Oxygen evolution reaction performance misjudgment caused by the self-oxidation process

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ABSTRACT

Based on the interference effect of surface self-oxidation peak on the oxygen evolution reaction (OER) performance, appropriate experimental strategies and data processing methods are crucial to correctly identify and address the oxidation peak in nickel-based materials to ensure data accuracy. Considering these facts that frequent OER performance misjudgment would confuse the readers, we revealed this reason and proposed the use of multi-potential step method to avoid non-steady-state currents caused by capacitive charging effects or intermediate oxidation. Additionally, combining electrochemical impedance spectroscopy (EIS) analysis, we discussed high-frequency response characteristics to further reveal the surface self-oxidation process. These research findings are crucial for accurately evaluating the actual performance of some special materials in electrochemical catalysis.

KEYWORDS

oxygen evolution reaction, self-oxidation reaction, electrochemical impedance spectroscopy, multi-potential step method

With the increasing severity of environmental pollution and energy shortages, sustainable energy conversion systems are crucial for the future development of energy solutions. Among these, water electrolysis for hydrogen production has garnered widespread attention due to its low cost, high efficiency, and minimal pollution. The water electrolysis process involves the hydrogen evolution reaction (HER) and the oxygen evolution reaction (OER), with the latter having slower kinetics and often requiring a higher overpotential [1]. Nickel foam (NF), with its unique three-dimensional interconnected structure, offers advantages such as lightweight, high porosity, high mechanical strength, chemical stability, and excellent electrical and thermal conductivity [2]. Consequently, it is widely used as a conductive substrate for catalyst preparation. However, in electrochemical testing, nickel- and cobalt-based active materials or substrates often exhibit a prominent oxidation peak before the onset of the OER reaction [3, 4]. This oxidation peak actually arises from the self-oxidation of the metal surface under applied voltage, leading to electron transfer and changes in the chemical state, where Ni^{2+} is oxidized to Ni^{3+} or higher oxidation states [5]. This peak is a normal phenomenon during testing and needs to be carefully considered to avoid interference with overpotential identification. Correctly identifying and distinguishing between the metal oxidation reaction and the OER region is crucial for accurately assessing the electrochemical performance of the material and avoiding misinterpretation of data due to the oxidation peak.

Under standard conditions, the thermodynamic equilibrium potential of OER is 1.23 V, but in the actual reaction process, there are adverse kinetic factors that hinder the reaction, and an additional potential is needed, that is, the overpotential (generally between 150–400 mV). However, the oxidation peak of nickel-based materials is generally between 1.2–1.6 V, and also produces a high current density, resulting in that if the oxidation peak is not fully considered and the voltage interval is set too small, the increase in current caused by the oxidation peak may be mistaken for the performance of catalytic activity, thus affecting the accurate evaluation of the true OER performance of the catalyst. A work by Liu et al., in *ACS catalysis*, on a nickel-based catalyst co-modified with iron and phosphate [6], produced a current density of over 100 mA·cm⁻² during testing, but the range was chosen to be only 1.2–1.45 V, a narrow voltage range that makes the electrochemical performance seriously unconvincing. Similarly, Zhou et al.'s work on the nitrate-coordinated cobalt-nickel-based catalyst published in *Energy & Environmental Sciences* showed the same phenomenon in the OER test, where the current density reached 300 mA·cm⁻² [7], but the material voltage window was only 1.15–1.4 V. Therefore, it is very important to correctly select the test voltage window, avoid the confusion between oxidation current and OER current, and explore the real OER performance in the electrochemical performance test of nickel-based catalysts. Referring to the work of Liu et al., we synthesized a related catalyst

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based on nickel foam. The results are shown in Fig. 1(a). Due to the use of a nickel-based material as the substrate, the catalyst also generated a current density of more than 100mA·cm⁻² during the test. At this point, the narrow test window makes it difficult to determine whether it is caused by metal oxidation or true reactivity.

As shown in Fig. 1(c), when the testing voltage range is extended to 1.7 V, the oxidation current peaks at 138 mA at 1.41 V and then rapidly decreases, with a noticeable hump between 1.3–1.5 V. Beyond this, the true OER catalytic activity becomes apparent. To effectively distinguish and avoid the interference of the oxidation peak in overpotential identification, a multiple potential step method is suggested to be used to detect the true OER performance on the Ni-based electrode, avoiding non-steady-state currents caused by capacitive charging effects or intermediate oxidation. This method involves increasing the voltage by a fixed increment, holding it for a certain period (t_s) at each voltage, mainly observing the steady-state current at different potentials to obtain several potential-steady-state current points, approximating a linear sweep voltammetry (LSV) curve when the potential transitions are small enough (Fig. 1(b)). By this means, researchers can more accurately distinguish between non-steady-state currents and steady-state currents resulting from water oxidation, and simulate the LSV curve of real OER without oxidation reaction. This method provides direct information about the dynamics of surface reactions on the electrode, avoiding the misinterpretation of the oxidation peak as catalytic activity. Practically, this approach can offer significant technical support

for the accurate assessment of nickel-based catalysts' true performance in electrochemical catalysis. In our tests within a voltage range of 1.15–1.7 V, using 10 mV increments and holding each voltage for 60 s, we simulated the true OER reaction LSV curve. The results, shown in Fig. 1(c), indicate no nickel oxidation current in the 1.3–1.5 V range, with the OER reaction beginning at 1.5 V as the current increased. By using the multiple potential step method, we successfully simulated the true OER reaction curve without nickel oxidation, eliminating interference from the oxidation peak and accurately assessing the true OER performance.

In electrochemical analysis, electrochemical impedance spectroscopy (EIS) is a valuable experimental tool. Beyond measuring equivalent charge transfer resistance (R_{ct}), EIS can characterize the dynamic interfacial kinetics, charge transfer, and mass transport evolution of catalysts [8]. Frequencies above 1 Hz mainly correspond to high-frequency regions associated with electron transfer at the interface between the catalytic layer and the catalyst bulk, while frequencies below 1 Hz pertain to low-frequency regions associated with the transfer of active species like OER intermediates. Y. Liang et al. found through Bode plot analysis that the high-frequency response of nickel-based materials is mainly related to the material's oxidation process, which is valuable for understanding and identifying the oxidation peak and its implications for data interpretation [9]. The high-frequency reaction characteristics indicate rapid changes in the nickel oxidation state, helping researchers distinguish between the oxidation peak and other electrochemical processes, such as water
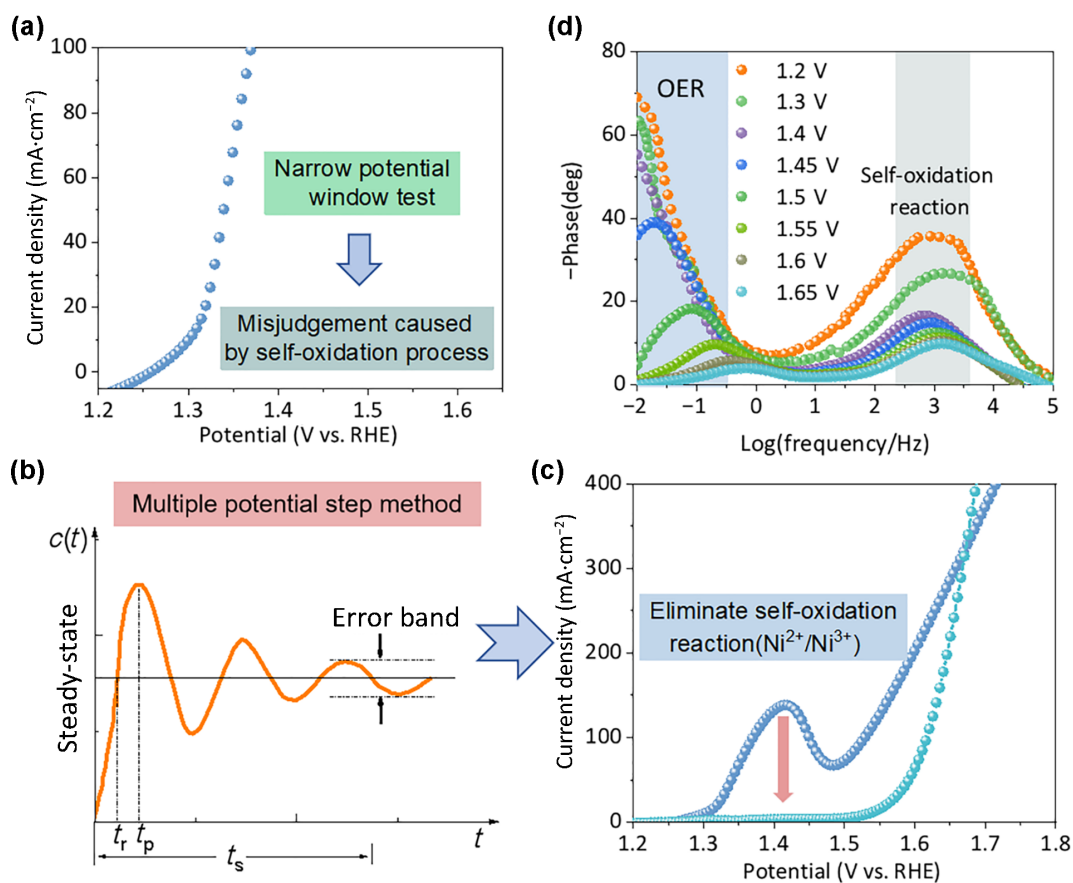

Figure 1 (a) LSV curve of OER reaction obtained under the condition of smaller set voltage interval. (b) The mechanism of multiple potential step method to avoiding non-steady-state currents caused by capacitive charging effects or intermediate oxidation. (c) The comparison OER performance between the LSV curve and result derived by fitting the multi-potential step current data. (d) Potential-dependent EIS Bode plots of reproduced material electrode when positive-going potentials varied from 1.2 to 1.65 V in 1 M KOH.

oxidation or urea oxidation. By performing electrochemical impedance tests at different potentials, we studied the charge transfer of the catalyst. The results in Fig. 1(d) show that after 1.2 V, the phase angle in the high-frequency region gradually decreases, representing electrocatalytic oxidation. In the 1.2–1.55 V range, the phase angle changes in the low-frequency region but no low-frequency interface reaction occurs, attributed to ion migration and adsorption at the catalyst-electrolyte interface during the discharge process, indicating that a pure nickel self-oxidation reaction (NSOR) occurs before 1.55 V. Simultaneously, the phase angle disappears in the low-frequency region after 1.55 V, indicating the start of low-frequency interface reactions due to the surface reconstruction of Ni^{2+} to Ni^{3+}, with OER reactions beginning on the Ni^{3+} active layer, synchronized with the OER test current. When the catalyst is active above 1.55 V, the OER occurs in the low-frequency region, while the high-frequency region associated with NSOR shows considerable stability, suggesting that the material's oxidation of H_2O may follow the electron transfer mechanism of the $Ni(OH)_2/NiOOH$ redox couple. In summary, EIS testing successfully demonstrated that the current peak observed before 1.55 V is due to the NSOR process, not the OER process.

In electrochemical testing, it is crucial to correctly identify and address the oxidation peak in nickel-based materials to ensure data accuracy. The oxidation peak often relates to the material's properties and its interaction with the electrolyte, necessitating careful consideration in experimental design and data interpretation. Researchers should use appropriate experimental strategies and data processing methods, such as different electrochemical techniques, to distinguish between oxidation peaks and actual catalytic activity signals. This approach ensures reliable and accurate test results. Continuous optimization of materials and electrochemical methods can further mitigate the impact of the oxidation peak on experimental outcomes, enhancing the performance of nickel-based materials in various applications. These comprehensive measures can more effectively utilize the potential of nickel-based materials in catalysis and energy conversion.

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Declaration of conflicting interests

The authors declare no conflicting interests regarding the content of this article.

Data availability

All data needed to support the conclusions in the paper are presented in the manuscript and/or the Supplementary Materials. Additional data related to this paper may be requested from the corresponding author upon request.

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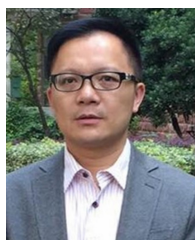
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