Composition Engineering of Amorphous Nickel Boride Nanoarchitectures Enabling Highly Efficient Electrosynthesis of Hydrogen Peroxide

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1. Introduction

Hydrogen peroxide (H$_2$O$_2$) is one of the most important chemicals in the world and has been extensively deployed as a disinfectant, blench, and combustion improver.[1–4] The current synthesis of H$_2$O$_2$ mainly focuses on the anthraquione process, which not only involves expensive catalysts and high gas pressures but also produces enormous energy consumption and organic wastes.[5–7] As an atomic economy, sustainable, and green method, the directional reduction of O$_2$ to H$_2$O$_2$ via electrocatalysis is a promising alternative to the conventional anthraquione process.[8–10] However, the oxygen reduction reaction (ORR) inherently bears the high tendency to undergo the four electron (4e$^-$) transfer to form H$_2$O, which inevitably suppresses the formation of...
H₂O₂ through two electron (2e⁻) pathway. In this regard, developing electrocatalysts with high 2e⁻ ORR selectivity is vitally important for the efficient production of H₂O₂.

Recently, several kinds of inexpensive transition metal-based compounds including oxides, chalcogenides, and phosphides have been exploited for selective reduction of O₂ to H₂O₂, by which their huge potential as 2e⁻ ORR electrocatalysts has been eloquently confirmed. For instance, in 2021, Jiang et al. found that the Cu₇.2Se₄ delivered the 2e⁻ selectivity up to 99% at 0.4 V and more than 93% in the high entropy perovskite oxides, which displayed a 2e⁻ ORR activity as high as 90%, and following this observation, Zhao et al. in 2022 reported that the 2e⁻ selectivity for Ni₂₋₃P could be reached higher than 92%. To further enhance the selectivity, very recently, Menezes and his coworkers synthesized high entropy perovskite oxides, which displayed a 2e⁻ selectivity up to 96%. Not only these remarkable new findings are appealing but also they are inspiring others to search for more diverse transition metal-based (TM) electrocatalysts toward 2e⁻ ORR. To the best of our knowledge, nearly all reported electrocatalysts with outstanding 2e⁻ ORR activity is mainly focused on the crystalline phases. Nevertheless, it has been widely accepted now that as compared to the crystalline phases, the corresponding amorphous materials hold the short-range local symmetry, apparent unsaturated coordination atoms, and more abundant defects, which are expected to enhance the number of intrinsic active sites as well as to induce the unique electronic structure, and thus providing the platform for optimizing the 2e⁻ ORR activity. Based on this premise, it can be envisioned that the construction of amorphous TM-based electrocatalysts for 2e⁻ ORR is highly promising and intriguing for both fundamental and industrial applications. However, the relevant investigation on amorphous TM-based electrocatalysts has received limited interest, and such amorphous electrocatalysts concurrently integrating the merits of low cost and high performance with admirable 2e⁻ ORR activity, selectivity, and stability have never been reported so far. Furthermore, a deep understanding of their composition-electronic structure–activity could be crucial to driving efficient 2e⁻ ORR catalysis and therefore requires special attention.

Motivated by the above concerns, in this contribution, a series of amorphous nickel boride nanoarchitectures with different atomic ratios between Ni and B have been fabricated by the reaction of NiSO₄ and NaBH₄ aqueous solution under an ambient condition in a nitrogen atmosphere. Such a hierarchical nanoarchitecture is believed to be beneficial for the active site exposure and mass transfer during catalysis. To further corroborate the above observations, the microstructures of these compounds were examined by transmission electron microscopy (FESEM) suggested a similar morphology for all borides displaying nanostructures as observed by TEM (Figure 1b; Figures S1–S4, Supporting Information). Such a hierarchical nanoarchitecture is believed to be beneficial for the active site exposure and mass transfer during catalysis. To further corroborate the above observations, the microstructures of these compounds were examined by transmission electron microscopy (FESEM) suggested a similar morphology for all borides displaying nanostructures as observed by TEM (Figure 1b; Figures S1–S4, Supporting Information). Such a hierarchical nanoarchitecture is believed to be beneficial for the active site exposure and mass transfer during catalysis.

### 2. Results and Discussion

A series of nickel borides with different atomic ratios were synthesized by a spontaneous redox reaction in the presence of NiSO₄ and NaBH₄ aqueous solution under an ambient condition in a nitrogen atmosphere. These compounds were first assessed by X-ray diffraction (XRD) and extended X-ray absorption fine structure (EXAFS) spectroscopy. It could be seen from the Ni K-edge XANES spectroscopy (Figure 2b) that the adsorption edge of NiB₂ was located in a nitrogen atmosphere (see the Experimental section, Table S1, Supporting Information). The phase structure for these compounds was first assessed by X-ray diffraction (XRD). As shown in Figure 1a, only broad diffraction peaks could be observed in these XRD patterns, indicating the amorphous feature of the as-prepared borides. A further morphological investigation by the field-emission scanning electron microscopy (FESEM) suggested a similar morphology for all borides displaying nanostructures as observed by TEM (Figure 1b; Figures S1–S4, Supporting Information). Such a hierarchical nanoarchitecture is believed to be beneficial for the active site exposure and mass transfer during catalysis.

The composition and the valence states of elements in NiB₄ were analyzed by X-ray photoelectron spectroscopy (XPS). High-resolution XPS spectrum of Ni 2p (Figure 2a) confirmed the presence of NiB₂ along with surface oxidized Ni²⁺ species (856.4 and 874.2 eV). Correspondingly, two peaks at 192.1 and 188.0 eV were observed in the B 1s spectrum (Figure S9, Supporting Information), which could be assigned to Ni=B bonds and surface passivated B⁺, respectively. To further verify the chemical state of Ni and decouple the local structure, the NiB₂ was examined by both the X-ray absorption near-edge structure (XANES) spectroscopy and extended X-ray absorption fine structure (EXAFS) spectroscopy. It could be seen from the Ni K-edge XANES spectroscopy (Figure 2b) that the adsorption edge of NiB₂ was located between those of Ni foil and NiO references, indicating that the average valence state of Ni in NiB₂ was between metallic Ni⁰ and oxidized Ni²⁺, which was consistent with the XPS results. Moreover, the Ni K-edge EXAFS curves, as well as corresponding fitting results toward the Ni foil, NiO, and NiB₂,
are also provided and compared (Figure 2c,d; Figures S10–S12, Supporting Information). Note that because the crystalline NiB₂ structure has not been previously reported, the structure model based on replacing Fe atoms by Ni atoms in the crystalline FeB₂ structure was selected for the EXAFS simulation trial.[40] Unexpectedly, the fitted R factor was quite good (0.0038), suggesting the rational and matched structure, that is, the local structure for amorphous NiB₂ alloy was similar to that for FeB₂. Specifically, it could be observed that NiB₂ displayed two main peaks at around 1.779 and 2.731 Å, respectively, accompanied by a submerged peak at around 2.110 Å, which were assigned to Ni–B coordination in the first shell, Ni–Ni coordination in the second shell and Ni–Ni coordination in the third shell, respectively. In order to further illustrate the coordination environment in NiB₂, wavelet transform (WT) was used to analyze the Ni K-edge EXAFS oscillations. The WT contour plots of Ni foil and NiO displayed the maximum intensity at 7.6 Å⁻¹ (Figure 2e) and 7.2 Å⁻¹ (Figure 2f), respectively, which could be due to their corresponding Ni–Ni coordination.[41,42] Compared to this, the maximum intensity was found to be positioned at 6.4 Å⁻¹ in the WT contour plot of NiB₂, which is ascribed to the coordination between Ni and B (Figure 2g).[43,44] According to the fitting results (Table S2, Supporting Information), unsaturated coordination numbers of B to Ni were observed in NiB₂, implying its defective structure, which might be beneficial to the ORR process.

Encouraged by the expected phase structure and micromorphology, the 2e⁻ ORR electrocatalytic activity of NiB₂ in 0.1 m O₂-saturated KOH was evaluated using a standard three-electrode system at room temperature, and compared with Ni₃B, Ni₂B, NiB, and NiB₃ phases. A rotating ring disk electrode (RRDE) was used to determine the selective oxygen reduction performance of the catalysts, and the collection efficiency was calculated as 0.37 (Figure S13, Supporting Information). The LSV curves of all five electrocatalysts toward ORR were compared and presented in Figure 3a. Evidently, NiB₂ exhibited a disk current close to the theoretical limit (3 mA cm⁻²) of 2e⁻ ORR accompanied by a large and fast-rising ring current. The H₂O₂ selectivity and electron-transfer number were also extracted from the LSV curves. In a wide potential range, the H₂O₂ selectivity of the NiB₂ was calculated to be more than 93%, especially approaching 99% at 0.4 V vs RHE (Figure 3b), which was much higher than those of Ni₃B (60%), Ni₂B (82%), NiB (50%), and NiB₃ (35%). Analogously, the average electron-transfer number attained for NiB₂ was about 2.06, suggesting an almost complete 2e⁻ ORR process (Figure 3c). Besides, the
electron-transfer number during ORR for Ni$_3$B, Ni$_2$B, NiB, and NiB$_2$ was around 2.81, 2.33, 2.99, and 3.32, respectively, which were much higher than that of NiB$_2$, suggesting that 4e$^-$ ORR was highly competitive during their ORR. These results also strongly demonstrated that the different atomic ratios between Ni and B played an important role in tuning the ORR pathway. Notably, the selectivity for amorphous NiB$_2$ toward 2e$^-$ ORR ranked in the top level among the currently reported transition-metal-based electrocatalysts in a wide potential range from 0.2 to 0.6 V (Figure 3d; Table S3, Supporting Information). It should be remarked that the produced H$_2$O$_2$ might undergo further decomposition reaction in the presence of electrocatalysts. To check this, the H$_2$O$_2$ decomposition ability of the electrocatalysts was firstly estimated by the disproportionation reaction test. After adding 5 mg electrocatalysts into the 0.1 m KOH containing 10$^{-3}$ m H$_2$O$_2$ solution, the results showed that NiB$_2$ exhibited a poor hydrogen peroxide disproportionation capability (Figure S14, Supporting Information). To further confirm this, the hydrogen peroxide reduction reaction measurement was then performed in Ar-saturated 0.1 m KOH containing 10$^{-3}$ m H$_2$O$_2$. Even when the applied overpotential was increased, the H$_2$O$_2$ decomposition current density by NiB$_2$ was still minimal, showing excellent H$_2$O$_2$ retention ability, which was expected to be conducive to bulk H$_2$O$_2$ production (Figure S14, Supporting Information).

On the other hand, stability is an indispensable indicator to evaluate the ORR performance in practical applications. Bearing this point in mind, chronoamperometry was also employed to determine the long-term stability of NiB$_2$. The current of ring and disk electrodes was recorded in O$_2$-saturated 0.1 m KOH electrolyte, where the working electrode was fixed at 0.4 V vs RHE (Figure 3e). Both the $i_{\text{disk}}$ and $i_{\text{ring}}$ almost showed no current decay even after the 12 h test, ensuring superior performance compared to previously reported TM-based electrocatalysts (Table S3, Supporting Information). Notably, the H$_2$O$_2$ selectivity kept fluctuating at around 95% during the entire testing process. In addition, the accelerated degradation test (ADT) was carried out to examine the stability of the catalysts. As shown in Figure 3f, quite a little attenuation could be observed for NiB$_2$ even after 5000 (5 K) ADT cycles. Moreover, both the selectivity toward H$_2$O$_2$ (%) and electron transferred number for NiB$_2$ were well retained even after 5 K ADT cycles (Figure S15, Supporting Information), signifying the excellent catalytic stability of NiB$_2$.

To further understand the origin of the outstanding stability, the phase structure, morphology, and chemical state of the NiB$_2$ electrocatalyst after the durability test were comprehensively analyzed. The XRD pattern of NiB$_2$ after the ORR test was almost unchanged as compared to the as-prepared one (Figure S16a, Supporting Information), implying high
structural stability. Similarly, the FESEM and TEM results also confirmed the high morphological stability (Figure S16b–i, Supporting Information), and the EDX results demonstrated that the elemental composition was preserved against ORR cycling (Table S4, Supporting Information). Furthermore, XPS was conducted to acquire the surface information of the NiB$_2$ after the chronoamperometry test (Figure S17, Supporting Information). The high-resolution XPS spectrum of Ni 2p was quite similar to the fresh NiB$_2$, suggesting a marginal surface reconstruction, which could be commonly observed in previous reports and believed to improve the oxygen adsorption ability to promote the 2e$^-$ ORR process.$^{[45–47]}$

Inspired by the outstanding 2e$^-$ ORR activity, selectivity and stability, the H$_2$O$_2$ production ability on a large scale was verified for NiB$_2$. First, an H-type electrolytic cell was employed to determine the H$_2$O$_2$ yield (Figure S18, Supporting Information). The H$_2$O$_2$ yield was measured in an O$_2$-saturated 0.1 m KOH electrolyte with an applied potential of 0.4 V vs RHE. Remarkably, the H$_2$O$_2$ yield was determined as 1.079 mol g$^{-1}$cat h$^{-1}$ by the UV–vis spectrum (Figure S19, Supporting Information). Given the fact that the production rate of H$_2$O$_2$ in the H-type electrolytic cell was restricted by the limitation of oxygen diffusion capability, the gas diffusion electrode was assembled to address this issue (Figure 4a; Figure S20, Supporting Information). As expected, the diffusion capability of oxygen to active sites was greatly improved, hence a larger oxygen reduction current and a higher H$_2$O$_2$ yield were achieved. The comparison of LSV curves recorded in O$_2$ and

Figure 3. a) LSV curves of the five Ni–B samples, where the disk current density ($j_{\text{disk}}$) together with the ring currents ($j_{\text{ring}}$) was fixed at a potential of 1.50 V vs RHE. b) The calculated H$_2$O$_2$ (%) of the corresponding LSV curves. c) The calculated $n$ of the corresponding LSV curves. d) Comparison of ORR selectivity of NiB$_2$ with previously reported electrocatalysts. e) Chronoamperometry of NiB$_2$ at 0.4 V vs RHE in O$_2$-saturated 0.1 m KOH for 12 h. f) Comparison of LSV curves of NiB$_2$ before and after 5 K ADT cycles.
Ar-saturated 0.1 M KOH electrolyte strongly suggested the oxygen reduction ability of NiB₂ (Figure 4b). Moreover, high current densities were observed with the assistance of gas diffusion electrodes, indicating the potential of H₂O₂ production on a large scale. When the potential applied to the working electrode was 0.4 V vs RHE, a current density of 125 mA cm⁻² was achieved by the gas diffusion electrode (Figure 4c). The H₂O₂ yield was determined up to around 1.9012 mmol h⁻¹ and 4.753 mol g⁻¹cat h⁻¹, which was greatly exceeded the value in the H-type electrolytic cell (Figure 4d). Moreover, NiB₂ delivered a Faradaic efficiency of 93%, which was close to the theoretical one. The reasons for less than 100% efficiency could be ascribed to the decomposition of H₂O₂ under alkaline conditions and/or the occurrence of 4e⁻ ORR on carbon paper. The exceptional durability of continuous operation of NiB₂ in gas diffusion electrodes further demonstrated the potential in practical application. Even after a continuous 12 h testing, the current density of the gas diffusion electrode was still well maintained at about 125 mA cm⁻², and little activity decay was observed (Figure 4c,d). Moreover, this H₂O₂ productivity and continuous H₂O₂ production capacity surpassed nearly all recently reported 2e⁻ ORR TM-based electrocatalysts (Figure 4e and Table S5, Supporting Information). It has been well documented that amorphous materials bear a higher density of surface defects (e.g., high density of coordinatively unsaturated sites) than their crystalline counterparts, which can usually enhance the electrocatalytic activities. Specifically, the presence of abundant defects not only contributes to the exposure of active metal sites, which increases the amount of catalytic sites during catalysis but also modifies the charge distribution of...
active metal sites, thus altering the charge-transfer ability and free adsorption energy toward surface-bound intermediates. To confirm this, the double-layer capacitance (C_{dl}) that was positively correlated to electrochemical active surface area (ECSA), electrochemical impedance spectroscopy (EIS), XPS spectra and ORR activity of amorphous Ni_{2}B and crystalline Ni_{1}B alloys were compared under the same testing condition as an illustration (Figures S21–S25, Supporting Information). Note that crystalline NiB_{2} was not selected because of the fact that it was hard to be achieved due to the high tendency to undergo the disproportionation-like reaction for amorphous NiB_{2} during annealing (Figure S26, Supporting Information). The amorphous NiB_{2} showed a much higher C_{dl} value (6.540 mF cm^{-2}) than that of the crystalline counterpart (1.080 mF cm^{-2}), demonstrating the larger amount of potential active sites (Figure S21, Supporting Information). Moreover, a slightly higher charge-transfer resistance was observed for amorphous Ni_{1}B than crystalline Ni_{1}B during catalysis, meaning the relatively slow charge-transfer kinetics (Figure S22, Supporting Information), which was probably beneficial for suppressing 4e^− ORR. Furthermore, the XPS spectra showed a slight change in both Ni and B valance states between crystalline Ni_{2}B and amorphous Ni_{1}B, implying the change in the electronic structure of Ni_{1}B (Figure S23, Supporting Information). Such a variation of the electronic structure in amorphous architecture probably effectively optimized the adsorption free energy of metal sites toward *OOH for improving 2e^− ORR.[57,58] As a result, benefiting from the above merits, the amorphous Ni_{1}B delivered about 10% selectivity higher than that of the corresponding crystalline one (Figure S24, Supporting Information). The ORR performance of the annealed NiB_{2} sample was also compared to the amorphous one under the same condition and lower activity and selectivity toward 2e^− ORR for the annealed sample was attained (Figure S25, Supporting Information), demonstrating again the advantages of amorphous structure. On the other hand, the C_{dl} value for five amorphous nickel borides was also compared. From the results, it could be seen that with the increase of metal amount in borides, the C_{dl} value was gradually increased, meaning the increase in the amount of catalytically active sites (Figure S27, Supporting Information).

To unveil the origin of the superior activity of NiB_{2} toward 2e^− ORR, the in situ Raman test was performed in 0.1 M KOH (0.3–0.7 V vs RHE) to gather insights into the possible active sites. As shown in Figure 5a, the bottom Raman curve was recorded at 0.7 V vs RHE, which is close to the onset potential and no obvious peaks can be observed. Moreover, the signals at 178, 435, and 731 cm^{-1} were gradually augmented as the ORR underwent (0.05 V as an interval), which can be attributed to the Ni–O signals.[52–54] Therefore, the reaction mainly occurred on Ni sites. Based on the in situ Raman test result, the density functional theoretical (DFT) calculation was carried out by taking the Ni site as the active site. Since the amorphous structure presented the short order arrangement feature, cluster models for amorphous Ni_{1}B, Ni_{2}B, NiB, NiB_{2}, and NiB_{3} phases were rationally created. Then, the free adsorption energy toward the intermediate *OOH (ΔG_{OOH}^*) was calculated and depicted in Figure 5b. Within different borides, NiB_{2} showed the closest ΔG_{OOH}^* value (3.75 eV) to the ideal value of 3.52 eV suggesting the best balance of adsorption and desorption ability toward *OOH,[9,21,55,56] which was in favor of the preservation of O–O bond and production of H_{2}O_{2}. The limiting potential–volcano plot for the 2e^− ORR pathway by using ΔG_{OOH} as a descriptor was further depicted. NiB_{2} cluster showed the nearest position to the top site of the volcano plot among the nickel boride samples, suggesting the most active H_{2}O_{2} production (Figure S28, Supporting Information). Such activity also surpassed some previously reported representative 2e^− ORR electrocatalysts and was also comparable to the noble metal ones.[3,13,10,55,57] To further demonstrate the high 2e^− ORR selectivity, we have provided the energy diagram for the reaction pathway of 4e^− ORR for NiB_{2} electrocatalyst for comparison. The free adsorption energy barrier was about +0.21 V for the conversion of *OOH to *O, which was larger than that (−0.23 eV) of the conversion of *OOH to *O under 0.7 V vs RHE, demonstrating the high two-electron selectivity (Figure S29, Supporting Information). Furthermore, when the ratio of Ni to B was high, such as for Ni_{2}B, Ni_{3}B, and NiB, the adsorption model for *OOH presented in the form of a side-on model (Figure 5c–e), which was believed to be hard for the preservation of O–O bond. However, when the ratio of B to Ni was high, the B atoms could effectively serve as the fence to isolate neighboring Ni atoms, which led to the end-on adsorption model of *OOH and facilitated the preservation of O–O bond (Figure 5f,g). Note that according to the deviation degree of ΔG_{OOH}^* value to 3.52 eV, it could be concluded that the activity showed the enhancement in the tendency of Ni_{2}B > Ni_{3}B > NiB_{2} > Ni_{1}B > NiB. This tendency was slightly different from the experimental observations (Ni_{2}B > Ni_{3}B > Ni_{1}B > NiB_{2} > NiB), which could be due to the comprehensive impact of the free adsorption energy toward *OOH, interfacial charge-transfer ability as well as the amount of active Ni sites as discussed below. Differential charge density distribution between the substrate and *OOH was decoupled and provided in Figure 5c–g. By comparing these patterns, the charge polarization occurred for all OOH-adsorbed cluster models. Among them, NiB_{2} showed a relatively weak charge interaction between *OOH and substrate, while Ni_{2}B, Ni_{3}B, and NiB showed a strong one. In comparison with these, NiB_{2} displayed a modest charge interaction between the substrate and *OOH resulting in an enhancement of catalytic activity. Notably, these results indicated that the electronic structure and adsorption model could be tuned by the atomic ratio between Ni and B, and thereby an optimization of ΔG_{OOH}^*. Motivated by the outstanding 2e^− ORR activity and selectivity in alkaline media, the 2e^− ORR performance for NiB_{2} was further investigated in 0.05 M H_{2}SO_{4}. Unfortunately, NiB_{2} delivered activity with a larger overpotential and a lower H_{2}O_{2} selectivity as compared to that under alkaline media (Figure S30, Supporting Information). The energy diagram for the reaction pathway from O_{2} to H_{2}O_{2} in the acidic solution was also calculated by DFT. The energy diagram showed that NiB_{2} bears a larger deviation of ΔG_{OOH}^* to 3.52 eV (U = 0.7 V) under acidic media than under alkaline media (Figure S31, Supporting Information).

In addition to DFT, the interfacial electron transfer process was analyzed to figure out the effect of electronic structure on ORR performance. A stimulation-response technique was developed based on a transient photoinduced voltage (TPV) to record the electron transfer process.[58–60] The TPV curves of Ni_{1}B and Ni_{2}B were first plotted in Figure 6a, from which
it could be observed that these two curves show similar decay tendency, that is, the intensity decreased with prolonged time. The decay time of Ni$_3$B and Ni$_2$B was simulated as 0.3299 and 0.3877 ms, respectively, meaning that the overall electron transfer process on the surface of Ni$_2$B was slower than that of Ni$_3$B. In general, the slower electron transfer kinetics would render the accumulation of electrons at the surface for a longer time rather than being quickly transformed into O$_2$ molecules, which could enhance the $2e^-$ ORR activity.\cite{61,62} Interestingly, NiB, NiB$_2$, and NiB$_3$ showed completely different curves where the signal intensity of the curves decayed even less than zero as time proceeded, which could be due to the electron-trap effect (Figure 6b). The emergence of the electron-trap effect usually signifies that the sample bears a strong ability to capture interfacial electrons and leads to slower electron transfer on the surface of the catalyst, thus facilitating the $2e^-$ ORR. Moreover, the decay times of the NiB, NiB$_2$, and NiB$_3$ were also simulated as 0.1526, 0.3032, and 0.2135 ms, respectively.

In order to deeply decouple the electron transfer on the surface of the electrocatalysts, fast Fourier transform (FFT) was adopted based on the TPV data. The FFT curves of the five electrocatalysts are displayed in Figure 6c, which showed a series of continuous signals. No obvious peaks were found in these FFT curves, revealing that there was no apparent static and periodic frequency component presented in the TPV relaxation signals. The continuous wavelet transformation (CWT) curves were also displayed to reveal different decay processes. Therefore, the CWT pattern of Ni$_3$B and Ni$_2$B were provided (Figure 6d and Figure S32, Supporting Information). The obtained CWT patterns were presented in the form 3D diagram, involving the time, frequency, and intensity, which provided time-scale/ frequency-scale analysis of these TPV curves. For different TPV curves, the relationship between peak intensity and time at different frequencies was compared to elucidate the dynamic electron transfer process, in which the low and high frequency represents slow and fast electron transfer, respectively. As shown in Figure 6e, the peak positions of Ni$_3$B and Ni$_2$B at 15 Hz were 0.6105 (t$_1$) and 0.6335 ms (t$_2$), respectively, which suggested that Ni$_2$B displayed a relatively slow interfacial electron transfer process in the low-frequency region. Moreover, even when the frequency was increased to 20 Hz, which corresponded to a faster interfacial electron transfer than 15 Hz, the position (0.4865 ms, t$_3$) of the peak observed in Ni$_2$B was still smaller than that (0.4725 ms, t$_4$) of Ni$_3$B (Figure 6f). The comparison of peak positions at other frequencies also showed that Ni$_2$B displayed lagging peaks as compared to those of Ni$_3$B (Figure S33, Supporting Information). The time difference ($\Delta t = t_2 - t_1$) at the fixed frequency was further achieved to investigate the difference in the different interfacial transport processes in which the $\Delta t$ were 0.0230 ms at 15 Hz and 0.0140 ms at 20 Hz. For some other higher frequencies, the $\Delta t$ was very close to zero (Table S6, Supporting Information). On the whole, the

Figure 5. a) In situ Raman spectra for NiB$_2$ electrocatalyst in O$_2$-saturated 0.1 m KOH within voltage window 0.3–0.7 V vs RHE. b) Free energy diagram at the limiting potential $U = 0.7$ V for nickel boride clusters with a different atomic ratio between Ni and B. c–g) Differential charge density distribution between OOH with Ni$_3$B (c), Ni$_2$B (d), NiB (e), NiB$_2$ (f), and NiB$_3$ (g) substrate. (The atoms in pink, green, red, and light pink represent Ni, B, O, and H, respectively; the red and blue colored isosurfaces mean the positive charge and the negative charge, respectively.)
Δt_{3,4} became minimal as the frequencies increased. It means that the most significant distinction in electron transfer was at low frequencies, and Ni_{2}B displayed a slower interfacial transport process than that of Ni_{3}B, which was beneficial to the 2e⁻ ORR and resulted in a higher H₂O₂ selectivity.

Next, the interfacial electron transfer for NiB, NiB₂, and NiB₃ electrocatalysts were also compared. At 15 Hz (Figure 6i), NiB₂ presented a lagging peak (t_{4} = 0.5975 ms) than those of NiB (t_{3} = 0.4330 ms) and NiB₃ (t_{5} = 0.5135 ms), indicating that NiB₂ exhibited the slowest interfacial electron transfer in low frequency region. As shown in Figure 6i, three samples presented obvious peak positions at 20 Hz, they were t_{3} = 0.362 ms for NiB, t_{4} = 0.465 ms for NiB₂ and t_{5} = 0.424 ms for NiB₃, respectively. NiB₂ also showed a hysteretic peak position than those of NiB and NiB₃, and NiB₃ displayed apparently lagging compared with that of NiB. Similarly, at other frequencies, the electron transfer kinetics still showed the enhanced tendency in the order of NiB₂ < NiB₃ < NiB (Figure S34, Supporting Information). Moreover, the time differences (Δt_{4,5} = t_{4} - t_{5} and Δt_{3,4} = t_{4} - t_{3}) were also achieved to illustrate the decisive frequency range that caused the electron transfer difference among the three electrocatalysts (Tables S7 and S8, Supporting Information). These results clearly indicated that the main difference in electron transfer occurred in the low-frequency region. This hysteresis may be beneficial in 2e⁻ ORR, as it caused electrons at the catalyst interface to stay at the interface for a longer period of time instead of being transferred to O₂ molecules. Therefore, NiB₂ possessed the slowest interfacial charge transfer kinetics among all the electrocatalysts, which would be the most effective to inhibit the binding of adjacent *OOH to form O₂. The above results show that NiB₂ has a favorable binding strength for OOH⁻ and the

Figure 6. a) TPV curves and corresponding decay times of Ni_{3}B and Ni_{2}B. b) TPV curves and corresponding decay times of NiB, NiB₂, and NiB₃. c) FFT patterns of the five TPV curves. d) CWT pattern of the corresponding Ni_{2}B TPV curve. e,f) Intensity–time curves comparison of Ni_{2}B and Ni_{3}B (t₁ and t₂ are the peak occurrence time of Ni_{3}B and Ni_{2}B, respectively). g) CWT pattern of the corresponding NiB₂ TPV curve. h,i) Intensity–time curves comparison of NiB, NiB₂, and NiB₃ (t₁, t₄, and t₅ are the peak occurrence time of NiB, NiB₂, and NiB₃, respectively).
slowest interfacial electron transfer kinetics, which synergistically assured the best activity and selectivity.

3. Conclusion

Several amorphous nickel borides nanosheets with different electronic structures were achieved by altering the composition ratio between Ni and B. The activity investigations showed that the optimized NiB<sub>2</sub> was an efficient electrocatalyst for the electrochemical reduction of O<sub>2</sub> to H<sub>2</sub>O<sub>2</sub>, which delivered the highest selectivity of close to 99% at 0.4 V vs RHE and produced over 93% of selectivity of H<sub>2</sub>O<sub>2</sub> across a wide potential range from 0.2 to 0.6 V vs RHE. Remarkably, the activity is stable with negligible current loss even after 12 h duration at 0.4 V vs RHE. Impressively, the sustainable bulk H<sub>2</sub>O<sub>2</sub> productivity in the rate of up to 4.753 mol g<sub>cat</sub><sup>-1</sup> h<sup>-1</sup> can be stably recorded for at least 12 h by assembling the gas diffusion electrode, together with a high FE of around 93%, which are superior to nearly all previously reported TM-based electrocatalysts, showing huge potential for practical application. Further in situ and ex situ investigations combined with the computational analysis unveiled that the electronic structure for the amorphous NiB<sub>2</sub> phase not only bears the closest ΔG<sub>O2H</sub> value to the ideal one but also reduced electron-transfer capability on the surface, thus enhancing the catalytic activity and selectivity for the efficient production of H<sub>2</sub>O<sub>2</sub>. The discovery of this work not only renders the amorphous NiB<sub>2</sub> as a new representative benchmark for 2e<sup>-</sup> ORR electrocatalyst in alkaline solution but also provides new mechanistic insights and opens up a new rational design strategy for economical, stable, and efficient TM electrocatalysts.

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

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Conflict of Interest

The authors declare no conflict of interest.

Data Availability Statement

The data that support the findings of this study are available from the corresponding author upon reasonable request.

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