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Ni₃N as an active hydrogen oxidation reaction catalyst in alkaline medium

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Abstract: Hydroxide-exchange membrane fuel cells can potentially utilize platinum-group-metal (PGM)-free electrocatalysts, offering cost and scalability advantages over more developed proton-exchange membrane fuel cells. However, there is a lack of non-precious electrocatalysts that are active and stable for the hydrogen oxidation reaction (HOR) relevant to hydroxide-exchange membrane fuel cells. Here we report the discovery and development of Ni₃N as an active and robust HOR catalyst in alkaline medium. A supported version of the catalyst, Ni₃N/C, exhibits by far the highest mass activity and break-down potential for a PGM-free catalyst. The catalyst also exhibits Pt-like activity for hydrogen evolution reaction (HER) in alkaline medium. Spectroscopy data reveal a downshift of the Ni d band going from Ni to Ni₃N and interfacial charge transfer from Ni₃N to the carbon support. These properties weaken the binding energy of hydrogen and oxygen species, resulting in remarkable HOR activity and stability.

Hydrogen fuel cell technology is a key component of a lowcarbon-emission hydrogen economy. Proton-exchange membrane fuel cell (PEMFC) has advanced significantly in recent years, and its commercial deployment in the automotive industry has started. Nevertheless, PEMFC remains a costly power device. Hydroxide-exchange membrane fuel cell (HEMFC) is an alternative fuel cell technology with potential cost advantages over PEMFC.^[1] HEMFC operates in alkaline medium where non platinum-group-metal (PGM) catalysts might be active and stable. Moreover, HEMFC might use more economical bipolar plates, air loop, and membranes than PEMFC.^[1b, 2] However, HEMFC is at a very early stage of development and many technical challenges are yet to be solved.

The possibility to use PGM-free electrocatalysts is one major advantage of HEMFC over PEMFC. Whereas PGM-free oxygen reduction reaction (ORR) catalysts exhibit comparable activity to PGM catalysts, PGM-free hydrogen oxidation reaction (HOR) catalysts are much inferior.^[1, 3] Despite several decades of research, only nickel and its metallic alloys have been shown to be active PGM-free HOR catalysts.^[3b, 3c, 4] Recently Yan and co-

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workers significantly improved the activity of Ni nanoparticles in HOR using a nitrogen-doped carbon nanotube support.[4d] This composite catalyst, however, is still one order of magnitude less active than state-of-the-art Pt catalysts. Besides modest activity, Ni also suffers from low stability at potential above ~0.1 V vs. reversible hydrogen electrode (RHE) due to relatively strong binding affinity towards oxygen species, which block the active sites. To achieve considerable power output, HOR catalysts should function at potentials up to 0.3 V vs. RHE.^[1b] Thus, there is great need for new PGM-free HOR catalysts, especially those with enhanced oxidative stability. Here we report the discovery of Ni₃N as an active HOR catalyst. When supported on carbon, the catalyst achieves by far the highest mass-averaged activity and break-down potential for a PGM-free catalyst. Spectroscopy data indicate a downshift of the Ni d band going from Ni to Ni₃N, as well as interfacial charge transfer from Ni₃N to the carbon support. These properties weaken the binding energy of hydrogen and oxygen species, which might result in higher HOR activity and stability than a typical Ni catalyst. For the same reason, the catalyst also exhibits superior activity in the hydrogen evolution reaction (HER).

Bulk and nanoparticle samples of Ni₃N were prepared by reducing an appropriate Ni precursor under a NH₃ atmosphere at an elevated temperature. The precursor for bulk Ni₃N was Ni(OH)₂ synthesized by a hydrothermal method and the precursor for nanoparticles was NiO nanoparticles, synthesized via an oleylamine-assisted method (see details in Methods and Figure S1 and S2, Supporting Information). To prevent the aggregation of the Ni₃N nanoparticles, they were prepared on a carbon black (Vulcan-XC 72R) support (labelled Ni₃N/C). According to thermal gravimetric analysis (TGA) in air, the loading of Ni₃N in Ni₃N/C was about 51.4 mass percentage. (Figure S3). Nickel nanoparticles were also prepared to serve as a reference sample (denoted as Ni-Ref).^[4d]

Powder X-ray diffraction (PXRD) analysis confirms the formation of Ni₃N without crystalline impurity (Figure 1a). In the Xray adsorption near-edge structure (XANES) spectra (Figure 1b), the adsorption edge of Ni₃N/C is positively shifted comparing to that of Ni₃N, suggesting a higher valence state of Ni in Ni₃N/C. According to extended X-ray adsorption fine structure (EXAFS) spectra and its fitting results (Figure S4 and Table S1), due to the interaction with nitrogen atom in the lattice, Ni-Ni bond length were elongated in both Ni₃N and Ni₃N/C comparing to Ni-Ref. The coordination number of Ni₃N/C is smaller than Ni₃N, indicating a smaller particle size, which was later confirmed by electron microscopy. In the high resolution Ni 2p_{3/2} X-ray photoelectron spectra (XPS) (Figure 1c and Figure S5), the peaks with a binding energy (BE) of about 853 eV are attributed to Ni in Ni₃N and Ni₃N/C. The binding energy is similar to that of Ni in Ni₂P, which is close to metallic nickel and was previously assigned as $Ni(\delta+)$.^[5] The peaks with BE of about 856 eV are attributed to surface oxidized Ni species, Ni(II).^[6] The binding energies of the same Ni species are higher in Ni₃N/C than in Ni₃N, again suggesting a higher valence state of Ni in the former. In the N 1s

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Figure 1. Characterization of Ni₃N and Ni₃N/C samples. (a). PXRD pattern. (b). XANES spectra. (c). Ni $2p_{3/2}$ and (d). N 1s high-resolution XPS spectra.

spectra (Figure 1d), a single peak with a BE of about 398 eV, corresponding to a nitride-type nitrogen, was observed for both Ni₃N and Ni₃N/C.^[6a, 7] The BE of N in Ni₃N/C is also positively shifted compared to that of Ni₃N. These data indicate an interfacial charge transfer from Ni₃N nanoparticle to the carbon support in Ni₃N/C.



Figure 2. Microscopic characterization of Ni₃N and Ni₃N/C composite. (a) TEM image of bulk Ni₃N. (b) TEM image of Ni₃N/C. (c) HRTEM image of Ni₃N/C. Inset is the Fast-Fourier Transform (FFT) image of the composite.

Transmission electron microscopy (TEM) revealed the morphology of Ni₃N and Ni₃N/C. Bulk Ni₃N (Figure 2a) contains large, sintered aggregates with a wide size distribution (42.2 \pm 18.5 nm, Figure S6). The large size is likely inherited from its precursor, while the large size range might be due to Ostwald ripening and high diffusivity of nickel atoms at an elevated temperature.^[8] Thanks to the carbon support, the Ni₃N nanoparticles in Ni₃N/C are evenly distributed (Figure 2b),

inheriting the morphology of its NiO/C precursor (Figure S2). The size distribution of Ni₃N/C is narrow (4.6 \pm 1.0 nm). High resolution TEM (HRTEM) image reveals an inter-planar spacing of ~0.20 nm in Ni₃N/C, corresponding to the (111) plane of Ni₃N (Figure 2c). Scanning transmission electron microscopy (STEM) and its corresponding elemental mapping indicate the homogeneous distribution of Ni and N elements (Figure S7).

The HOR activity of Ni₃N and Ni₃N/C was examined with a standard three-electrode system at a scan rate of 1 mV/s in H₂-saturated 0.1 M KOH solution (See details in Methods). The Ni₃N/C sample has a much higher current density than bulk Ni₃N and Ni-Ref (Figure 3a). Its activity approaches that of 20 wt% Pt/C. Importantly, the break-down potential of Ni₃N/C is about 0.26 V vs RHE, the highest potential achieved by an Earth-abundant catalyst. Control experiments conducted in N₂-saturated electrolytes showed negligible anodic currents across the whole potential range (Figure S8). *In situ* XANES and EXAFS measurements (Figure S9 and Table S2) of Ni₃N/C revealed a stable catalyst at 0-0.25 V vs. RHE.

The kinetic current densities were calculated using data from LSV curves at different rotating speeds (Figure 3b). When the current is controlled by both reaction kinetics and H_2 diffusion, Koutecky-Levich equation (eq. 1) applies:

 $1/j = 1/j_k + 1/j_d = 1/j_k + 1/Bc_0 \, \omega^{0.5} \qquad (1)$ Here j is the measured current density, j_k and j_d are kinetic and diffusional current density, respectively, B is the Levich constant related to the diffusivity of H₂ and kinematic viscosity of electrolyte, c₀ is the solubility of H₂ in 0.1 M KOH, and ω is the rotating speed. By fitting the data at an overpotential of 50 mV ($\eta = 50$ mV) with eq. 1, a linear plot of $\omega^{-1/2}$ with j⁻¹ was obtained (Figure S10). The slope is 4.75 cm²/mA·s^{1/2}, close to the theoretical value (4.87 cm²/mA·s^{1/2}).^[9] The kinetic current density of Ni₃N/C is 3.9 mA/cm²_{disk} at $\eta = 50$ mV. The corresponding mass activity of Ni₃N/C is 24.38 mA/mg_{Ni3N} at $\eta = 50$ mV, the highest among all reported earth-abundant HOR catalysts (Table S3). The mass activity of bulk Ni₃N (1.73 mA/mg_{Ni3N}) and Ni-Ref (1.07 mA/mg_{Ni}) are an order of magnitude lower.



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at different rotating speeds. (c) HER/HOR Tafel plots of kinetic current density on Ni₃N/C and Ni₃N. (d) Accelerated durability test results of Ni₃N/C. The durability test was performed by doing cyclic voltammetry scans in H₂-saturated 0.1 M KOH from -0.05 V to 0.1 V vs RHE with a scan rate of 150 mV/s. The LSV curves were recorded after 0, 1000, 3000, 5000 scans. The catalyst loading was 0.28 mg/cm² for Ni₃N and Ni-Ref and 0.16 mg_{Ni3N}/cm² for Ni₃N/C.

The kinetic current density from Eq. 1 (Figure 3c) was further fitted to the Butler-Volmer equation (eq. 2) to obtain the exchange current density j_0 :

$$j_k = j_0 (e^{\alpha F \eta/RT} - e^{(1-\alpha)F \eta/RT})$$
⁽²⁾

Here α is charge transfer coefficient, F is Faraday constant (96485 A/mol), R is universal gas constant (8.314 J/mol \cdot K), η is overpotential and T is temperature. The exchange current densities were then normalized by electrochemical surface area (ECSA; Figure S11) as well as the catalyst loading (Table S3). Comparison with Ni-ref and other state-of-the-art non-precious HOR catalysts reveals the origin of the remarkable mass activity of $Ni_{3}N/C.^{[3b,\,4d]}$ The specific activity, that is, the ECSA-normalized exchange current density of Ni₃N/C and Ni₃N is similar and more than 7 times higher than that of Ni-ref. But this specific activity is slightly lower than that of most active hybrid Ni catalysts.[3b, 4d] Recently a Ni/Ni₃N/nickel foam catalyst was reported to have very high geometric activity in HOR.^[10] The active site was proposed as the interfacial sites of Ni and Ni₃N, instead of Ni₃N itself. The direct comparison to that catalyst is difficult due to the use of different measurement methods. A rough estimate of ECSAaveraged exchange current density was 0.003 mA/cm², lower than the present Ni₃N catalysts. The mass-normalized exchange current density of Ni₃N/C is 10 times higher than that of bulk Ni₃N and about 4 times higher than most active hybrid Ni catalysts.[3b, ^{4d]} Thus, dispersion of Ni₃N nanoparticles on a carbon support leads to a high surface area/mass ratio, which contributes to its exceedingly high mass activity.

An accelerated long-term durability test (ADT) for Ni₃N/C was conducted by running repetitive CV from -0.05 V to 0.1 V vs RHE at a scan rate of 150 mV/s in 0.1 M H₂-saturated KOH. To prevent Pt contamination, the working and counter electrodes were separated by a frit. After 1000, 3000, 5000 CVs, the exchange current density of the electrode decreased to 81.0 %, 71.7 % and 59.8 % of the initial value, respectively (Figure 3d). TEM image (Figure S12) shows that after the measurement the catalyst retains its morphology. Size distribution analysis indicates a slightly increased particle size (4.7 ± 1.2 nm). HRTEM shows no formation of an extra phase at the surface. Some catalyst fell off from the electrode after 5000 CVs, which led to a decreased ECSA (Figure S13). The ECSA-normalized activity decreased to 74.4 % of the initial value after 5000 CVs, indicating good stability of Ni₃N/C (Table S4, Supporting Information).

Since HER is the reverse reaction of HOR, the good HOR activity of Ni₃N/C promoted us to examine its HER activity. The experiments were conducted 1 M N₂-saturated KOH solutions. Ni₃N/C exhibits remarkable HER activity, close to the benchmark 20 wt% Pt/C catalyst. The overpotential to reach 10 mA/cm² is only 64 mV for Ni₃N/C, among the lowest for earth-abundant HER catalysts in alkaline media (Table S5). The geometric activity of Ni₃N/C is much higher than that of Ni₃N and Ni-ref. The Tafel slopes are 32, 48, 122, 88 mV/decade for Pt/C, Ni₃N/C, Ni₃N and Ni-Ref, respectively. The durability of Ni₃N/C in HER was



Figure 4. Electrochemical HER performance. (a) HER polarization curves of Ni₃N/C, Ni₃N, Ni-Ref and commercial 20 wt% Pt/C in N₂-saturated 1 M KOH with a scan rate of 1 mV/s. All the catalysts were casted onto a 5 mm glassy carbon electrode with an overall loading of 0.28 mg/cm² except that Ni₃N/C had a loading of 0.31 mg/cm² (loading includes the carbon support). (b) HER Tafel slopes measured according to the HER performance in (a). (c) Durability test for Ni₃N/C. To prevent the catalyst detachment, hydrophilic carbon cloth was used as working electrode here.

Ultraviolet photoemission spectroscopy (UPS) was applied to study the electronic structure of Ni₃N/C, Ni₃N, and Ni-Ref. As shown in Figure 5a and Fig. S14, all the materials have electronic bands crossing the Fermi level. The presense of such a Fermi edge in the UPS spectra indicates a metallic nature of these materails.^[11] This result is consistent with previous studies which showed Ni₃N as an intrinsic metallic material.^[12] The reporetd electronic electronic resistivity was about $1.09 \times 10^{-4} \Omega \cdot m$ at 300 K.^[12a] For Ni₃N and Ni₃N/C, the signals located at 5-10 eV are tentatively attributed to hybridized Ni 3d and N 2p emissions, as observed in similar regions for other transition metal nitrides such as TiN and VN.^[13] The peaks located at 0-1 eV arise from nickel's 3d band.^[14] The Ni 3d band reaches it maximum at 0.305 eV. 0.65 eV and 0.805 eV for Ni-Ref, Ni₃N, and Ni₃N/C, respectively. These data indicate that from Ni to Ni₃N and to Ni₃N/C, the 3d band is pushed away from the Fermi level. According to the *d*-band theory, the interaction of adsorbate with transition metal catalysts can be simplified as electronic coupling between the adsorbate's valence states and the catalyst's d band, which results in bonding and antibonding states. A higher *d*-band center (closer to the Fermi level) leads to more empty antibonding states above the Fermi level, hence a stronger adsorption.^[15] Thus, the absorption energy should have the order of $Ni > Ni_3N > Ni_3N/C$.

The mechanism of HOR on PGM catalysts in alkaline medium is studied only in recent years.^[16] A prevailing theory is that hydrogen bonding energy (HBE) determine the rate of HOR.^[16a-c, 16i] However, there is a vivid debate on whether and how surfaceadsorbed OH species influence HOR kinetics.^[16c-h, 17] In addition, the pH-dependent potential of zero point charge was proposed to affect the transportation of OH⁻ through the double layer region and hence the HOR rate.^[16h] Dedicated mechanistic studies of

measured in a 24-hour electrolysis at a constant current density of -10 mA/cm². The potential remained nearly constant, indicating good stability (Figure 4c).

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non-PGM HOR catalysts are rare,^[1a, 1c, 18] although the modest activity of Ni in HOR was commonly attributed to a too high HBE.^[3b, 19] Accordingly, the higher specific activity of Ni₃N over Ni might be explained by a weakening of HBE. Going from Ni₃N to Ni₃N/C, the mass activity is much higher due to the much higher surface area per mass, but the specific activity is slightly lower. The decrease of specific activity might be due to an overcorrection of the hydrogen binding strength to an unfavorable weak region. It should be pointed out that the hydroxide bonding energy (OHBE) changed in the same direction as HBE for these samples (see below), thus, the improved activity might be due to more optimal OHBE, or both HBE and OHBE. A recent study indicated that both HBE and OHBE (from density functional theory (DFT) computations) were important parameters in describing the HOR activity of Ni alloys.^[16e]



Figure 5. (a) UPS spectra of Ni₃N, Ni₃N/C and Ni-Ref. The excitation photon energy (He II) is hu = 40.82 eV. (b) Anodic LSV scans in 0.1 M N₂-saturated KOH electrolyte showing the OH⁻ oxidative adsorption peaks, scan rate: 50 mV/s. Current here were normalized in order to make three curves in the same graph.

The higher break-down potential in HOR for Ni₃N and Ni₃N/C compared to Ni-Ref can be, at least partially, explained by attenuated adsorbate binding. It was reported that catalysts with high affinity to oxygen species, especially those based on Ru and Ni, deactivate readily at positive potentials vs RHE.[3b, 20] The deactivation was attributed to the oxidative adsorption of oxygen species from the electrolyte. In Pt-based ORR catalysts, a downshift d-band decreases the binding strength of O species.[21] The UPS data above show that nickel's d-band is downshifted from metallic Ni to Ni₃N to Ni₃N/C. Thus, the oxygen binding strength should follow the order Ni > Ni₃N > Ni₃N/C. The decreased oxygen binding in Ni_3N/C results in its high break-down potential. To further corroborate this hypothesis, the OH⁻ oxidative adsorption peaks in the three catalysts are compared (Figure 5b). Indeed Ni₃N/C has the most positive peak. Besides, it is noted that XANES and XPS data show an interfacial charge transfer from Ni₃N to the carbon support in Ni₃N/C. This charge transfer decreases the electron density of Ni₃N, making it more difficult to be oxidized. Enhanced oxidative resistance due to interfacial charge transfer observed by XPS was reported for other supported catalysts such as Cu/WO2.72. [22] Whether the charge transfer is the cause of the downshift of the *d*-band, or works in parallel to it, remains unclear.

In summary, we discover the significant activity of Ni_3N for HOR in alkaline medium. By dispersing Ni_3N nanoparticles onto a

carbon support, we obtain a Ni₃N/C catalyst with the highest mass activity and break-down potential in HOR for a base metal catalyst. The catalyst also exhibits excellent HER activity in alkaline medium, comparable to the benchmark Pt/C. Spectroscopy data reveal a downshift of the Ni *d* band and interfacial charge transfer from Ni₃N to the carbon support as factors that lead to weak binding of hydrogen and oxygen species in Ni₃N/C. This weak binding might be the origin of its remarkable HOR activity and stability.

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