

Catalytic Performance and Near-Surface X-ray Characterization of Titanium Hydride Electrodes for the Electrochemical Nitrate Reduction Reaction

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ABSTRACT: The electrochemical nitrate reduction reaction (NO₃RR) on titanium introduces significant surface reconstruction and forms titanium hydride (TiH_x, 0 < x ≤ 2). With *ex situ* grazing-incidence X-ray diffraction (GIXRD) and X-ray absorption spectroscopy (XAS), we demonstrated near-surface TiH₂ enrichment with increasing NO₃RR applied potential and duration. This quantitative relationship facilitated electrochemical treatment of Ti to form TiH₂/Ti electrodes for use in NO₃RR, thereby decoupling hydride formation from NO₃RR performance. A wide range of NO₃RR activity and selectivity on TiH₂/Ti electrodes between −0.4 and −1.0 V_{RHE} was observed and analyzed with density functional theory (DFT) calculations on TiH₂(111). This work underscores the importance of relating NO₃RR performance with near-surface electrode structure to advance catalyst design and operation.

The conversion of wastewater nitrate to ammonia can simultaneously remediate widespread nitrogen pollution and electrify ammonia manufacturing. The electrochemical nitrate reduction reaction (NO₃RR) has been actively studied because of its potential to circularize nitrogen management.^{1–9} As with other electrocatalytic reactions, NO₃RR electrocatalysts may undergo substantial structural evolution during the reaction, creating a need to understand how the altered catalyst structure influences reaction performance (activity and selectivity).^{10–15} Titanium, an inexpensive and abundant metal, has recently been identified as a robust electrocatalytic material for NO₃RR.¹⁶ The reasons for its catalytic performance remain unclear, especially regarding the role of titanium hydride (TiH_x, 0 < x ≤ 2), a water-stable titanium species that forms during NO₃RR. The rational operation of Ti-catalyzed NO₃RR requires improved understanding of how TiH_x forms and influences NO₃RR performance.

Metal hydrides have attracted attention for their ability to perform thermal or mechanocatalytic ammonia synthesis from N₂ gas^{17–23} but remain underexplored for aqueous electrochemical ammonia synthesis (e.g., from nitrate). Electrochemical metal hydride formation proceeds at moderate potentials, acting as a side reaction that convolves electrocatalytic performance with an evolving electrode surface structure. Studies on TiH_x have demonstrated either quantitative bulk characterization to determine hydrogen content (e.g., X-ray diffraction,²⁴ weight loss,²⁵ outgassing measurements²⁶) or qualitative to semiquantitative near-surface (topmost nanometers) characterization (e.g., time-of-flight secondary ion mass spectrometry²⁷). Quantitative near-surface characterization has not been reported and is key to overcoming the challenge of decoupling hydride formation from reaction performance. In this work, we combined

systematic synchrotron X-ray characterization of Ti electrodes with electrochemical testing to link near-surface structure (chemical composition, crystal structure, coordination number, and interatomic distance) with NO₃RR performance. Through *ex situ* grazing-incidence X-ray diffraction (GIXRD) and total electron yield X-ray absorption spectroscopy (TEY XAS) measurements, we demonstrated the electrochemically tunable enrichment of near-surface TiH₂ by controlling NO₃RR duration (2 to 8 h) and applied potential (−0.4, −0.6, −0.8, and −1.0 V_{RHE}). These results informed us about the electrochemical treatment of Ti to produce TiH₂/Ti electrodes for use in NO₃RR. Faradaic efficiency (FE) on TiH₂/Ti varied greatly with applied potential for the production of ammonia (38.0% to 74.7%) and nitrite (23.9% to 52.3%) but not hydrogen (<2.6%). Meanwhile, partial current density toward ammonia formation on TiH₂/Ti increased monotonically with applied potential, reaching −1.83 mA cm^{−2} at −1.0 V_{RHE}. A surface Pourbaix diagram for the TiH₂(111) surface was developed from density functional theory (DFT) calculations. Adsorbate free energy diagrams demonstrated that, on TiH₂(111), nitrogen species were competitive with H atoms for adsorption in the experimentally studied potential range (−0.4 to −1.0 V_{RHE}), which may have contributed to the relatively small amounts of hydrogen evolved. Notably, no appreciable difference in NO₃RR rate or selectivity was

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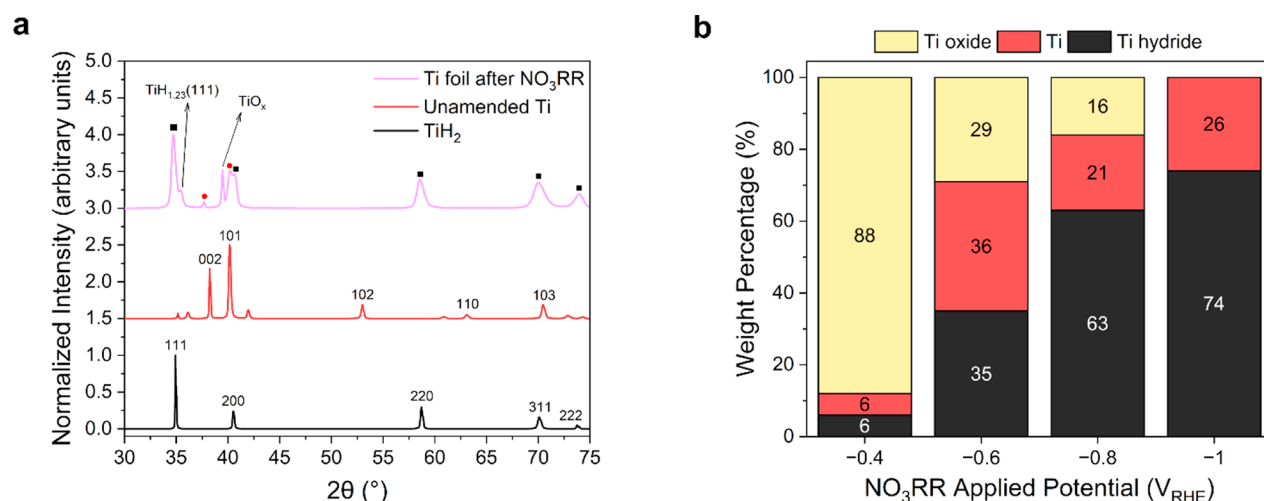


Figure 1. (a) Representative GIXRD of Ti foils before and after electrochemical NO_3RR ($-0.6 \text{ V}_{\text{RHE}}$ for 8 h in $0.1 \text{ M HClO}_4 + 0.8 \text{ mM KNO}_3$) at a nominal probe depth of 3.2 nm. (b) Ti foil chemical compositions calculated from GIXRD after 4 h of NO_3RR ($0.1 \text{ M HClO}_4 + 0.8 \text{ mM KNO}_3$) at varying applied potentials (12.6 nm nominal probe depth).

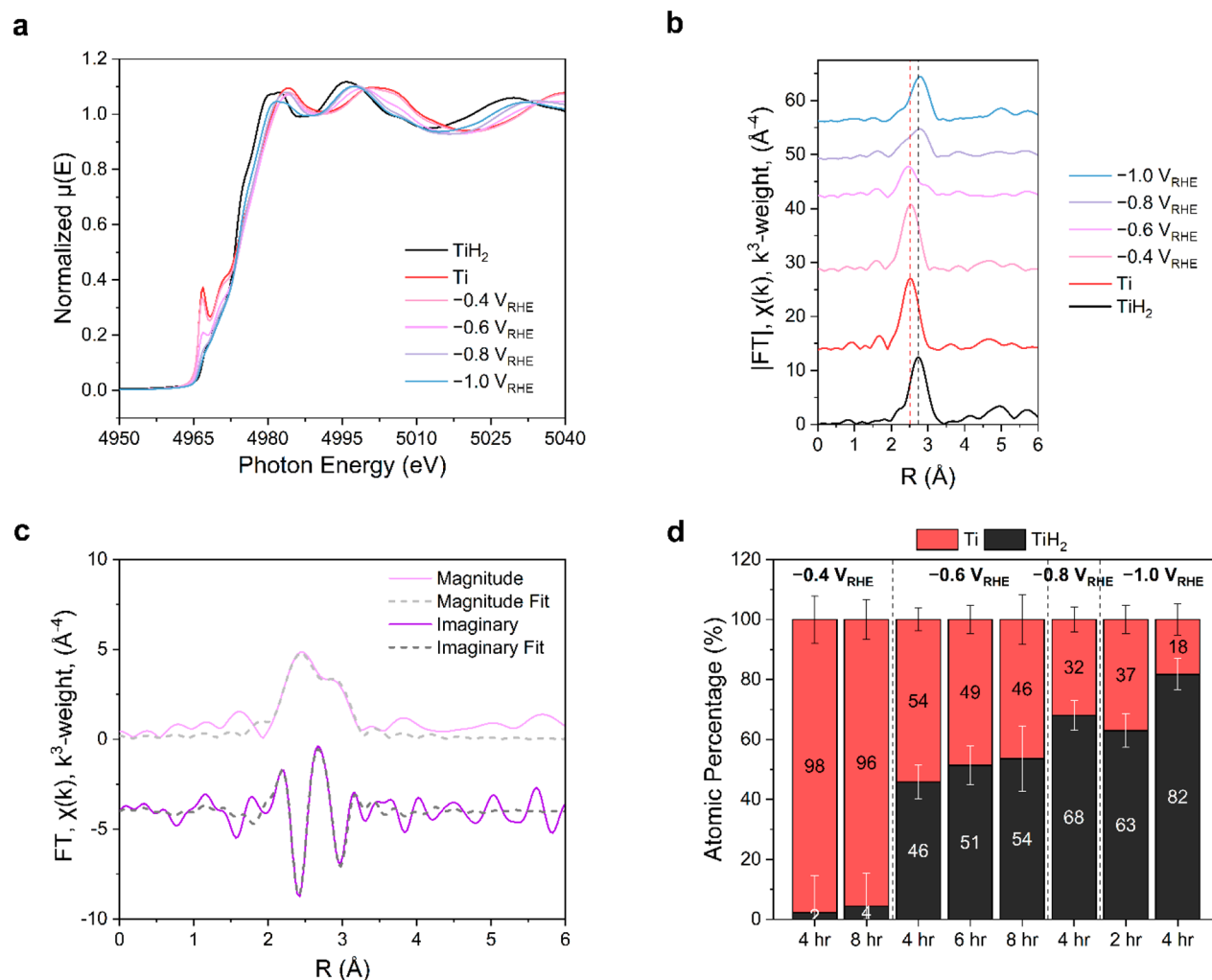


Figure 2. (a) Normalized Ti K-edge XANES characterizing Ti foil cathodes after 4 h NO_3RR ($0.1 \text{ M HClO}_4 + 0.8 \text{ mM KNO}_3$) at different applied potentials. (b) Magnitude of the k^3 -weighted Fourier-transformed EXAFS data calculated using a k -range of $3.3\text{--}11.6 \text{ \AA}^{-1}$. Dashed lines correspond to Ti–Ti single-scattering paths for Ti (red) and TiH_2 (black) references. (c) k^3 -weighted Fourier-transformed EXAFS data and best-fit model characterizing the Ti foil cathode after NO_3RR ($-0.6 \text{ V}_{\text{RHE}}$ for 8 h in $0.1 \text{ M HClO}_4 + 0.8 \text{ mM KNO}_3$). The k -range and R -range used in the fit were $3.3\text{--}11.6 \text{ \AA}^{-1}$ and $1.90\text{--}3.25 \text{ \AA}$, respectively. (d) Ti atomic percentages obtained from the EXAFS modeling. Error bars represent $\pm$ one standard deviation scaled by the regression standard error.

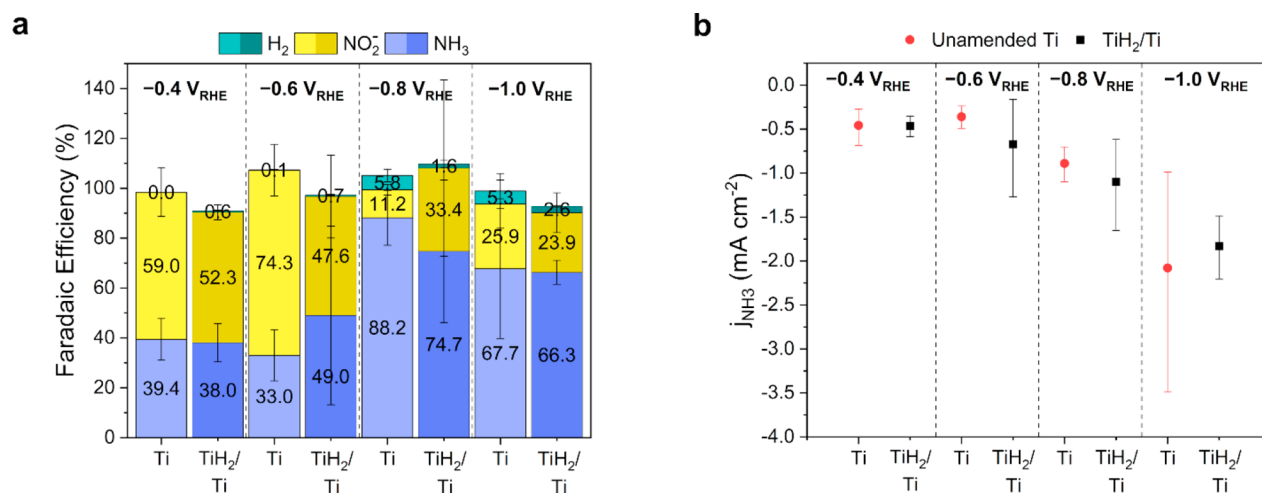


Figure 3. (a) Faradaic efficiencies toward the production of ammonia, nitrite, and hydrogen gas on unamended Ti and TiH₂/Ti electrodes (1 M NaClO₄ + 10 mM HNO₃ electrolyte). Error bars represent $\pm$ one standard deviation. (b) Partial current density toward ammonia production on unamended Ti and TiH₂/Ti electrodes (1 M NaClO₄ + 10 mM HNO₃ electrolyte). Asymmetric error bars come from propagating error (one standard deviation) in total current density and FE_{NH_3} .

observed between unamended Ti (cleaned but not chemically nor electrochemically treated) and TiH₂/Ti electrodes, suggesting that both the rate-determining and selectivity-determining steps were negligibly affected by the initial near-surface structure of the electrodes.

With GIXRD, we characterized the crystalline structure of commercially pure, polycrystalline Ti foil cathodes before and after NO₃RR (experimental matrix in Table S3). α -Ti was the major phase in the diffractograms of unamended Ti foil. Over the course of NO₃RR, the Ti electrodes shared significant and consistent structural alterations across the applied potentials, durations, and nominal probe depths tested (chemical composition estimates from each diffractogram in Figures S4–S15). The α -Ti diffraction peaks decreased in relative peak area, often becoming the nondominant phase (Figure 1a). Meanwhile, diffraction patterns for TiH_x appeared, the most intense of which came from TiH₂ and the less intense of which corresponded to crystalline, substoichiometric TiH_x. Altogether, α -Ti, TiO_x ($0 < x \leq 2$), and TiH_x coexisted in post-NO₃RR electrodes, and no other crystalline titanium species (e.g., titanium nitride) were observed. For a fixed NO₃RR duration and nominal probe depth, a more negative applied potential led to enriched hydride content (Figure 1b). Likewise, longer NO₃RR durations led to enriched hydride content though to a lesser extent than the applied potential.

To complement GIXRD, Ti K-edge TEY XAS measurements (nominal probe depth of 5–10 nm^{28–31}) were used to sample the ensemble average of local Ti coordination environments at the electrode near-surface. The X-ray absorption near-edge structure (XANES, Figure 2a) of unamended Ti showed a characteristic pre-edge peak corresponding to a Ti 1s $\rightarrow$ 3d transition.³² The peak was absent in TiH₂, indicating its cubic (fcc) structure³³ and facilitating TiH₂ assignment in samples of various applied potentials and durations. Ti foil from 4 h of NO₃RR at -0.4 and -0.6 V_{RHE} showed a pre-edge peak similar to that of the Ti foil but diminished in intensity, while analogous samples from NO₃RR at -0.8 and -1.0 V_{RHE} showed no pre-edge peak, suggesting a near-surface structure transition from α -Ti (hcp) to TiH₂ (fcc). In the Fourier transform of the extended X-ray absorption fine structure (EXAFS), a pronounced peak

corresponding to Ti–Ti scattering occurred at 2.52 Å for Ti foil and -0.4 and -0.6 V_{RHE} NO₃RR samples (Figure 2b). This peak was shifted to 2.79 Å for TiH₂ and -0.8 and -1.0 V_{RHE} NO₃RR samples, corresponding to a 10.7% expansion. EXAFS modeling was performed with bonding distance Ti–Ti scattering paths from both Ti and TiH₂ (representative fits in Figure 2c). The resulting coordination numbers from each sample are given in Table S1 and shown as atomic percentages in Figure 2d. XANES, k³-weighted EXAFS, Fourier-transformed EXAFS, and EXAFS fits for the complete set of samples are presented in Figures S24–S36. The number of Ti atoms belonging to TiH₂ consistently increased with both applied potential and duration, while Ti belonging to α -Ti exhibited the opposite trend. In agreement with GIXRD, a more negative applied potential enriched near-surface hydride content more drastically than longer applied durations. For example, more TiH₂ was formed at -1.0 V_{RHE} (2 h) than -0.6 V_{RHE} (8 h). The evident control over the near-surface structure enabled electrochemical treatment of Ti to produce TiH₂/Ti electrodes (Section S3.2 and Figure S37) for use in NO₃RR.

The electrochemical NO₃RR performance of unamended Ti and preformed TiH₂/Ti electrodes was assessed with 30-min chronoamperometry experiments at -0.4, -0.6, -0.8, and -1.0 V_{RHE} (1 M NaClO₄ + 10 mM HNO₃, Section S3.2). GIXRD of unamended Ti electrodes after chronoamperometry showed no TiH_x phase, while the persistence of near-surface TiH₂ was observed on TiH₂/Ti electrodes (Figures S16–S23). Faradaic efficiency toward H₂ (FE_{H_2}) remained below $5.8 \pm 2.5\%$ (Figure 3a), indicating that NO₃RR was the dominant reaction and that TiH₂/Ti electrodes did not introduce appreciable HER competition. Nitrite was the major reaction product at -0.4 and -0.6 V_{RHE} while ammonia dominated at -0.8 and -1.0 V_{RHE} ; negligible N₂ production was observed (50 ppm detection limit). FE_{NH_3} ratios of TiH₂/Ti to unamended Ti showed no significant difference between the applied potentials investigated (Figure S38). The ratios of NH₃ N-selectivity (fraction of reacted nitrate converted to ammonia) followed a similar trend (Figure S39), suggesting that the selectivity-determining step of NO₃RR remained unchanged between unamended Ti and TiH₂/Ti electrodes. An analogous conclusion was reached by examining the

performance metrics for electrocatalytic activity (j_{NH_3} in Figure 3b and nitrate conversion in Figure S40). Several reasons may explain the similar NO_3RR performance. Although both electrodes began with different near-surface structures, *in situ* catalytic conditions may have led to a convergence of surface structure and therefore similar reactivity. Alternatively, the electrode surfaces may have remained distinct, yet other factors played a more dominating role in conferring reaction performance, such as surface roughness or contributions to surface electronic state imparted by the coexistence of Ti, TiO_x , and TiH_x .

To provide insights into the reactivity of TiH_2 , periodic DFT calculations on the thermodynamics of surface coverage were performed using the RPBE xc-functional in the Vienna Ab-initio Simulation Package (Section S4).^{34–36} A surface Pourbaix diagram (Figure 4a, surface and adsorption structures in Figure 4c) was developed for $\text{TiH}_2(111)$, the most intense TiH_2 peak observed via GIXRD, to summarize H^* coverage (θ_{H}) under standard conditions. For TiH_2 , θ_{H} is defined as the coverage of hydrogen following a full monolayer in all available hcp sites. The hydrogen evolution reaction (HER) is thermodynamically favorable over H^* adsorption once the hcp sites become occupied, and if HER is kinetically available, this will lead to a lowering of θ_{H} . From thermodynamics, θ_{H} increases with more negative applied potentials up to a TiH_2 -terminated surface. For a fixed applied potential, θ_{H} may sharply decrease with increasing pH, which we indeed observed in the catholyte for all electrochemical experiments (as drastic as pH 1.70 to 11.85, Figure S41). We therefore hypothesize that transient θ_{H} plays a role in steering the reaction selectivities seen in Figure 3a, such as by controlling hydrogenation of surface intermediates to form NO_x^* and NH_y^* species.^{37,38} Our calculated potential of zero charge (negative of $-1.0 \text{ V}_{\text{RHE}}$ for nearly all θ_{H} , Table S5) leads to a positively charged surface, likely promoting anionic nitrate adsorption, which is often the rate-determining step of NO_3RR .^{7,39} The DFT calculations predict that, regardless of the initial θ_{H} , nitrogen species are competitive for surface sites compared to H (Figure 4b). While molecular nitrate (NO_3^*) exhibits weak adsorption that gets weaker with increasing NO_3RR overpotential, dissociative adsorption into nitrite (NO_2^*) and surface (hydr)oxide, $\text{O}(\text{H})^*$, is favorable. The stability of coadsorbed O^* and OH^* relative to the oxidized $\text{H}_2\text{O}_{(\text{aq})}$ state varies significantly with potential (Figures 4b and S43 for high coverage), and understanding the competition between nitrogen and oxygen surface species may elucidate the potential dependence of NO_3RR products over TiH_2 . Lastly, preliminary DFT calculations on $\text{Ti}(0001)$ indicate that the integral free energies of H^* under one monolayer are lower than the integral free energy to evolve H_2 (Figure S44), implying that unamended Ti will eventually form surface TiH_2 under NO_3RR conditions. The analysis suggests that similar reactivity to TiH_2/Ti electrodes may be conferred to unamended Ti *in situ*; this *in situ* modification may be more influential than *ex situ* pretreatment.

In summary, electrochemical preparation and testing of TiH_2/Ti electrodes was enabled by systematically characterizing the Ti near-surface. Electrochemical experiments paired with DFT calculations indicate that the applied potentials explored in this work correspond to a fundamentally dynamic range of NO_3RR activity and selectivity on TiH_2 . Our investigation advances direct relationships between NO_3RR performance with *ex situ* near-surface electrocatalyst compo-

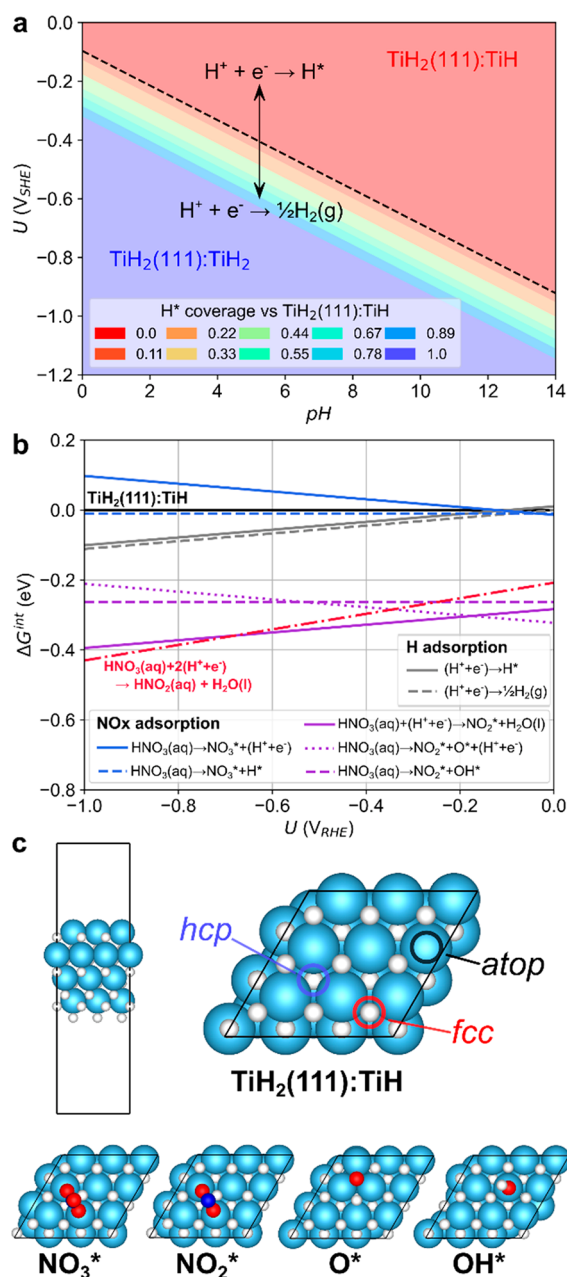


Figure 4. (a) Surface Pourbaix diagram for the $\text{TiH}_2(111)$ surface with TiH termination (Section S4.2 and Figure S42), denoted as $\text{TiH}_2(111):\text{TiH}$. Color scale indicates prevalent surface H^* (hcp site) coverage evaluated on a 3×3 unit cell. The black dotted line indicates where $\text{H}_2(\text{g})$ formation is thermodynamically favored over H^* adsorption. (b) Integral free energy (normalized by number of sites), ΔG^{int} , at the standard state of NO_3RR intermediates for low coverage on $\text{TiH}_2(111):\text{TiH}$. (c) $\text{TiH}_2(111):\text{TiH}$ surface and optimized adsorption structures of NO_3RR intermediates. Adsorption sites on the surface are depicted with additional H^* , preferring the hcp hollow site by 0.58 eV/H over the atop site occupied in epitaxial growth. NO_3^* and NO_2^* adsorb in bidentate mode on the atop sites; O^* sits in the hcp site, and OH^* sits on the atop site.

sition and identifies key opportunities for further research, such as kinetic DFT calculations and *in situ* characterization of Ti electrodes.

■ ASSOCIATED CONTENT

SI Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/jacs.2c01274>.

Experimental details; supporting tables; data processing and fitting; DFT methodology; additional GIXRD, XAS, and electrochemical data (PDF)

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Notes

The authors declare no competing financial interest.

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