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Boosting alkaline water electrolysis by asymmetric temperature modulation

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ABSTRACT: Hydrogen production by water electrolysis is a sustainable and promising pathway to store surplus electricity from intermittent renewable energy. In conventional electrolyzers, hydrogen evolution and oxygen evolution reactions at the two electrodes run at the same temperature. In this work, we implement asymmetric temperature modulation to enhance the water electrolysis rate in an alkaline solution. We revisit the thermodynamics of water electrolysis and determine by both simulations and experiments that the Gibbs free energy change required for alkaline water electrolysis under asymmetric temperature is lower than that under uniform average temperature. With the temperature difference of 40 K (possible for low-grade waste heat), the required voltage of asymmetric configuration decreases by 100 mV at the current density of 10 mA cm⁻² compared to the system operated at the same average temperature. Moreover, the thermal efficiency reaches a maximum value of 7% under optimized operating current density. The asymmetric-temperature water electrolysis opens a promising way for utilization of low-grade heat.

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Hydrogen has been regarded as a promising alternative to traditional fossil resources,^{1, 2} which can be produced by environmental-friendly electrochemical water electrolysis.³ The water electrolysis approach is capable to store the surplus power generated by intermittent photovoltaics, wind, ocean and other renewable energy sources, in the form of hydrogen.⁴⁻⁸ The current technology of hydrogen generation is via reforming fossil fuels which generates carbon dioxide emissions.^{9, 10} Therefore, water electrolysis could be a key and sustainable technology for future large-scale hydrogen production.¹¹ Generally, water electrolysis encompasses two half reactions on the two electrodes, viz., hydrogen and oxygen evolution reactions (HER and OER). Under a standard condition, the thermodynamic reaction energy of water electrolysis is 1.23 eV.¹² Considering kinetic and ohmic overpotentials, water electrolysis is a strong uphill reaction. To improve the performance of water electrolysis, immense efforts have been devoted to electrocatalyst engineering¹³⁻¹⁷ and electrolyzer design.¹⁸⁻²⁴ Recently, it was reported that decoupling the HER and OER process in alkaline water electrolysis may produce hydrogen with high efficiency.²⁵⁻²⁷ This strategy requires several processing steps and thus increases the complexity of operation. Another approach to promote water electrolysis is to increase the electrolysis operation temperature, which can effectively lower the thermodynamic reaction voltage,²⁸ enhance HER/OER reaction kinetics and decrease the overpotentials.^{29, 30} These electrolyzers typically operate at low-grade heat region, ranging from 333 to 363 K.^{31, 32} However, there has been no discussion on how thermodynamics and temperature affect the performance and energy efficiency of water electrolysis.

In this work, we propose an asymmetric temperature modulation strategy for water electrolysis in alkaline condition. We show that the Gibbs free energy change of water electrolysis under asymmetric temperature is obviously lower than that of uniform average temperature. This approach is validated by kinetics simulation and experiments based on commercial catalysts. When the temperature difference is 40 K, the required voltage for water electrolysis can be decreased by 100 mV at the current density of 10 mA cm⁻² compared to that of a uniform-temperature system operated at the same average temperature. In addition, the thermal efficiency is comparable to or higher than existing advanced thermoelectric devices, demonstrating the asymmetric temperature system has great promise in harvesting low-grade waste heat and efficient water electrolysis.

Under alkaline conditions, the HER/OER reactions occur as

The temperature of OER and HER electrode is set as T_{O} and T_{H} , respectively, as illustrated in Fig. 1a. We can calculate the Gibbs free energy change ΔG_{g} (unit kJ mol^{-1}) of alkaline water electrolysis (details are shown in Supplementary Note 1) at certain temperature gradient condition (T_{O} , T_{H}) as

$$\Delta G_{\text{g}} = 285.80 - (0.19T_{\text{O}} - 0.03T_{\text{H}}) \quad (3)$$

Eq (3) indicates that thermodynamic effects of temperature on OER and HER reactions are different. This is due to the different entropy change of OER ($0.19 \text{ kJ mol}^{-1} \text{ K}^{-1}$) and HER ($-0.03 \text{ kJ mol}^{-1} \text{ K}^{-1}$) processes in the alkaline solution. The Gibbs free energy change caused by increasing the temperature of the OER electrode is much greater than that of the HER electrode. For a vivid illustration, here we also calculated the Gibbs free energy changes of two systems with uniform temperature for comparison. One is under an average temperature, $T_{\text{a}} = (T_{\text{O}} + T_{\text{H}})/2$

$$\Delta G_{\text{a}} = 285.80 - 0.16T_{\text{a}} \quad (4)$$

The other one is under a maximum temperature, $T_{\text{m}} = (T_{\text{O}}, T_{\text{H}})_{\text{max}}$

$$\Delta G_{\text{m}} = 285.80 - 0.16T_{\text{m}} \quad (5)$$

The Gibbs free energy change in the three cases are mapped in Fig. 1b. It is shown that ΔG_{g} is always the smallest when T_{O} is larger than T_{H} . A greater temperature difference corresponds to larger difference in Gibbs free energy change. For example, when T_{O} and T_{H} is 333 and 293 K, respectively, ΔG_{g} is $231.32 \text{ kJ mol}^{-1}$. As a comparison, ΔG_{a} and ΔG_{m} is 235.72 and $232.52 \text{ kJ mol}^{-1}$, respectively. The corresponding thermodynamic voltages for water electrolysis in the three cases are 1.199, 1.222 and 1.205 V. From a purely thermodynamic point of view, about 2% energy (23 mV promoted) can be saved when the electrolyzer is working under the temperature of (333 K, 293 K) compared to (313 K, 313 K). When compared to the case of (333 K, 333 K), the asymmetric operation will save 0.5% of the electricity, showing the thermodynamics advantage of water electrolysis under a temperature gradient. We emphasize that this superiority is an intrinsic property of alkaline water electrolysis, which is only associated with the temperatures of electrodes and has no dependence on the electrolyzer or electrode catalyst states.

In addition to the thermodynamic potential, overpotentials of HER/OER and electrolyte resistance need be considered in water electrolysis. Subsequently, the current-voltage characteristics of alkaline water electrolysis

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are simulated (Fig. 1c). The electrolyzer working under the temperature of (333 K, 293 K) shows better performance than that of (313 K, 313 K). After iR-correction, the electrolyzer performance under the temperature of (333 K, 293 K) is almost same as that of (333 K, 333 K) (Fig. 1d). Such results indicate that the superiority of asymmetric temperature operation in alkaline water electrolysis will be more significant in membrane electrolysis system, since the resistance of the membrane is quite small.³³

After subtracting the thermodynamic equilibrium voltage and ohmic overpotential, we can obtain the temperature effects on the HER/OER reactions (Fig. S1). The compositive overpotentials of HER/OER reactions working under the temperature of (333 K, 293 K) shows slightly smaller than that of (313 K, 313 K). It should be noted that, the actual situation of HER/OER overpotentials may have some fluctuations due to the states of electrode catalysts. Considering both the kinetic overpotentials and superior thermodynamics, it can be inferred that alkaline water electrolysis demonstrates a better performance at the temperature of (333 K, 293 K) than that at (313 K, 313 K).

The advance of asymmetric temperature strategy is an intrinsic feature of alkaline water electrolysis, and it is not suitable for acidic water electrolysis (Supplementary Note 2, Fig. S2 and S3). It's worth noting that, if T_O is lower than T_H , the alkaline water electrolysis is suppressed (Fig. S4). This is partly due to the increased Gibbs free energy change when T_H is larger than T_O . This is also understandable since the OER overpotential dominates the water electrolysis because of the more sluggish four-electron process than HER.

To verify the feasibility of the asymmetric temperature strategy, an experiment is carried out using the well-established Pt catalyst on carbon cloth in a two-electrode system for alkaline water electrolysis. Fig. 2a shows the photograph of the electrolyzer under asymmetric temperature modulation. The linear sweep voltammograms at a scan rate of 10 mV s^{-1} under different temperature conditions are demonstrated in Fig. 2b. When $\Delta T=40 \text{ K}$, a voltage of 1.83 V is required for the (333 K, 293 K) case to reach a current density of 10 mA cm^{-2} (U_{10}), which is 100 mV lower than that of (313 K, 313 K) (1.93 V), and even comparable to that of (333 K, 333 K) (1.79 V). This means that the use of temperature difference can reduce electricity consumption by 5.2% compared to uniform average condition. The cases with $\Delta T=30 \text{ K}$ and 20 K (T_H is fixed at 293 K) show similar results with $\Delta T=40 \text{ K}$ (Fig. S6). Combined with stability experiments under a fixed current density of 10 mA cm^{-2} (Fig. 2c), these results confirm the determinate and solid advantage of asymmetric

temperature modulation for alkaline water electrolysis.

The Tafel slope for the (333 K, 293 K) configuration is 297 mV dec^{-1} , which is marginally higher than that of (313 K, 313 K) (291 mV dec^{-1}) (Fig. 2d). There is a slight difference on gas evolution kinetics between the experimental results and the simulations, which can be partly attributed to the deviation in parameters as well as details ignored in the simulation model, such as bubble dynamics and catalyst states. Since the Tafel slopes appear similar in the two cases with gradient and average temperatures, it can be inferred that the influences of convection and non-equilibrium Soret effect (with small Seebeck coefficient of $\sim 0.2 \text{ mV K}^{-1}$ in aqueous electrolytes),³⁴ induced by temperature gradient to reaction kinetics in experiments is negligible. The Tafel slope versus U_{10} value for all the studied cases is plotted in Fig. 2e. Although the gas evolution kinetics under the temperature of (333 K, 293 K) is slightly slower than that of (313 K, 313 K), the asymmetric case demonstrates a much lower operating voltage at given current densities.

To further confirm the kinetics differences on various test conditions, electrochemical impedance was measured (Fig. 2f). The equivalent circuit proposed for data fitting is shown in inset. The Ohmic resistance is represented by the high frequency interception (R_0), which is dependent on temperatures, electrolyte, and electrodes. The high, medium, and low frequency arc is attributed to the HER process (R_1), OER process (R_2) and mass transport (R_3), respectively.³⁵ At high temperatures, the mass transport process has negligible effect and do not appear in the impedance spectra. The OER charge transfer resistance under the temperature of (333 K, 293 K) and (313 K, 313 K) are 13.4 and $12.8 \text{ } \Omega \text{ cm}^2$, respectively. This result indicates slightly slower kinetics of catalysts under the temperature of (333 K, 293 K) compared to the case of (313 K, 313 K), which is consistent with results of the Tafel slope. Based on the above results and analysis, we may conclude that the improved water electrolysis under asymmetric temperature operation is mainly rooted in the thermodynamic advantage rather than kinetics.

The ratio of higher heating value (HHV) voltage to voltage applied to the electrolyzer is a descriptor to evaluate the energy efficiency (η_{HHV}) of water splitting.³¹ Here we summarize the energy efficiencies under various operating conditions (Fig. 3a). The η_{HHV} at the case of (333 K, 293 K) is comparable to that of (333 K, 333 K), and obviously higher than that of (313 K, 313 K). At a current density of 10 mA cm^{-2} , the η_{HHV} of electrolyzer under (313 K, 313 K) is 76%, and it increases to 81% when the electrolyzer is operated under (333

K, 293 K), demonstrating the benefits of asymmetric temperature water electrolysis.

Thermal efficiency of the system is also calculated from the electricity saving and thermal energy input (Supplementary Note 3). To illustrate the benefit of the asymmetric temperature operation, here the thermal energy input is taken as the heat flow due to the temperature gradient across the electrodes. The electricity saving is taken as the decreased electrical power as compared with symmetric systems with the same hydrogen production or current density. Fig. 3b shows the thermal efficiency as a function of current density. With the ΔT of 40 K, the thermal efficiency is 0.7% at the current density of 10 mA cm^{-2} . With a higher current density of 20 mA cm^{-2} , the thermal efficiency achieves 1.7%, which is comparable to advanced thermoelectric devices, such as electrochemical heat engine,³⁶ thermogalvanic cells^{37, 38} and thermally regenerative electrochemical cycle batteries,^{39, 40} as illustrated in Fig. S8. Moreover, as the current density further increases, the efficiency can indeed increase to a maximum value of 7% and then decrease, because a large amount of joule heating generated by high current density will offset the saved power induced by asymmetric temperatures. Considering such a high thermal efficiency, our asymmetric temperature modulation strategy not only presents its advantages in water electrolysis, but also provide a tactic for low-grade heat recovery.

In summary, an asymmetric temperature operation is proven useful to boost the alkaline water electrolysis based on thermodynamic simulation and experiments. The advantage of the asymmetric temperature is manifested when it is compared with a uniform temperature under the same average temperature. While further enhancement in performance can be achieved by selecting better electrodes and catalysts, the demonstrated approach in this study originates from intrinsic thermodynamics and independent of the catalysts, thus possess potential to all alkaline OER catalysts. Additionally, a competitive high thermal efficiency is obtained at optimized current density. Considering that low-grade heat is ubiquitous in industrial processes, our results provide an opportunity for industry alkaline water electrolysis with improved energy utilization efficiency.

See the supplementary material for the calculation notes and characterization methods.

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The authors declare no conflict of interest.

DATA AVAILABILITY

The data that support the findings of this study are available within this article and its supplementary material.

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FIG. 1. The principle of low-grade heat promoted alkaline water electrolysis. (a) Schematic of alkaline water electrolysis under a temperature gradient (top) and uniform average temperature (bottom). (b) Gibbs free energy change required for alkaline water electrolysis under a temperature gradient and uniform temperatures. (c) Simulated polarization curves and (d) iR-free polarization curves at different temperature conditions.

FIG. 2. The performance of alkaline water electrolysis using Pt catalyst under asymmetric temperature modulation. (a) Photograph of the electrolyzer. The effective cross-sectional area of the electrode is 1 cm^2 , and the distance between the two electrodes is 2 cm. (b) Polarization curves at 10 mV s^{-1} . (c) Stability measurements (voltage versus time) at a current density of 10 mA cm^{-2} . (d) Tafel plots. (e) Comparison of U_{10} values and Tafel slopes. (f) Nyquist plots at 10 mA cm^{-2} . Inset shows an equivalent circuit.

FIG. 3. Efficiency of thermal assisted alkaline water electrolysis. (a) Voltage efficiencies of the alkaline water electrolyzer. (b) Thermal efficiency of the heat flux under the temperature of (333 K, 293 K).

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