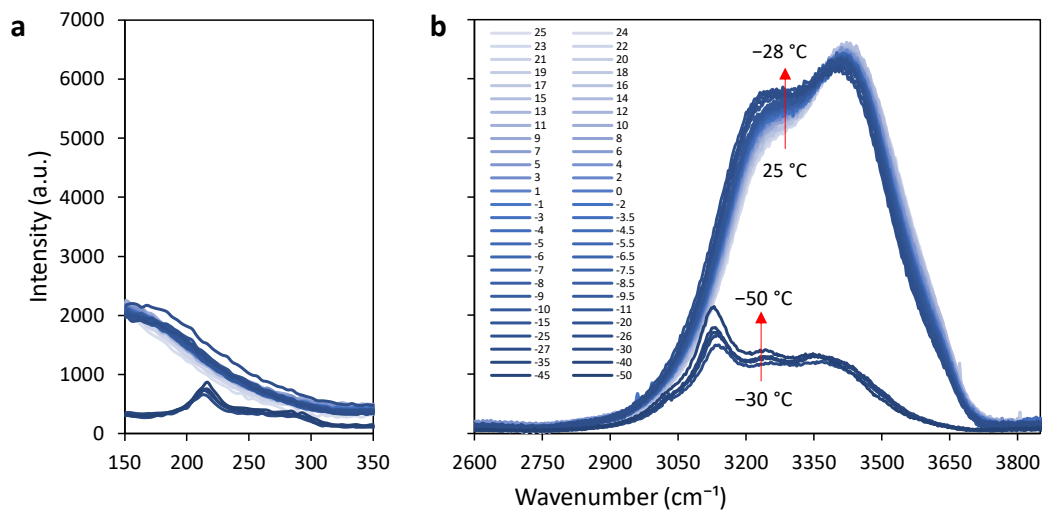
Supplementary Figure 15. Long-term stability test at lower applied current densities above and below 0 °C.

CP measurements of $\gamma\text{-MnO}_2/\text{FTO}$ at 50 mA cm^{-2} (a, d) and 25 mA cm^{-2} (b, e) in 1 M H_2SO_4 and 0.5 M Na_2SO_4 . CP was also conducted in only 1 M H_2SO_4 (c, f). Even only in 1 M H_2SO_4 , the catalytic lifetime decreased upon lowering the temperature from 4 to -4 °C. Vertical error bars show mean value $\pm$ s.d. from $n = 3$ independent experiments.



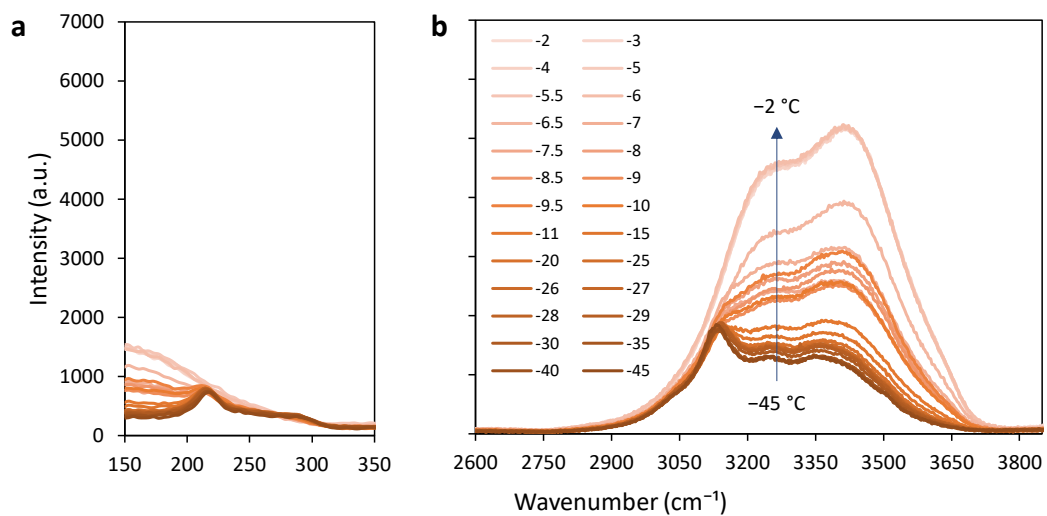
Supplementary Figure 16. Raman spectra of dissociated SO_4^{2-} and HSO_4^- from H_2SO_4 and Na_2SO_4 at temperatures between 80 to -15 $^{\circ}\text{C}$.

(a) Intensity changes of SO_4^{2-} and HSO_4^- peaks at 982.2 and 1052.2 cm^{-1} , and (b) ratio of SO_4^{2-} and HSO_4^- peak intensities as a function of temperature. Vertical error bars show mean value $\pm$ s.d. from $n = 3$ independent experiments.



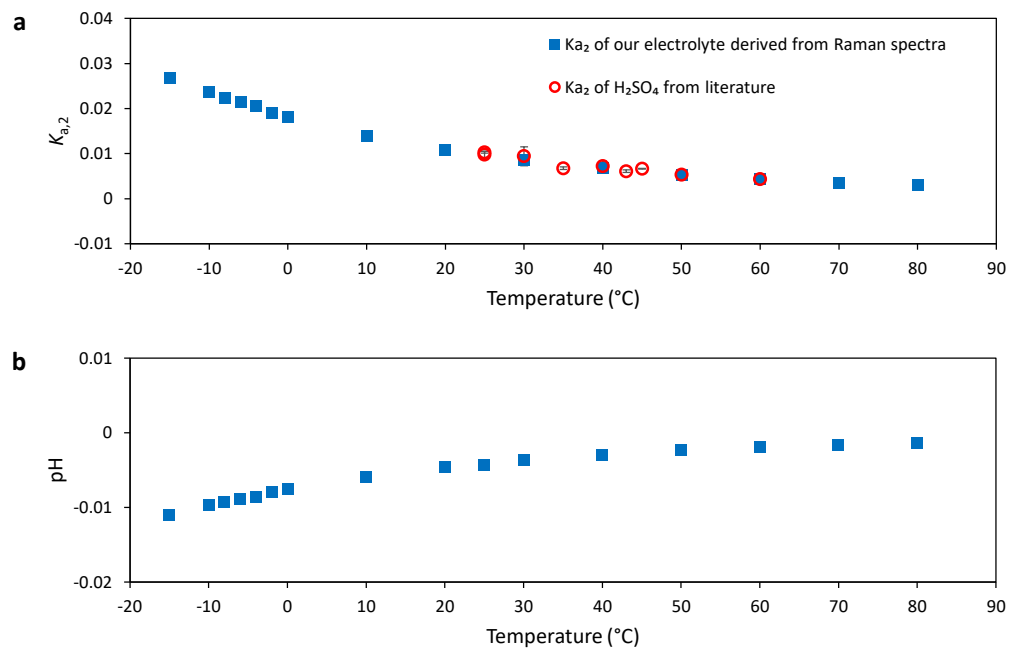
Supplementary Figure 17. Raman spectra of the bulk electrolyte upon cooling from 25 °C to -50 °C.

The spectra show broad features in the low-frequency region (a) and OH-stretching bands in the high-frequency region (b). The Raman spectra upon heating from -45 to -2 °C can be seen in Supplementary Fig. 18.



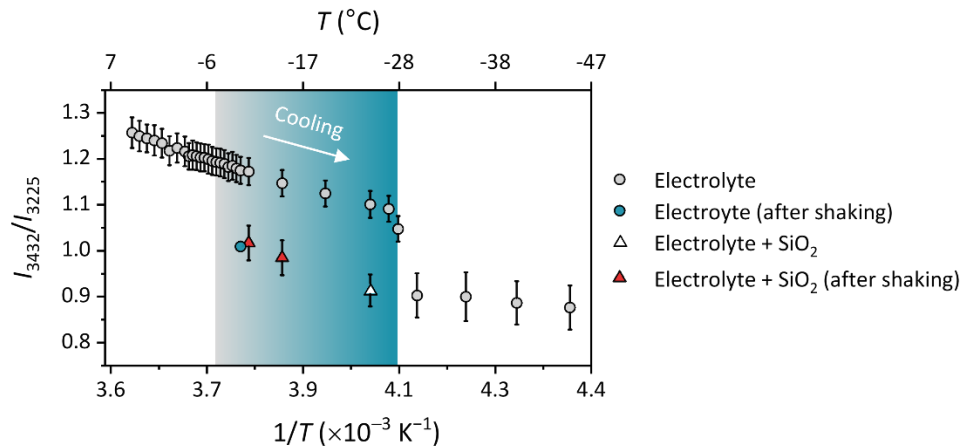
Supplementary Figure 18. Raman spectra of the bulk electrolyte upon heating from $-45\text{ }^{\circ}\text{C}$ to $-2\text{ }^{\circ}\text{C}$.

The spectra show broad features in the low-frequency region (a) and OH-stretching bands in the high-frequency region (b).



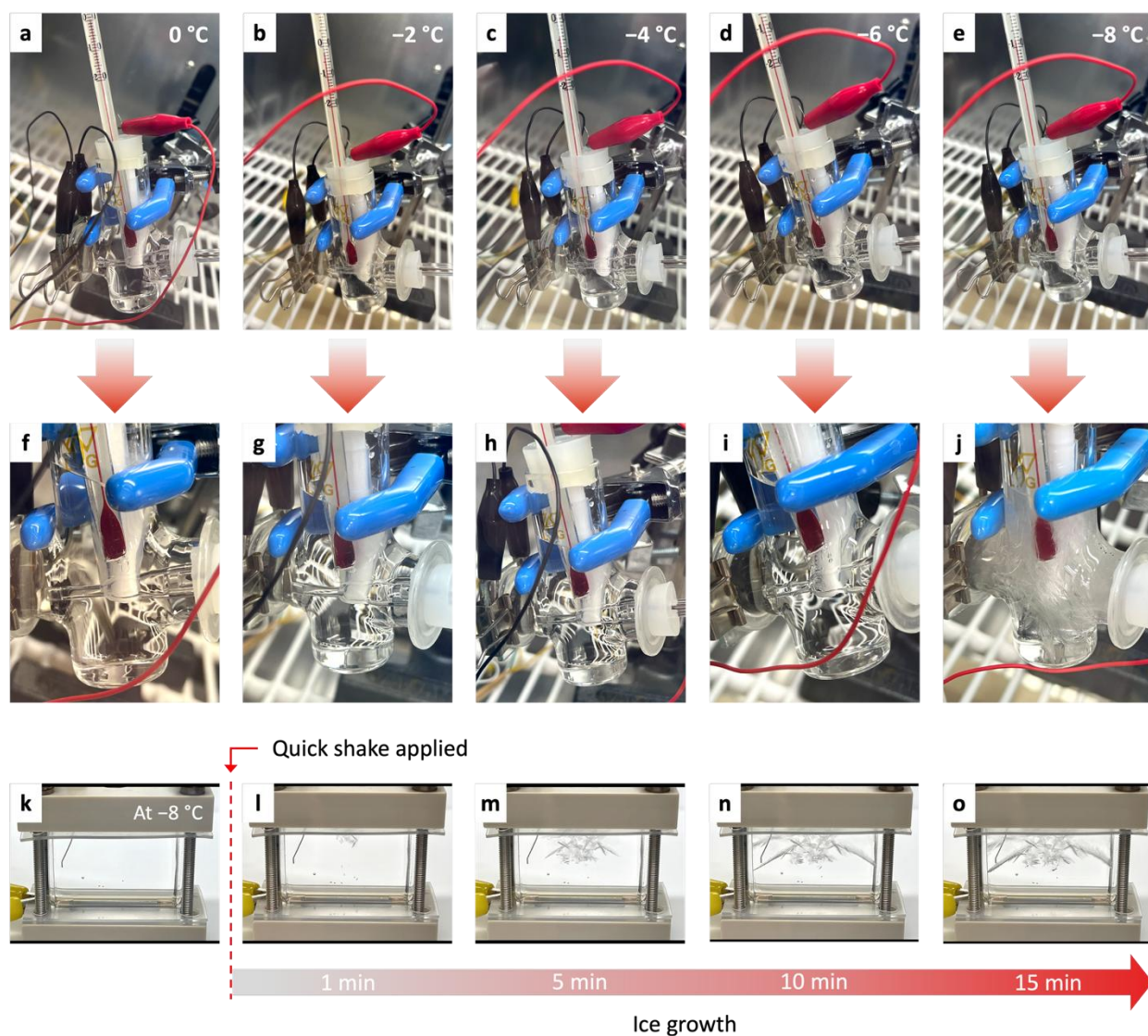
Supplementary Figure 19. Temperature-dependent second dissociation constant and pH of the electrolyte.

(a) Second dissociation constant ($K_{a,2}$) and (b) calculated pH of the electrolyte used in this study over the range 80 to -15 °C without freezing. Blue squares indicate data derived from the Raman spectra (Supplementary Figure 16b), and open red circles are the values reported by Marshall et al.¹⁰



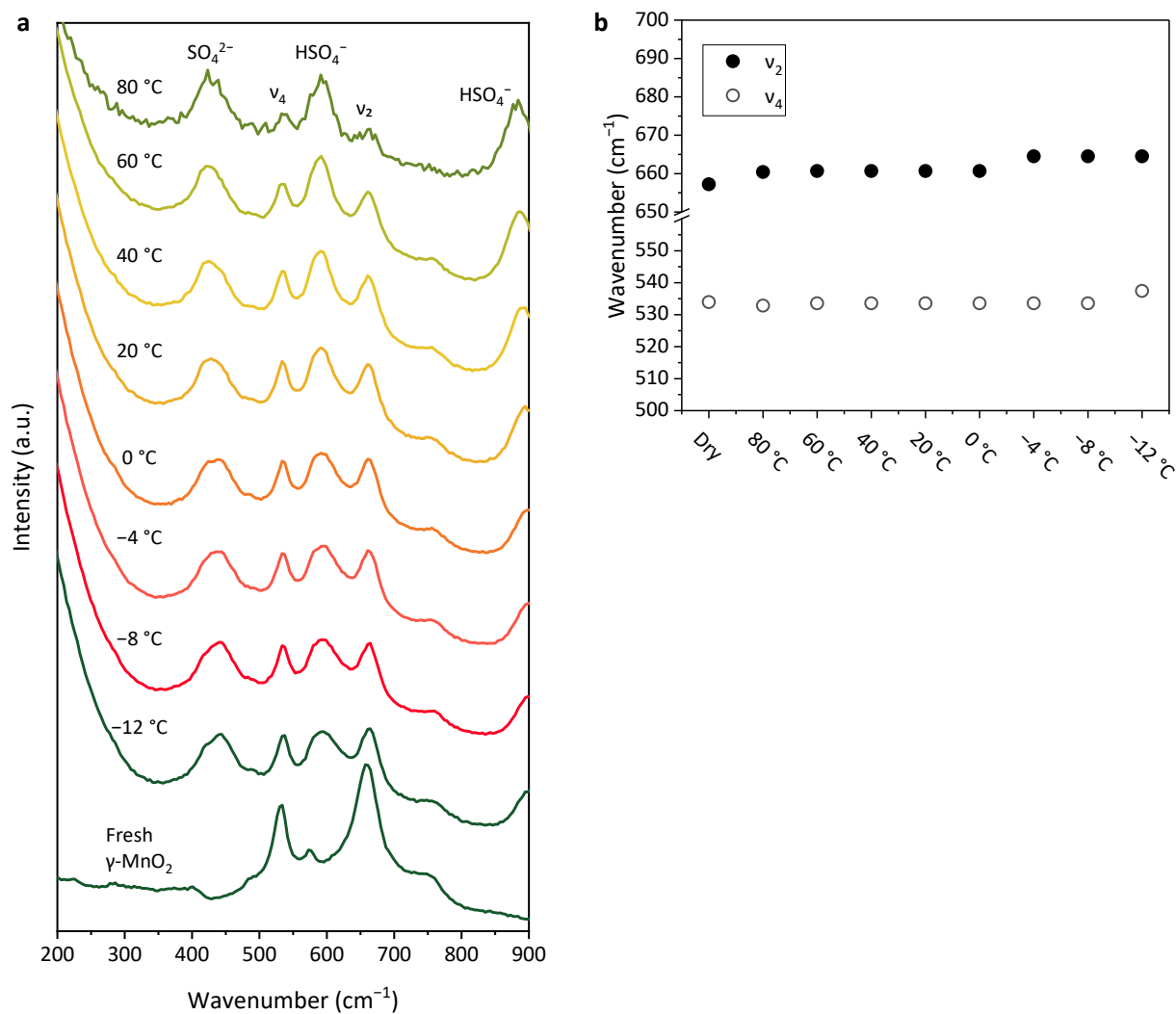
Supplementary Figure 20. Perturbation effects on the Raman intensity ratio of di-coordinated (3432 cm^{-1}) to tetra-coordinated (3225 cm^{-1}).

The tests include shaking the electrolyte at -10°C (blue circle) and adding colloidal silica as an ice-nucleating agent and shaking at -11°C and -15°C (red triangles) and without shaking at -25°C (white triangle) in the supercooled regime (blue shaded window). Data were obtained using the line-scan Raman imaging (400 scanned lines), except for the shaken electrolyte, which were measured in point mode.



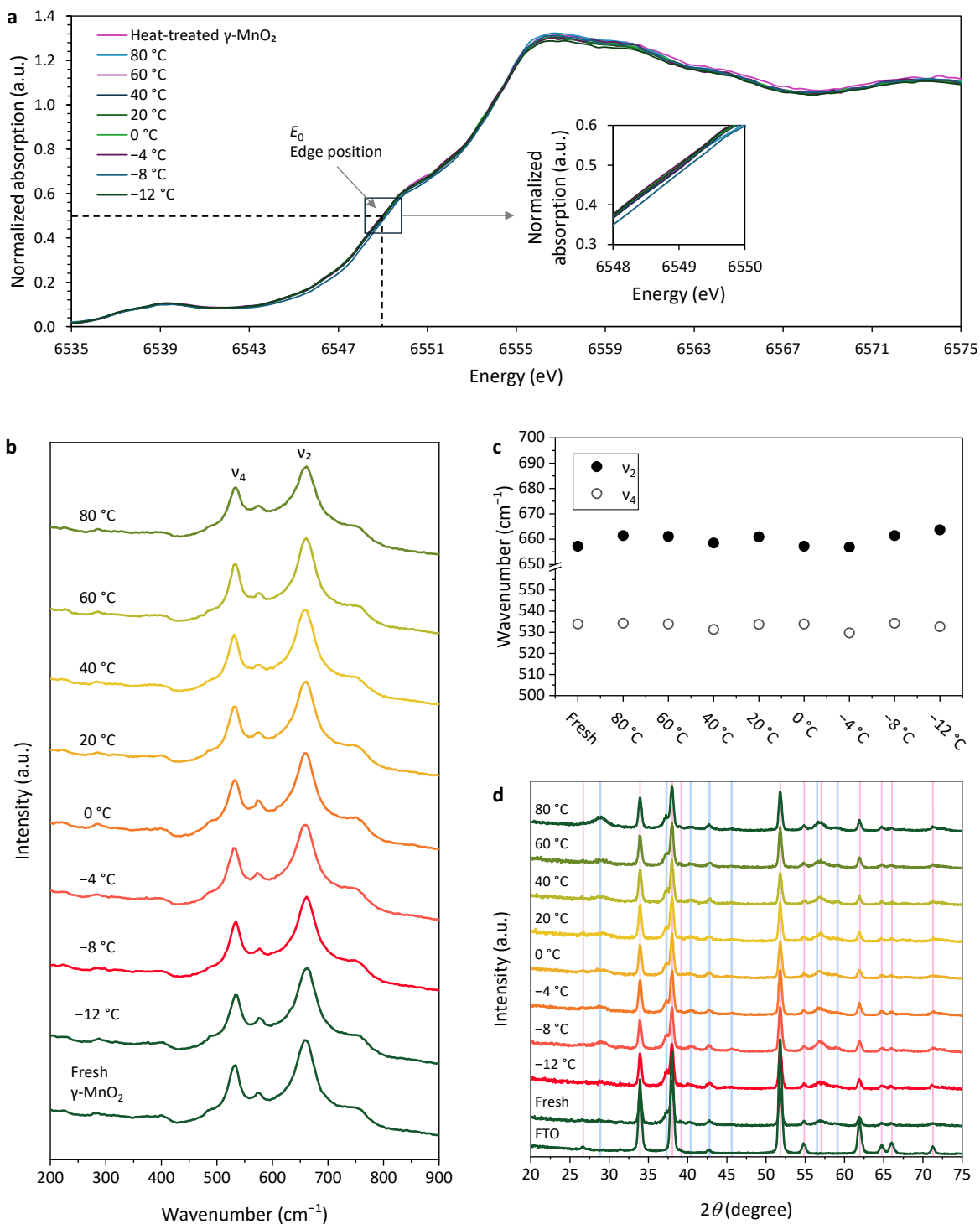
Supplementary Figure 21. Photographs of the three-electrode system before (a–e) and after a quick shake (f–j) at 0, -2, -4, -6, and -8 °C, without applying electrochemical bias. (k–o) Photographs of the two-electrode system at -8 °C, showing the ice crystal growth supercooled after a quick shake.

Clear ice formation was observed after shaking at -8 °C in all of the figures, indicating the electrolyte is in a supercooled state. No visible precipitation occurred between 0 and -8 °C, suggesting that the electrolyte remained supersaturated.



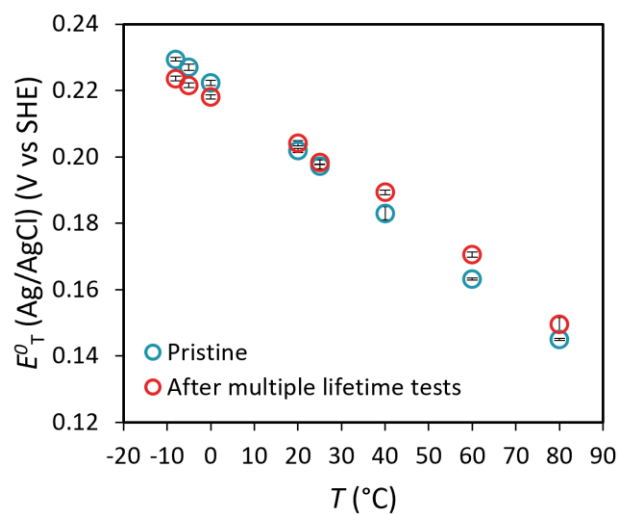
Supplementary Figure 22. Temperature-dependent Raman spectra of $\gamma\text{-MnO}_2$ immersed in the electrolyte over the temperature range from 80 and -12 °C.

(a) The characteristic v_2 and v_4 vibrational mode of $\gamma\text{-MnO}_2$ together with bands from the electrolyte. (b) Variation of v_2 and v_4 Raman shift as a function of temperature.



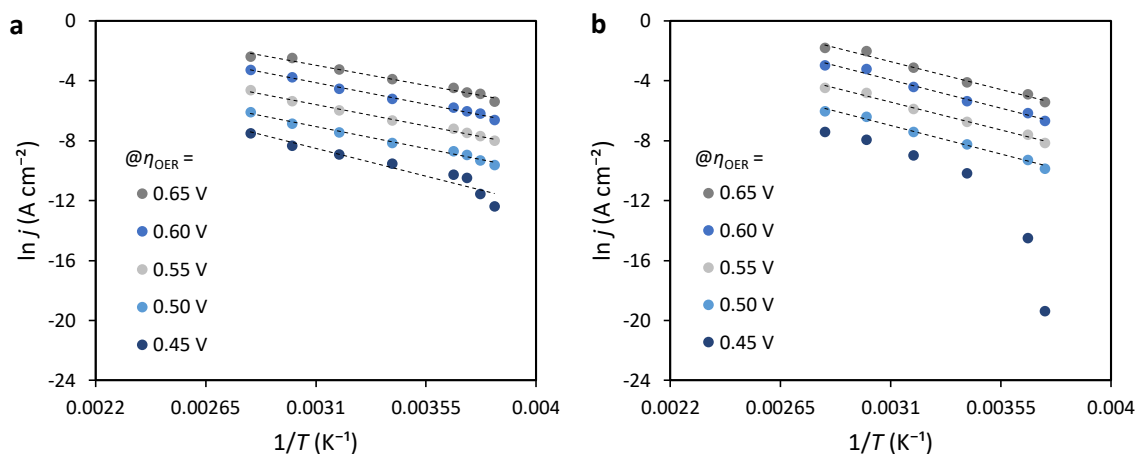
Supplementary Figure 23. Characterization of γ - MnO_2 after lifetime testing between 80 and -12 °C at 100 mA cm^{-2} .

(a) Normalized Mn K-edge XANES spectra. (b) Raman spectra of γ - MnO_2 , showing v_2 and v_4 vibration modes. (c) Variation of v_2 and v_4 wavenumbers as a function of testing temperature. (d) GI-XRD patterns; γ - MnO_2 and FTO are marked by blue and red lines, respectively.



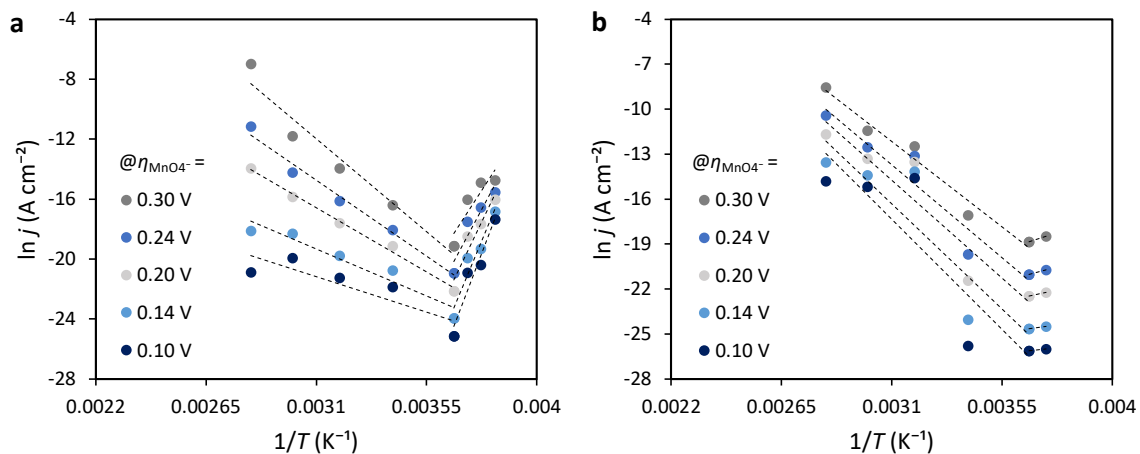
Supplementary Figure 24. Temperature-dependence of the Ag/AgCl (sat. KCl) reference electrode potential from -8 to 80 °C before and after lifetime tests longer than 10 h.

The values can be seen in Supplementary Table 1.



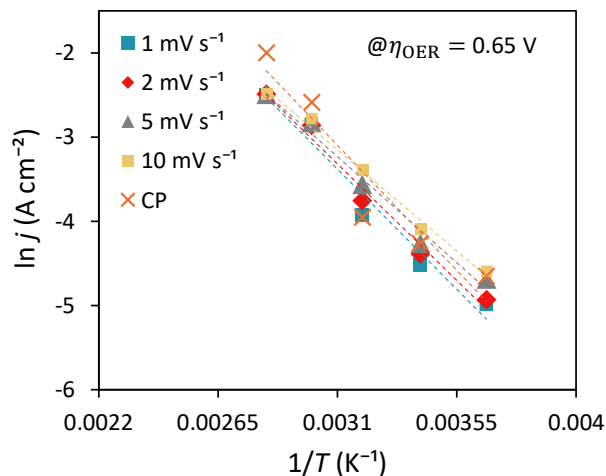
Supplementary Figure 25. Arrhenius plot of OER at different overpotentials under unstirred (a) and stirred conditions (b).

The relatively large deviation from linearity was observed at the lowest overpotential ($\eta_{\text{OER}} = 0.45$ V) at 0 and -5 °C under stirred conditions. As this deviation was observed under both unstirred and stirred conditions, it cannot be attributed solely to hydrodynamic effects. At this low overpotential, the OER current is close to the onset region, where the measured current becomes more susceptible to background contributions and experimental uncertainty.



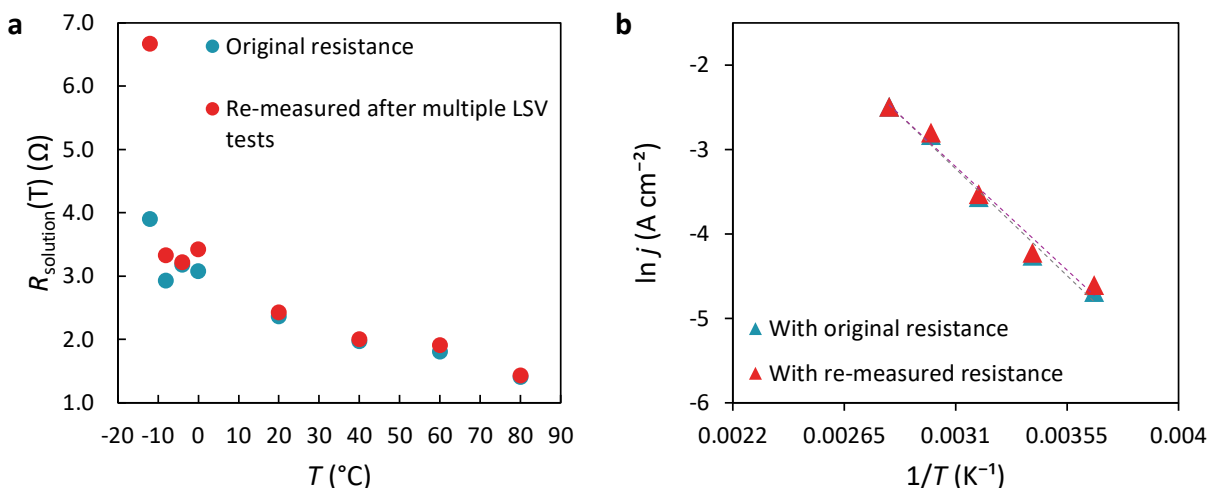
Supplementary Figure 26. Arrhenius plot of MnO_4^- dissolution at different overpotentials.

The plots are generated from the experiments under unstirred conditions over the temperature range from 80 to -12 °C (a) and stirred conditions over the temperature range from 80 to -5 °C (b).



Supplementary Figure 27. Arrhenius plots of OER obtained at different scan rates and from CP measurements between 80 °C and 0 °C.

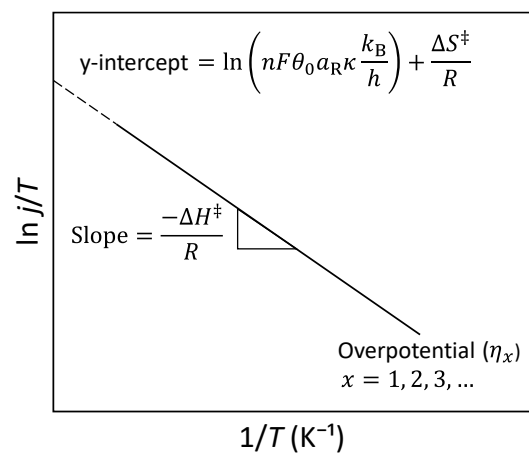
Arrhenius plots of OER at $\eta_{\text{OER}} = 0.65 \text{ V}$ obtained from LSV measurements at scan rates of 1, 2, 5, and 10 mV s^{-1} . The orange crosses show values obtained from chronopotentiometric measurements at $\eta_{\text{OER}} = 0.65 \pm 0.02 \text{ V}$. Dashed lines represent linear fits used to estimate the apparent activation energies.



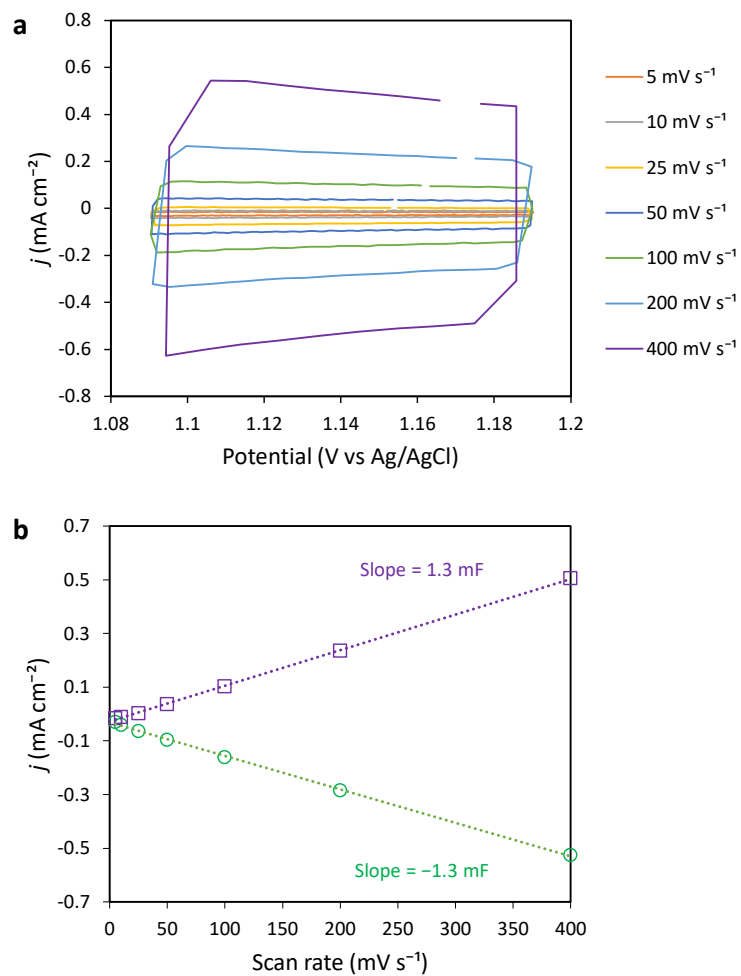
Supplementary Figure 28. Effect of repeated LSV measurements on solution resistance and Arrhenius analysis.

(a) Temperature-dependence of the solution resistance measured before any OER measurements and re-measured after six consecutive LSV scans under quiescent conditions. The increase in resistance after LSV measurements indicates that gas evolution and/or residual bubbles can affect the measured resistance to some extent. The large increase observed at -12°C is attributable to ice formation during the experiment. (b) Arrhenius plots of OER $\geq 0^{\circ}\text{C}$ corrected using the original resistance values and the re-measured resistance values after the repeated LSV scans.

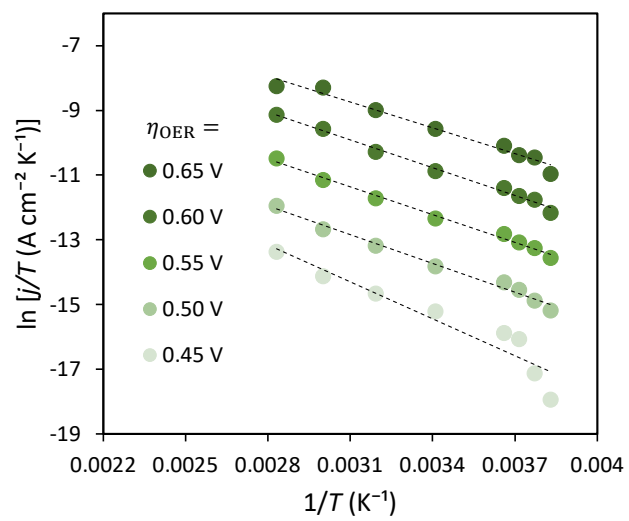
The apparent activation energy for OER above 0°C was essentially unchanged when the post-LSV solution resistances were used for iR correction: 23.5 kJ mol^{-1} using the original resistance values and 22.9 kJ mol^{-1} using the post-LSV resistance values. This small difference indicates that gas-evolution-induced changes in the uncompensated resistance have a negligible effect on the extracted apparent activation energy for OER.



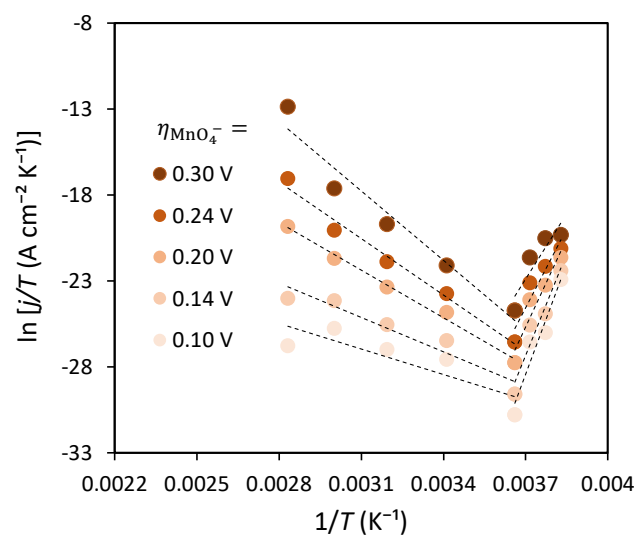
Supplementary Figure 29. Eyring plot for heterogeneous electrochemical reactions.



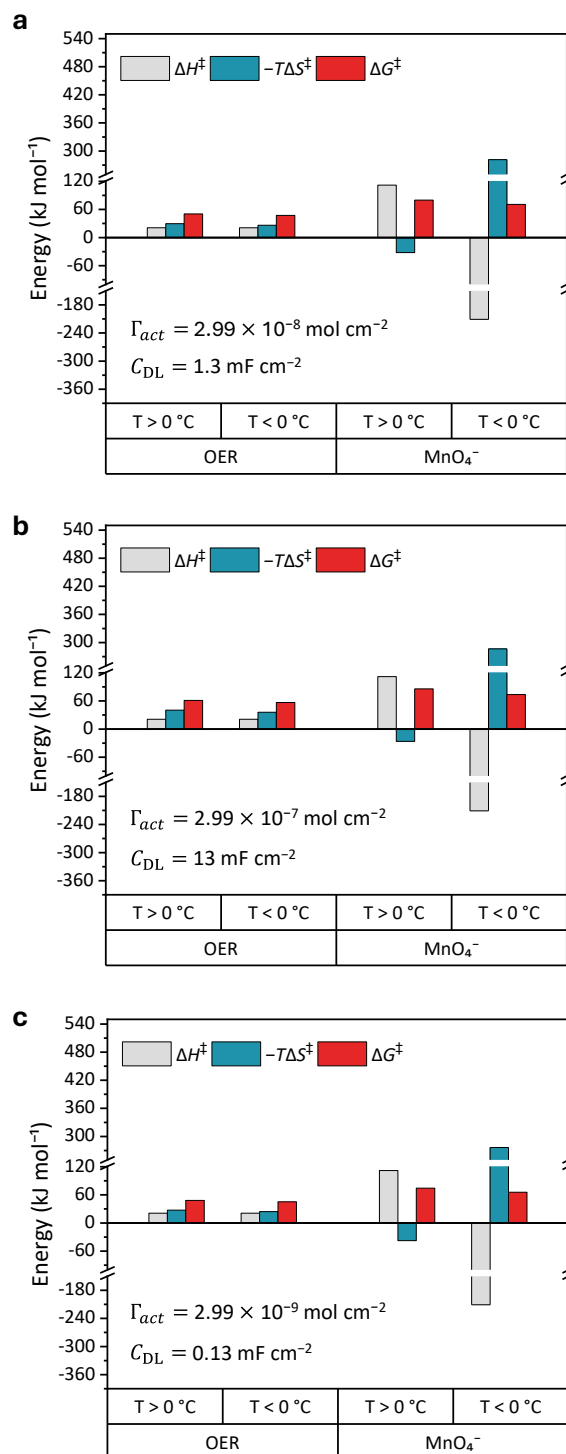
Supplementary Figure 30. Double-layer capacitance measurements on γ -MnO₂ in 1 M H₂SO₄.



Supplementary Figure 31. Eyring plot for the OER.

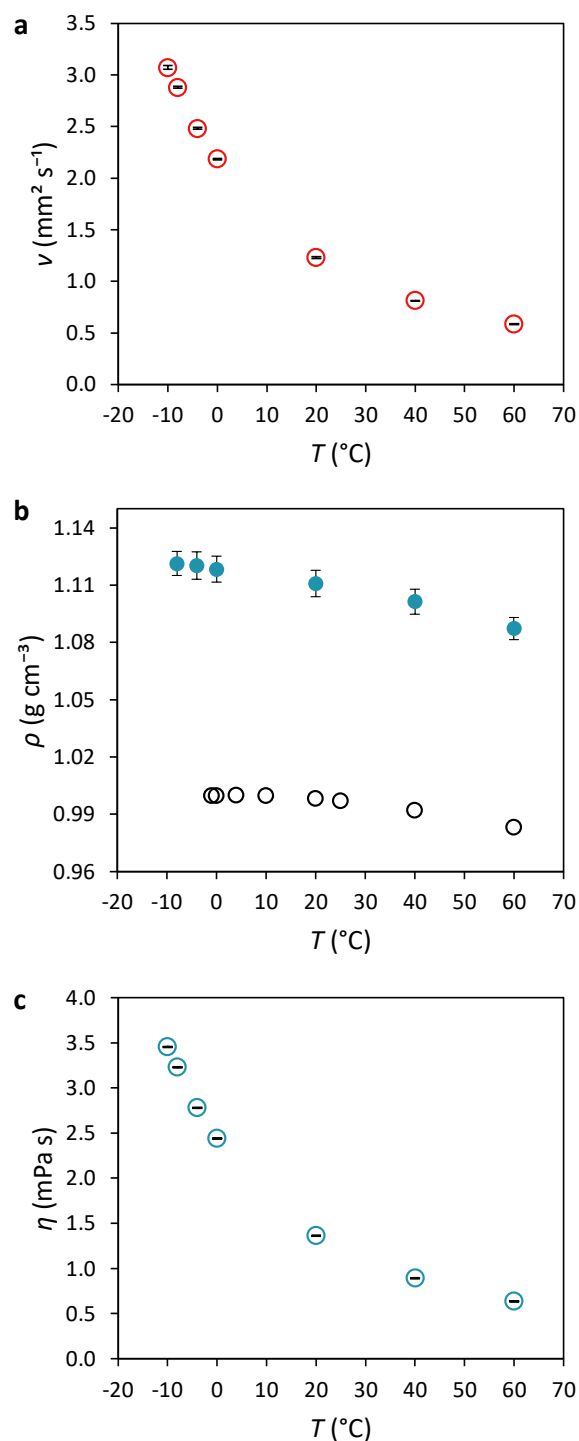


Supplementary Figure 32. Eyring plot for MnO_4^- dissolution.



Supplementary Figure 33. Enthalpy–entropy compensation derived using the specified active site concentrations: one order of magnitude higher (b) and lower (c) active site concentrations than the estimated value (a).

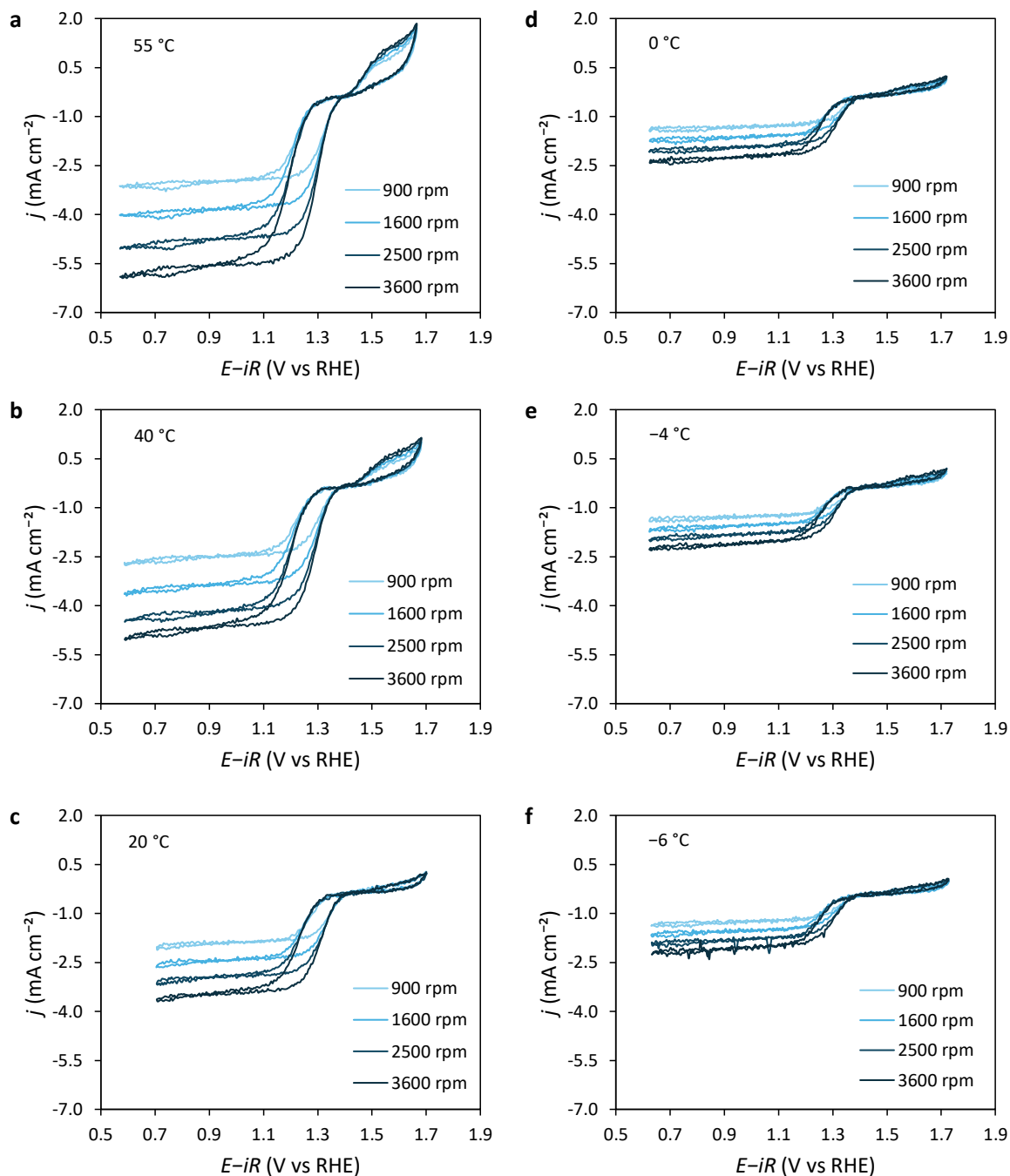
Two orders of magnitude differences are also provided in Supplementary Table 10–13.



Supplementary Figure 34. Temperature-dependent viscosity and density of 1 M H₂SO₄ + 0.5 M Na₂SO₄.

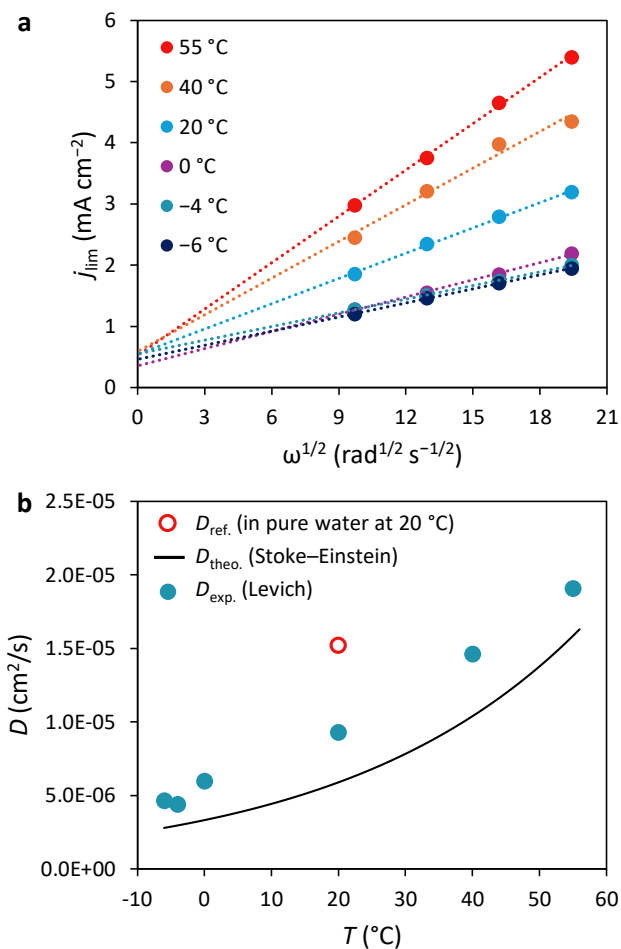
(a) The kinematic viscosity was measured using an *Ubbelohde* viscometer. Vertical error bars show mean value $\pm$ s.d. from $n = 5$ independent experiments. (b) The density was measured using a 25 mL pycnometer (blue-green circles), together with pure water from literature shown for

comparison (white circles). Vertical error bars show mean value $\pm$ s.d. from $n = 4$ independent experiments. (c) Dynamic viscosity calculated from the measured kinematic viscosity and density using $\eta = \nu\rho$. η at $-10\text{ }^{\circ}\text{C}$ was calculated using ρ extrapolated from the measured data in Supplementary Figure 34b.



Supplementary Figure 35. Cyclic voltammograms of MnO_4^- reduction over the temperature range of -6 to 55 °C recorded using RDE.

The voltammograms were recorded using a Pt disk in N_2 -purged $\text{H}_2\text{SO}_4 + 0.5$ M Na_2SO_4 containing 0.5 mM KMnO_4 at rotation rates of 900, 1600, 2500, and 3600 rpm. Measurements were conducted at (a) 55 °C, (b) 40 °C, (c) 20 °C, (d) 0 °C, (e) -4 °C, and (f) -6 °C.



Supplementary Figure 36. Levich analysis for estimating MnO_4^- diffusion coefficients over the temperature range of -6 to 55 °C.

(a) Levich plots obtained from the cathodic limiting currents of MnO_4^- reduction at different temperatures. (b) Temperature dependence of the MnO_4^- diffusion coefficient estimated from the Levich analyses. The diffusion coefficient generally decreased upon cooling, also consistent with the increase in electrolyte viscosity. The calculation assumed a five-electron reduction of MnO_4^- to Mn^{2+} in acidic media.

Supplementary Table

Supplementary Table 1. Equilibrium potentials of Ag/AgCl reference electrode before and after lifetime tests longer than 10 h.

T (°C)	V vs SHE (before CP test)	V vs SHE (after multiple CP tests)	% change
−12	0.233 ± 0.00049	N/A	N/A
−8	0.229 ± 0.00091	0.224 ± 0.00069	2.54
−4	0.227 ± 0.00080	0.222 ± 0.00071	2.37
0	0.222 ± 0.00069	0.218 ± 0.00067	1.91
20	0.202 ± 0.00066	0.204 ± 0.00078	1.11
25	0.197 ± 0.00202	0.198 ± 0.00068	0.62
40	0.183 ± 0.00031	0.189 ± 0.00070	3.44
60	0.163 ± 0.00032	0.171 ± 0.00077	4.53
80	0.145 ± 0.00066	0.150 ± 0.00212	3.17

After the reference electrode was re-calibrated, we note that the maximum potential drift was 8 mV, that is too small to significantly affect the end-of-life measurement by chronopotentiometry (Figure 3a, Supplementary Figure 15).

Supplementary Table 2. Standard equilibrium potential of water oxidation and equilibrium potential of MnO_4^- at temperatures between -12 and 80 °C.

T (°C)	E^0_{T} ($\text{O}_2/\text{H}_2\text{O}$) (V vs NHE)	E_{T} ($\text{Mn}^{\text{IV}}/\text{Mn}^{\text{VII}}$) (V vs SHE)
-12	1.262	1.596
-8	1.258	1.595
-4	1.255	1.593
0	1.251	1.592
20	1.234	1.584
25	1.230	1.582
40	1.217	1.576
60	1.201	1.568
80	1.184	1.560

Supplementary Table 3. E_a of the OER and MnO_4^- dissolution at different overpotentials under unstirred conditions. The values were estimated from the negative slopes of the Arrhenius plots.

OER				MnO_4^- dissolution			
η_{OER} (V)	Slope	R^2	E_a (kJ mol ⁻¹)	$\eta_{\text{MnO}_4^-}$ (V)	Slope	R^2	E_a (kJ mol ⁻¹)
0.45	-3639	0.92	30.3	0.10	-5249	0.75	43.6
0.50	-3169	0.99	26.3	0.14	-6959	0.93	57.9
0.55	-3101	0.99	25.8	0.20	-9523	0.99	79.2
0.60	-3085	0.99	25.7	0.24	-11233	0.98	93.4
0.65	-2814	0.98	23.4	0.30	-13786	0.96	114.6

The Arrhenius plots resulting from the unstirred conditions are shown in Supplementary Figure 25a.

Supplementary Table 4. E_a of the OER and MnO_4^- dissolution at different overpotentials under stirred conditions. The values were estimated from the negative slope of the Arrhenius plots.

OER				MnO_4^- dissolution			
η_{OER} (V)	Slope	R^2	E_a (kJ mol ⁻¹)	$\eta_{\text{MnO}_4^-}$ (V)	Slope	R^2	E_a (kJ mol ⁻¹)
0.45	N/A	N/A	N/A	0.10	-16315	0.77	135.6
0.50	-4026	0.99	33.5	0.14	-15585	0.82	129.6
0.55	-3985	0.99	33.1	0.20	-14491	0.88	120.5
0.60	-4119	0.98	34.2	0.24	-13761	0.92	114.4
0.65	-4024	0.98	33.5	0.30	-12667	0.97	105.3

The potential-dependence curves of OER and MnO_4^- , lifetime tests, and Arrhenius plots resulting from the stirred conditions are shown in Supplementary Figure 9, 11, and 25b.

Supplementary Table 5. E_a of MnO_4^- dissolution at different overpotentials under unstirred conditions. The values were estimated from the positive slopes of the corresponding anti-Arrhenius plots.

MnO_4^- dissolution			
$\eta_{\text{MnO}_4^-}$ (V)	Positive slope	R^2	E_a (kJ mol $^{-1}$)
0.10	42612	0.92	−354.3
0.14	39139	0.92	−325.4
0.20	33929	0.91	−282.1
0.24	30457	0.88	−253.2
0.30	25247	0.81	−209.9

E_a for MnO_4^- dissolution was determined over 0 to −12 °C.

Supplementary Table 6. E_a of MnO_4^- dissolution at different overpotentials under stirred conditions. The values were estimated from the positive slopes of the anti-Arrhenius plots.

MnO_4^- dissolution			
$\eta_{\text{MnO}_4^-}$ (V)	Positive slope	R^2	E_a (kJ mol ⁻¹)
0.10	1805	1	-15.0
0.14	2527	1	-21.0
0.20	3610	1	-30.0
0.24	4331	1	-36.0
0.30	5414	1	-45.0

E_a for MnO_4^- dissolution was determined over 0 to -5 °C. The potential-dependence curves of OER and MnO_4^- , lifetime tests, and Arrhenius plots resulting from the stirred conditions are shown in Supplementary Figure 9, 11, and 25b.

Supplementary Table 7. Apparent activation energies of OER obtained from LSV measurements at different scan rates and from chronopotentiometry.

η_{OER} (V)	Scan rate (mV s ⁻¹)	Slope	R ²	E_a (kJ mol ⁻¹)
0.60	1	-3560	0.96	29.6
	2	-3406	0.98	28.9
	5	-3442	0.97	28.6
	10	-3351	0.98	27.9
0.62	1	-3325	0.96	27.6
	2	-3350	0.98	27.9
	5	-3078	0.97	25.6
	10	-3078	0.98	25.6
0.65	1	-3146	0.96	26.2
	2	-3083	0.97	25.6
	5	-2827	0.97	23.5
	10	-2776	0.98	23.1
0.65 ± 0.02	*Chronopotentiometry	-3306	0.91	27.5

*Chronopotentiometry was conducted at fixed current densities selected to give overpotentials at $\eta_{\text{OER}} = 0.65 \pm 0.02$ V, depending on temperature. Each measurement was held for at least 60 s, and the reported overpotential represents the average of the collected potential values.

Supplementary Table 8. Apparent activation parameters of the OER and MnO_4^- dissolution at different overpotentials estimated above 0 °C from the corresponding Eyring plots.

OER					MnO_4^- dissolution				
η_{OER} (V)	$\Delta H^\ddagger$ (kJ mol^{-1})	$\Delta S^\ddagger$ (kJ mol^{-1} K^{-1})	$-T\Delta S^\ddagger$ at 25 °C (kJ mol^{-1})	$\Delta G^\ddagger$ (kJ mol^{-1})	$\eta_{\text{MnO}_4^-}$ (V)	$\Delta H^\ddagger$ (kJ mol^{-1})	$\Delta S^\ddagger$ (kJ mol^{-1} K^{-1})	$-T\Delta S^\ddagger$ at 25 °C (kJ mol^{-1})	$\Delta G^\ddagger$ (kJ mol^{-1})
0.45	27.7	-0.12	37.1	64.8	0.10	41.1	-0.19	56.1	97.2
0.50	23.8	-0.12	37.1	60.9	0.14	55.3	-0.13	38.5	93.8
0.55	23.3	-0.11	33.9	57.2	0.20	76.6	-0.04	11.9	88.5
0.60	23.1	-0.10	30.5	53.6	0.24	90.8	0.02	-5.80	85.0
0.65	20.9	-0.10	29.7	50.5	0.30	112.0	0.10	-32.0	80.0

See Supplementary Note 11 for calculation details. From the negative slopes of the Eyring plots, $\Delta H^\ddagger$ of OER at η_{OER} 0.65 V was estimated to be 20.9 kJ mol^{-1} . The corresponding $\Delta S^\ddagger$ was -0.10 kJ mol^{-1} K^{-1} , giving a Gibbs free energy of activation ($\Delta G^\ddagger$) of 50.8 kJ mol^{-1} at 25 °C. At a lower overpotential (η_{OER} = 0.45 V), $\Delta G^\ddagger$ is 64.8 kJ mol^{-1} , comparable to that of a Co-Pi OER catalyst⁴⁰ (70.4 kJ mol^{-1} at η_{OER} = 0.41 V).

Supplementary Table 9. Apparent activation parameters of the OER and MnO_4^- dissolution at different overpotentials estimated below 0 °C from the corresponding Eyring plots.

OER					MnO_4^- dissolution				
η_{OER} (V)	$\Delta H^\ddagger$ (kJ mol ⁻¹)	$\Delta S^\ddagger$ (kJ mol ⁻¹ K ⁻¹)	$-T\Delta S^\ddagger$ at -8 °C (kJ mol ⁻¹)	$\Delta G^\ddagger$ (kJ mol ⁻¹)	$\eta_{\text{MnO}_4^-}$ (V)	$\Delta H^\ddagger$ (kJ mol ⁻¹)	$\Delta S^\ddagger$ (kJ mol ⁻¹ K ⁻¹)	$-T\Delta S^\ddagger$ at -8 °C (kJ mol ⁻¹)	$\Delta G^\ddagger$ (kJ mol ⁻¹)
0.45	27.7	-0.12	33.0	60.7	0.10	-356.5	-1.65	436.7	80.2
0.50	23.8	-0.12	33.0	56.8	0.14	-327.6	-1.53	405.9	78.3
0.55	23.3	-0.11	30.2	53.4	0.20	-284.3	-1.36	359.8	75.5
0.60	23.1	-0.10	27.1	50.2	0.24	-255.5	-1.24	329.0	73.6
0.65	20.9	-0.10	26.4	47.3	0.30	-210.8	-1.06	281.6	70.7

See Supplementary Note 11 for calculation details. In the temperature range between 80 and 0 °C, $\Delta H^\ddagger$ of MnO_4^- dissolution ($\eta_{\text{MnO}_4^-} = 0.30$ V) was estimated to be 112.0 kJ mol⁻¹, and $\Delta S^\ddagger$ to be 0.10 kJ mol⁻¹ K⁻¹, giving $\Delta G^\ddagger$ of 80.0 kJ mol⁻¹ at 25 °C. Between 0 and -12 °C, $\Delta H^\ddagger$ and $\Delta S^\ddagger$ were -210.8 and -1.06 kJ mol⁻¹ K⁻¹, respectively, corresponding to $\Delta H^\ddagger = 70.7$ kJ mol⁻¹ at -8 °C.

Supplementary Table 10. Effect of active site concentrations on the activation parameters of OER. $T > 0$ °C ($\eta_{\text{OER}} = 0.65$ V, $\Delta H^\ddagger = 20.9$ kJ mol⁻¹, $T = 25$ °C).

Active site concentration (mol cm ⁻²)	$\Delta S^\ddagger$ (kJ mol ⁻¹ K ⁻¹)	$-T\Delta S^\ddagger$ (kJ mol ⁻¹) at 25 °C	$\Delta G^\ddagger$ (kJ mol ⁻¹)
2.99×10^{-6}	-0.148	44.1	65.8
2.99×10^{-7}	-0.136	40.4	61.3
2.99×10^{-8}	-0.114	33.9	54.8
2.99×10^{-9}	-0.092	27.4	48.2
2.99×10^{-10}	-0.061	18.1	41.5

Supplementary Table 11. Effect of active site concentrations on the activation parameters of OER. $T < 0$ °C ($\eta_{\text{OER}} = 0.65$ V, $\Delta H^\ddagger = 20.9$ kJ mol⁻¹, $T = -8$ °C).

Active site concentration (mol cm ⁻²)	$\Delta S^\ddagger$ (kJ mol ⁻¹ K ⁻¹)	$-T\Delta S^\ddagger$ (kJ mol ⁻¹) at -8 °C	$\Delta G^\ddagger$ (kJ mol ⁻¹)
2.99×10^{-6}	-0.148	39.2	60.9
2.99×10^{-7}	-0.136	36.0	56.8
2.99×10^{-8}	-0.114	30.2	51.1
2.99×10^{-9}	-0.092	24.3	45.2
2.99×10^{-10}	-0.061	16.1	39.5

Grey shaded row indicates the effective active site concentration determined by the relative surface area.

Supplementary Table 12. Effect of active site concentrations on the activation parameters of MnO_4^- dissolution. $T > 0\text{ }^\circ\text{C}$ ($\eta_{\text{MnO}_4^-} = 0.30\text{ V}$, $\Delta H^\ddagger = 112.0\text{ kJ mol}^{-1}$, $T = 25\text{ }^\circ\text{C}$).

Active site concentration (mol cm^{-2})	$\Delta S^\ddagger$ ($\text{kJ mol}^{-1}\text{ K}^{-1}$)	$-T\Delta S^\ddagger$ at $25\text{ }^\circ\text{C}$ (kJ mol^{-1})	$\Delta G^\ddagger$ (kJ mol^{-1})
2.99×10^{-6}	0.070	-20.6	91.4
2.99×10^{-7}	0.089	-26.3	85.7
2.99×10^{-8}	0.108	-32.0	80.0
2.99×10^{-9}	0.127	-37.7	74.3
2.99×10^{-10}	0.146	-43.4	68.6

Supplementary Table 13. Effect of active site concentrations on the activation parameters of MnO_4^- dissolution. $T < 0\text{ }^\circ\text{C}$ ($\eta_{\text{MnO}_4^-} = 0.30\text{ V}$, $\Delta H^\ddagger = -210.8\text{ kJ mol}^{-1}$, $T = -8\text{ }^\circ\text{C}$).

Active site concentration (mol cm^{-2})	$\Delta S^\ddagger$ ($\text{kJ mol}^{-1}\text{ K}^{-1}$)	$-T\Delta S^\ddagger$ at $-8\text{ }^\circ\text{C}$ (kJ mol^{-1})	$\Delta G^\ddagger$ (kJ mol^{-1})
2.99×10^{-6}	-1.100	291.7	80.9
2.99×10^{-7}	-1.081	286.6	75.8
2.99×10^{-8}	-1.062	281.6	70.7
2.99×10^{-9}	-1.043	276.5	65.7
2.99×10^{-10}	-1.024	271.4	60.6

To assess the reliability of this approximation, $\Delta S^\ddagger$ was also evaluated assuming active site concentrations varied by ± 2 orders of magnitude. Despite the absolute uncertainty, the results consistently exhibited a linear enthalpy–entropy compensation trend, indicating that the observed relationship is intrinsic to the reaction mechanism rather than an artifact of the assumed site concentration. Grey shaded row indicates the effective active site concentration determined by the relative surface area (Supplementary Note 12).

Supplementary Table 14. The average values of $E_{\text{stable}}(T)$ and $E_{\text{fail}}(T)$.

T (°C)	E_{stable} (V vs RHE) (unstirred)	E_{fail} (V vs RHE) (unstirred)
80	1.81	2.01
60	1.85	2.05
40	1.91	2.11
20	2.07	2.27
0	2.10	2.30
−4	2.12	2.32
−8	2.13	2.33

$E_{\text{stable}}(T)$ is the initially stabilized potential during chronopotentiometry at temperature T . The catalyst lifetime, $\tau(T)$, is defined as the first time at which the electrode potential reaches $E_{\text{stable}}(T) + \Delta E_{\text{crit}}$, where $\Delta E_{\text{crit}} = 0.2 \text{ V}^{41}$.

Supplementary Table 15. Temperature dependence of solution resistance before and after repeated LSV measurements.

Temperature-dependence of solution resistance			
T (°C)	Before LSVs	After LSVs	% change
80	1.41	1.43	1.45
60	1.81	1.92	5.82
40	1.98	2.00	1.54
20	2.36	2.43	2.90
0	3.08	3.43	11.39
−4	3.18	3.22	1.13
−8	2.93	3.33	13.55
−12	3.90	6.67	70.93

Supplementary Table 16. Estimated classical Debye length of the electrolyte at selected temperatures.

Temperature	* ϵ_r	Estimated λ_D at $I = 3$ M
80 °C (353.15 K)	60.8	0.168 nm
20 °C (293.15 K)	80.2	0.176 nm
0 °C (273.15 K)	87.9	0.178 nm

Supplementary Table 17. Summary of temperature-dependent physicochemical and transport properties that are considered in interpreting the apparent activation parameters in this study.

Property	Trend upon cooling	Source and method
Dynamic viscosity, η	Increases	Measured in 1 M H ₂ SO ₄ + 0.5 M Na ₂ SO ₄ at –10–60 °C
Density, ρ	Slightly increases	Measured in 1 M H ₂ SO ₄ + 0.5 M Na ₂ SO ₄ at –8–60 °C
MnO ₄ [–] diffusion coefficient, $D_{\text{MnO}_4^-}$	Decreases	Determined by rotating disk electrode in 1 M H ₂ SO ₄ + 0.5 M Na ₂ SO ₄ at –6–55 °C
H ⁺ diffusion coefficient, D_{H^+}	Decreases	Reported for aqueous acidic media at 0–50 °C
Ionic conductivity, κ	Decreases	Relative trend inferred from $1/R_{\text{solution}}(T)$ using the same cell geometry
O ₂ solubility	Increases	Reported for 1 M H ₂ SO ₄ at 25–55 °C
Classical Debye length, λ_{D}	Slightly increases	Estimated at $I = 3$ M using the classical Debye–Hückel model

Supplementary References

1. deBethune, A. J., Licht, T. S. & Swendeman, N. The Temperature Coefficients of Electrode Potentials: The Isothermal and Thermal Coefficients—The Standard Ionic Entropy of Electrochemical Transport of the Hydrogen Ion. *J. Electrochem. Soc.* **106**, 616 (1959).
2. Salvi, G. R. & deBethune, A. J. The Temperature Coefficients of Electrode Potentials: II . The Second Isothermal Temperature Coefficient. *J. Electrochem. Soc.* **108**, 672 (1961).
3. Lamas, C. P., Vega, C. & Noya, E. G. Freezing point depression of salt aqueous solutions using the Madrid-2019 model. *J. Chem. Phys.* **156**, 134503 (2022).
4. HORIBA Ltd. Electrical potential of Reference Electrode. <https://www.horiba.com/int/water-quality/support/electrochemistry/the-basis-of-ph/electrical-potential-of-reference-electrode/>.
5. Sensortechnik Meinsberg. Standard potentials of reference electrodes. <https://www.meinsberger-elektroden.de/en/ueberblick/potential>.
6. Bard, A. J., Parsons, R. & Jordan J. Manganese, Technetium, and Rhenium. in *Standard Potentials in Aqueous Solution (1st ed.)* 436–438 (CRC Press, New York, 1985).
7. Wagman, D. D. *et al.* The NBS Tables of Chemical Thermodynamic Properties. in *J. Phys. Chem. Ref. Data* vol. 11 191 (1982).
8. Li, A. *et al.* Stable Potential Windows for Long-Term Electrocatalysis by Manganese Oxides Under Acidic Conditions. *Angew. Chem. Int. Ed.* **58**, 5054–5058 (2019).
9. Kong, S. *et al.* Acid-stable manganese oxides for proton exchange membrane water electrolysis. *Nat. Catal.* **7**, 252–261 (2024).
10. Marshall, W. L. & Jones, E. V. Second dissociation constant of sulfuric acid from 25 to 350° evaluated from solubilities of calcium sulfate in sulfuric acid solutions. *J. Phys. Chem.* **70**, 4028–4040 (1966).
11. Tomikawa, K. & Kanno, H. Raman Study of Sulfuric Acid at Low Temperatures. *J. Phys. Chem. A* **102**, 6082–6088 (1998).
12. Lund Myhre, C. E., Christensen, D. H., Nicolaisen, F. M. & Nielsen, C. J. Spectroscopic Study of Aqueous H₂SO₄ at Different Temperatures and Compositions: Variations in Dissociation and Optical Properties. *J. Phys. Chem. A* **107**, 1979–1991 (2003).
13. Muñoz-Iglesias, V., Bonales, L. J. & Prieto-Ballesteros, O. pH and salinity evolution of Europa’s brines: Raman spectroscopy study of fractional precipitation at 1 and 300 bar. *Astrobiology* **13**, 693–702 (2013).
14. Zeleznik, F. J. Thermodynamic Properties of the Aqueous Sulfuric Acid System to 350 K. *J. Phys. Chem. Ref. Data* **20**, 1157 (1991).
15. Krumgalz, B. S. Temperature Dependence of Mineral Solubility in Water. Part 3. Alkaline and Alkaline Earth Sulfates. *J. Phys. Chem. Ref. Data* **47**, (2018).
16. Butler, B. M., Papadimitriou, S., Santoro, A. & Kennedy, H. Mirabilite solubility in equilibrium sea ice brines. *Geochim. Cosmochim. Acta* **182**, 40–54 (2016).

17. Christov, C. & Moller, N. Chemical equilibrium model of solution behavior and solubility in the H-Na-K-OH-Cl-HSO₄-SO₄-H₂O system to high concentration and temperature. *Geochim. Cosmochim. Acta* **68**, 1309–1331 (2004).
18. Vinal, G. W. & Craig, D. N. The viscosity of sulphuric acid solutions used for battery electrolytes. *Bur. Stand. J. Res.* **10**, 781 (1933).
19. Clegg, S. L. & Wexler, A. S. Densities and Apparent Molar Volumes of Atmospherically Important Electrolyte Solutions. 1. The Solutes H₂SO₄, HNO₃, HCl, Na₂SO₄, NaNO₃, NaCl, (NH₄)₂SO₄, NH₄NO₃, and NH₄Cl from 0 to 50 °C, Including Extrapolations to Very Low Temperature and to the Pure Liquid State, and NaHSO₄, NaOH, and NH₃ at 25 °C. *J. Phys. Chem. A* **115**, 3393–3460 (2011).
20. Desideri, P. G. The reduction mechanism of permanganic ion in mineral acid media. *J. Electroanal. Chem.* **6**, 344–356 (1963).
21. Han, J., Mariani, A., Passerini, S. & Varzi, A. A perspective on the role of anions in highly concentrated aqueous electrolytes. *Energy Environ. Sci.* **16**, 1480–1501 (2023).
22. Hutter, J. *et al.* The nature of the hydrated excess proton in water. *Nature* **397**, 601–604 (1999).
23. Lee, S. H. & Rasaiah, J. C. Proton transfer and the mobilities of the H⁺ and OH⁻ ions from studies of a dissociating model for water. *J. Chem. Phys.* **135**, 124505 (2011).
24. Mizuhata, M. Electrical Conductivity Measurement of Electrolyte Solution. *Electrochemistry* **90**, 102011–102011 (2022).
25. Owen, B. B., Miller, R. C., Milner, C. E. & Cogan, H. L. THE DIELECTRIC CONSTANT OF WATER AS A FUNCTION OF TEMPERATURE AND PRESSURE^{1,2}. *J. Phys. Chem.* **65**, 2065–2070 (1961).
26. Kaskiala, T. Determination of oxygen solubility in aqueous sulphuric acid media. *Miner. Eng.* **15**, 853–857 (2002).
27. Brown, T. E. *et al.* Properties of Solutions. in *Chemistry: The Central Science (14th ed.)* 545–546 (Pearson, 2018).
28. Johnson, T. R. *et al.* A Low-Cost and Simple Demonstration of Freezing Point Depression and Colligative Properties with Common Salts and Ice Cream. *J. Chem. Educ.* **99**, 3590–3594 (2022).
29. Atkins, P. & de Paula, J. Physical Chemistry for the Life Sciences. in *Physical Chemistry for the Life Science* (ed. W. H. Freeman and Company) 134–126 (Oxford University Press, New York, 2006).
30. Duan, Y. *et al.* Revealing the Impact of Electrolyte Composition for Co-Based Water Oxidation Catalysts by the Study of Reaction Kinetics Parameters. *ACS Catal.* **10**, 4160–4170 (2020).
31. McCrory, C. C. L. *et al.* Benchmarking Hydrogen Evolving Reaction and Oxygen Evolving Reaction Electrocatalysts for Solar Water Splitting Devices. *J. Am. Chem. Soc.* **137**, 4347–4357 (2015).

32. Bard, A. J. & Faulkner, L. R. Chapter 13. in *Electrochemical Methods: Fundamentals and Applications (2nd Edition)* (John Wiley & Sons, 2000).
33. Tombácz, E. *et al.* Polyelectrolyte coating on superparamagnetic iron oxide nanoparticles as interface between magnetic core and biorelevant media. *Interface Focus* **6**, (2016).
34. Wachs, I. E., Chen, Y., Jehng, J. M., Briand, L. E. & Tanaka, T. Molecular structure and reactivity of the Group V metal oxides. *Catal. Today* **78**, 13–24 (2003).
35. Ross-Medgaarden, E. I. *et al.* New insights into the nature of the acidic catalytic active sites present in ZrO₂-supported tungsten oxide catalysts. *J. Catal.* **256**, 108–125 (2008).
36. Takashima, T., Hashimoto, K. & Nakamura, R. Mechanisms of pH-dependent activity for water oxidation to molecular oxygen by MnO₂ electrocatalysts. *J. Am. Chem. Soc.* **134**, 1519–1527 (2012).
37. Watzele, S. A., Katzenmeier, L., Sabawa, J. P., Garlyyev, B. & Bandarenka, A. S. Temperature dependences of the double layer capacitance of some solid/liquid and solid/solid electrified interfaces. An experimental study. *Electrochim. Acta* **391**, 138969 (2021).
38. Nicotera, I., Coppola, L., Rossi, C. O., Youssry, M. & Ranieri, G. A. NMR Investigation of the Dynamics of Confined Water in Nafion-Based Electrolyte Membranes at Subfreezing Temperatures. *J. Phys. Chem. B* **113**, 13935–13941 (2009).
39. Kong, S., Fushimi, K., Li, A. & Nakamura, R. Effects of dissolved 3d-block metal ions on PEM water electrolysis performance. *Chem. Commun.* **60**, 14621–14624 (2024).
40. Lee, K. G. *et al.* Importance of entropic contribution to electrochemical water oxidation catalysis. *ACS Energy Lett.* **4**, 1918–1929 (2019).
41. Shi, W. *et al.* Ultrastable supported oxygen evolution electrocatalyst formed by ripening-induced embedding. *Science* **387**, 791–796 (2025).