Significance of Slight Ambient Temperature Variation on the Electrocatalyst Performance toward Oxygen Evolution Reaction

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Abstract

Hundreds of oxygen evolution reaction (OER) electrocatalysts have been developed over the past few decades, and their performances are evaluated and compared at ambient temperature. However, the effect of ambient temperature variation on OER electrocatalyst performance has received less attention, which may play a remarkable role in the electrocatalytic activity. In this work, we systematically investigated the influence of ambient temperature variation on electrocatalyst performance toward OER. The results show that the slight ambient temperature variation has a significant effect on OER catalyst performance based on the changes of overpotential (10 mA cm^{-2}) and Tafel slope. Both remarkable chances are observed on transition metal (Ni) and noble metal (IrO_2) electrocatalysts, and the overpotentials decrease around 81 mV with a temperature increase by 20 °C (from 10 to 30 °C) for both Ni and IrO_2 electrocatalysts with the Tafel slope drops of 36.9 and 29.5 mV dec^{-1}, respectively. A similar trend is also found in the electrochemically active surface (ECSA) normalized performance and the charge transfer resistance. This study demonstrates that reporting the actual operating temperature for OER is not only recommended but also necessary to evaluate and compare electrocatalyst activities from different materials systems properly, and neglecting the ambient temperature variation effect can highly mislead conclusions.

Keywords: Ambient temperature effect; Oxygen evolution reaction; Electrochemical water splitting; Electrocatalyst performance

1. Introduction

The growing global energy crisis, along with environmental pollution caused by fossil fuels, has heightened the urgent search for renewable energy sources. Green hydrogen (H_2), produced from renewable energy sources such as wind and solar, is considered a viable alternative to fossil fuels due to its high energy density, reliable energy storage, and emission of only water upon combustion [1-4]. Electricity-driven water splitting is a promising method for H_2 production and has garnered significant interest [5]. In electrochemical water splitting, the oxygen evolution reaction (OER) – a four-electron transfer reaction at the anode – is more kinetically sluggish than the hydrogen evolution reaction (HER) – a two-electron transfer reaction at the cathode. As a result, the OER is the critical process that determines the overall efficiency of water splitting [6]. Currently, iridium (Ir) and ruthenium (Ru)-based catalysts are state-of-the-art electrocatalysts for OER, particularly in acidic media. However, the large-scale application of noble-metal-based OER catalysts is severely hindered by their limited crustal reserves and high costs [7, 8]. This situation has substantially stimulated research into non-noble-metal-based OER electrocatalysts. In practice, the durability of non-noble-metal-based catalysts in acidic media presents a significant challenge. Consequently, extensive efforts have been dedicated to developing non-noble and completely Platinum Group Metal (PGM)-free catalysts for OER in alkaline media [9-11].

Over the past few decades, hundreds of PGM-free OER electrocatalysts have been developed, displaying remarkable electrocatalytic activity and, in some cases, even outperforming noble-metal-based electrocatalysts [12-15]. A crucial reported parameter for comparing OER electrocatalyst performance is the overpotential value at a geometric current density of 10 mA cm^{-2}, while another one is the Tafel slope obtained from linear sweep voltammetry (LSV). Besides the overpotential and Tafel slope, the electrochemically active surface (ECSA) obtained from

electrical double-layer capacitance (C_{dl}) and electrochemical impedance spectroscopy (EIS) are also very important parameters for evaluating the performance of catalysts. According to a literature review [16-19], most researchers have reported the performance of OER electrocatalysts at ambient temperature, often without specifying the exact and measured values [20-24]. As a result, researchers tend to compare OER catalyst performance among materials from different families based on ambient temperature, and the effect of ambient temperature variation on OER catalyst performance has received far less attention. According to Arrhenius' law, as shown in equation (1):

$$k = Ae^{(-\frac{Ea}{RT})} \quad (1)$$

It is well known that the chemical reaction rate (k) is related to temperature (T) and activation energy (Ea). A reaction rate usually accelerates with increasing temperature, given the same activation energy. Simultaneously, the OER requires energy input to drive its process, as it is a thermodynamically "up-hill" reaction [25]. Therefore, a lower overpotential at the same current density for OER can be theoretically achieved by raising the temperature.

Doha et al. investigated the effect of catalyst preparation temperature (T_p) and performance measurement temperature (T_m) on the OER performance of Ni-based catalysts and observed that the catalyst performance was enhanced with the increase of T_m from 25 to 50 °C for the same catalyst at the same T_p [26]. Additionally, Zhang et al. studied the effect of abnormal temperature on the OER performance of Co-based catalysts and found that the performance reached a peak at 65 °C [25]. The authors proposed that the rate-determining step switched from OH- adsorption dominant to a mixed mode that both the adsorption and the cleavage of the OH groups can be rate-

determining steps, leading to the fastest kinetics at the optimal temperature range (around 55-65 °C).

It is well known that Ambient temperature varies with latitudes, seasons, and even daily fluctuations within the same lab. Consequently, ambient temperature variation may play a significant role in evaluating and comparing OER catalyst performance, and neglecting the effect of the temperature variation could potentially lead to misleading conclusions. Consequently, we thoroughly investigated the influence of ambient temperature variation (from 10 to 30 °C) on the electrocatalyst performance toward OER in this work, while three different electrodes were evaluated in alkaline media. The results indicate that ambient temperature variation significantly affects OER catalyst performance.

2. Materials and methods

All experiments were performed in a one-compartment glass cell, as shown in Fig. S1a and b, and the electrolyte temperature was controlled by a Julabo 200F refrigerated/heating circulator with temperature accuracy of ±0.03 °C. The real temperature of the electrolyte was monitored by a thermocouple, and three ambient temperatures (10, 20, and 30 °C) were evaluated. The Ni foam (commercially available), 316 stainless steel (SS) mesh (FuelCellStore with SKU number 590663), and IrO_2-coated Ti mesh (Dimensionally Stable Anode, DSA; De Nora) electrodes connected with Ti wires with a geometric area of 1 cm^2 (1.0×1.0 cm) were investigated as working electrodes in this work, respectively, as shown in Fig. S1c, as IrO_2 is the state-of-the-art electrocatalyst toward oxygen evolution reaction (OER) and we found the 316 SS mesh electrode exhibited promising activity and outperformed the Ni foam for OER [18]. A Pt gauze (52 mesh woven from 0.1 mm diameter wire, 99.9% metals basis, Alfa Aesar) with a geometric area of 6.25 cm^2 (2.5×2.5 cm) was employed as the counter electrode (CE), and a hydrogen reference electrode (Gaskatel with

SKU number 81010) was used. In all the experiments, 150 ml 1 M KOH (pH of 13.5, prepared with KOH pellets, 85+%, ACS reagent, Sigma-Aldrich) electrolyte was used.

All electrochemical measurements were carried out via a potentiostat (Pine, WaveDriver 200). The electrolyte was bubbled with O_2 for 20 minutes to maintain the equilibrium potential at the standard value before starting an electrochemical experiment. Linear sweep voltammetry (LSV) measurements were performed at a scan rate of 10 mV s^{-1} and repeated at least 5 times to ensure repeatability. The Tafel plot was obtained based on the LSV data with a current density range of around 0.5-20 mA cm^{-2}. Durability tests were performed via chronopotentiometry (CP) at a current density of 10 mA cm^{-2} for 300 s, and the corresponding potential was recorded. Internal resistance (iR) correction was applied to all potentials with the resistance obtained in EIS, and the EIS measurement was performed from 100K Hz to 1 Hz with the potential corresponding to the current density of 10 mA cm^{-2}. The C_{dl} of electrodes was measured by performing cyclic voltammetry (CV) in the non-Faradic region under different scan rates ranging from 10 to 200 mV s^{-1}. The double-layer charging current (non-faradaic current) was plotted vs. the CV scan rate, and the slope of the linear regression indicates the C_{dl}. The ECSA of SS mesh electrodes was estimated based on the C_{dl}. For estimating the ECSA of the Ni foam electrodes, a specific capacitance of 0.04 mF cm^{-2} in 1 M KOH was employed according to the literature report [27]. All the potentials reported in this work are in the reversible hydrogen electrode (RHE, throughout the text) scale.

3. Results and discussion

Fig.1 displays LSV at different experimental temperatures and electrodes in 1 M KOH electrolytes. All LSV curves were repeated five times, as shown in Figs. S2, 3, and 4, to obtain reliable data, and the LSV curves shown in Fig. 1 are the fourth scan curves. According to Figs. 1a, b, and c, all LSV curves shift negatively with increasing temperature, indicating that the electrocatalytic activity of the electrodes is enhanced with temperature. The overpotentials at a current density of 10 mA cm^{-2} are recorded and summarized, as shown in Fig. 1d, and all overpotentials decrease significantly with a slight increase in experimental temperature.

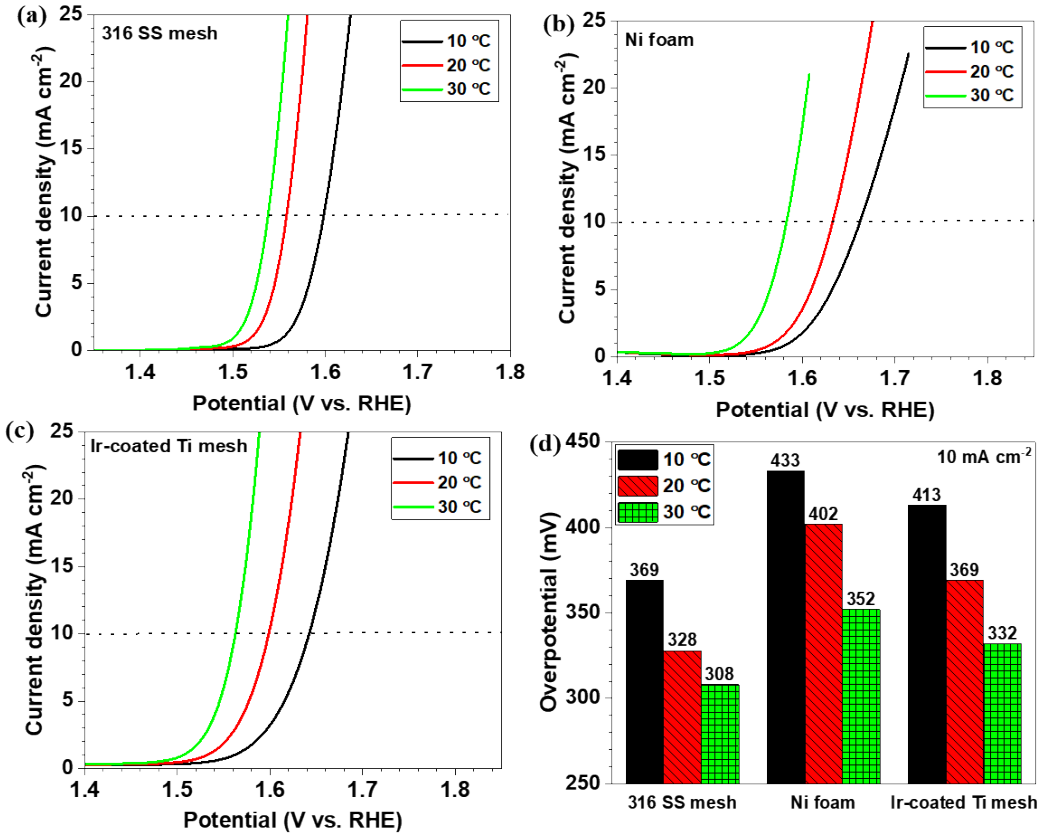

Fig. 1 LSV curves at different ambient temperatures in 1 M KOH electrolytes. (a) 316 SS mesh electrode, (b) Ni foam electrode, (c) Ir-coated Ti mesh electrode, and (d) overpotentials obtained from LSV at the current density of 10 mA cm^{-2}.

Figs. S5 a and b show overpotential (at 10 mA cm^{-2}) change treand with temperature and the total overpotential changes under experimental temperature variation of 20 °C, respectively. According to Fig. S5a, the average overpotentials decrease by 4.1 mV for both Ni foam and IrO_2-coated Ti mesh electrodes and by 3.1 mV for 316 SS mesh electrodes when the temperature rises by one degree. The overall overpotential changes under the experimental temperature variation of 20 °C are 61, 81, and 81 mV for the 316 SS mesh, Ni foam, and IrO_2-coated Ti mesh electrodes, respectively, as shown in Fig. S5b. The results suggest that the slight ambient temperature variation has a remarkable impact on OER catalyst performance, which cannot be ignored.

Empirically, the Tafel equation has been expressed as the following equation (2):

$$\eta = a + b\,log(j) \qquad (2)$$

Where η is the overpotential, j is the current density, and b denotes the Tafel slope. Meanwhile, according to the Butler-Volmer equation, simple electrochemical redox reactions can be represented as the following equation (3):

$$j = j_0[e^{-\alpha f \eta} - e^{(1-\alpha) f \eta}] \qquad (3)$$

Where j_0 defines the exchange current density, α is the transfer coefficient, and f denotes the F/RT (R: the universal gas constant, T: the absolute temperature, F: the Faraday's constant). This equation describes the total currents from oxidation and reduction reactions (opposite pathway). The following equation (4) can be derived if we only consider forward or backward reaction rates, which are sufficiently larger than the corresponding opposite reaction rates [28].

$$\eta = \frac{RT}{\alpha F}\ln(j_0) - \frac{RT}{\alpha F}\ln(j) \qquad (4)$$

For analyzing electrochemical performances, the Tafel analysis (from equation (2)) is usually conjugated with the derived Butler-Volmer equation (equation (4) in many studies, and the Tafel slope can be expressed as the following equation (5) integrating experience and theory.

$$b = -2.3\frac{RT}{\alpha F} \qquad (5)$$

According to equation (5), it is evident that the Tafel slope is highly related to temperature; thus, it is crucial and necessary to evaluate the Tafel slope change with ambient temperature variation. Fig. 2 shows the Tafel slopes at different experimental temperatures and electrodes in 1 M KOH electrolytes, and all Tafel slopes decrease with increasing temperature. Fig. 2d displays a summary of the Tafel slope change. The results indicate that the slight temperature increase is kinetically significantly favorable for OER for all electrodes, particularly for Ni foam and IrO_2-coated Ti mesh electrodes. Figs. S6a and b display the Tafel slope change trend with temperature and the total Tafel slope change with the experimental temperature variation of 20 °C. According to Fig. S6a, the average Tafel slopes decrease by 0.5, 1.8, and 1.5 mV dec^{-1} for the 316 SS mesh, Ni foam, and IrO_2-coated Ti mesh electrodes, respectively, when the temperature rises by one degree. The overall Tafel slope changes with an ambient temperature variation of 20 °C are 10.3, 36.9, and 29.5 mV dec^{-1} for the 316 SS mesh, Ni foam, and IrO_2-coated Ti mesh electrodes, respectively, based on Fig. S6b. Combining Figs. 1 and 2, it can be concluded that the influence of ambient temperature variation on electrodes with poorer performance (higher overpotentials and Tafel slopes) is more severe. The possible reason is that the slight temperature increase changes the rate-determining steps (RDS) toward OER for poor-performed electrodes, whose Tafel slopes decrease significantly from high to low values. In contrast, the moderate change in Tafel slopes for the high-performed electrode indicates the RDS for OER remains the same.

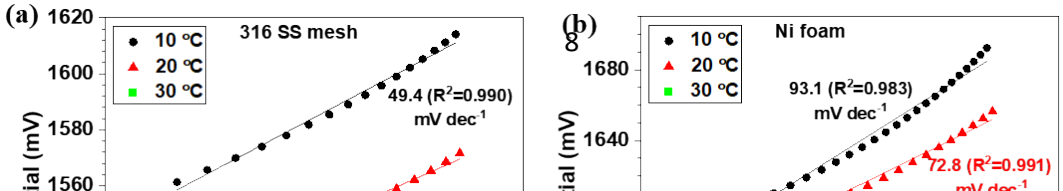

Fig. 2 Tafel slopes at different ambient temperatures in 1 M KOH electrolytes. (a) 316 SS mesh electrode, (b) Ni foam electrode, (c) Ir-coated Ti mesh electrode, and (d) a summary of Tafel slopes.

Figs. S7-9 show the CV curves of all three electrodes at different temperatures and the obtained C_{dl}, respectively. It can be seen that no noticeable change of C_{dl} is observed from 316 SS mesh electrodes from 10 to 30 °C based on Fig. S7(d), indicating the ECSA of 316 SS mesh electrodes keep constant with slight variations in ambient temperature. Additionally, a slight increase of C_{dl} is observed from Ni foam (around 9% increase) and Ir-coated Ti mesh (about 8% increase) electrodes from 10 to 30 °C based on Fig. S8(d) and Fig. S9(d), respectively. We chose the Ni foam electrode as an example to normalize its performance based on ECSA, as the highest increase of C_{dl} is observed from the Ni foam electrode. Fig. S10 displays the LSV curves and

overpotentials of Ni foam electrodes after normalization based on ECSA, it can be seen clearly that a significant improvement of overpotential at the same current density is noticed, which is consistent with the results based on geometric areas. All of those results indicate that the intrinsic activities of catalysts toward OER are enhanced with a slight increase in ambient temperature. Moreover, the EIS was performed to investigate the effect of slight ambient temperature variation on the charge transfer resistance of catalysts toward OER, as shown in Fig. 3. A higher temperature exhibits a smaller charge transfer resistance for all three catalysts, demonstrating that better electronic conductivity and faster reaction kinetics could be achieved for the same catalyst with a slight increase in ambient temperature.

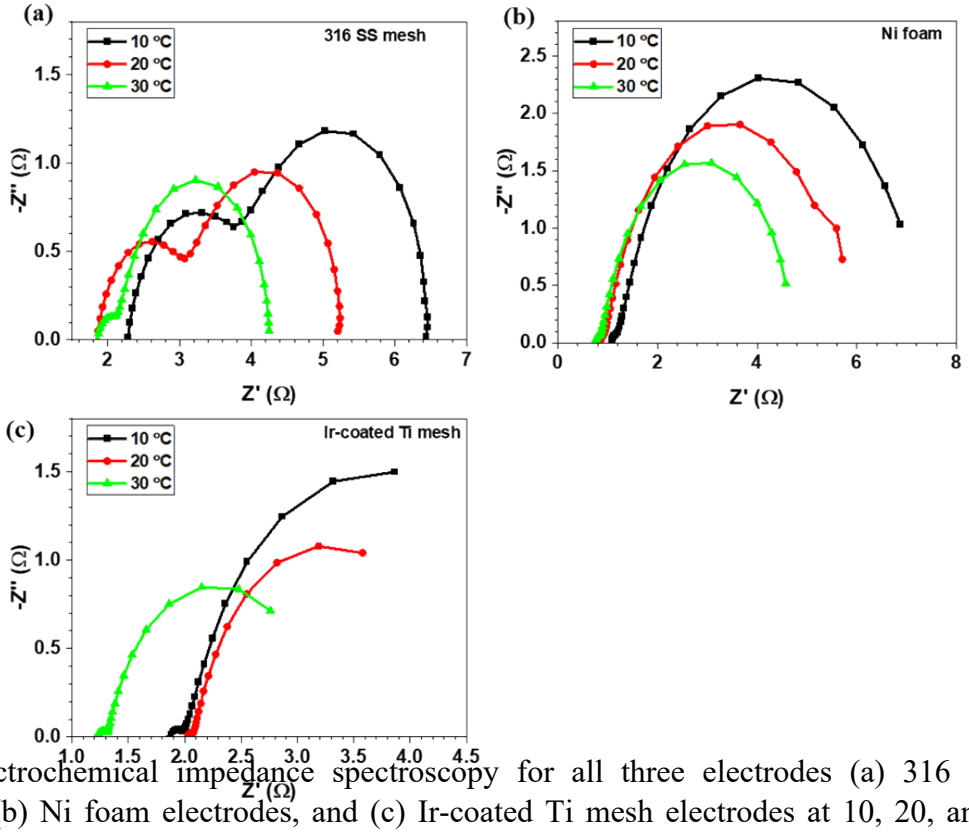

Fig. 3. Electrochemical impedance spectroscopy for all three electrodes (a) 316 SS mesh electrodes, (b) Ni foam electrodes, and (c) Ir-coated Ti mesh electrodes at 10, 20, and 30 °C, respectively.

Fig. S11 displays the chronopotentiometry (CP) at a current density of 10 mA cm^{-2} with different electrodes in 1 M KOH electrolytes. The overpotentials at 200 s are recorded and summarized, as shown in Fig. S7d. The overpotential changes obtained from the CP are consistent with those obtained from LSV, confirming the significant impact of ambient temperature variation on OER catalyst performance.

4. Conclusion

In summary, we systematically investigated the influence of ambient temperature variation on electrocatalyst performance toward OER in this work, which is a critical topic in electrochemical water splitting but has received less attention. The results indicate that the slight ambient temperature variation has a remarkable impact on OER catalyst performance based on overpotential changes at a current density of 10 mA cm^{-2} and Tafel slope changes. The overpotential and Tafel slope with the Ni foam electrode decrease from 433 mV and 93.1 mV dec^{-1} to 352 mV and 56.2 mV dec^{-1}, respectively, when the ambient temperature climbs from 10 to 30 °C. The same performance trend is observed after normalizing based on ECSA, and the charge transfer resistance decreases from EIS study with the slight increase of temperature.The overpotential changes are also confirmed by CP experiments. This finding suggests that reporting the actual operating temperature for OER is not only recommended but also necessary to properly evaluate and compare electrode performances from different materials systems, and neglecting the ambient temperature variation effect can highly mislead conclusions. Moreover, it is supposed that this finding can be extended to electrochemical hydrogen evolution reaction (HER), CO_2 reduction reaction (CO_2RR), and nitrogen reduction reaction (NRR).

Declaration of competing interest

The authors declare that they have no competing financial interests in this paper.

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