Selective electrochemical reduction of nitric oxide to hydroxylamine by atomically dispersed iron catalyst

Dong Hyun Kim¹,⁸, Stefan Ringe²,⁸, Haesol Kim¹, Sejun Kim³, Bupmo Kim⁴, Geunsu Bae¹, Hyung-Suk Oh⁵, Frédéric Jaouen⁶, Wooyul Kim⁷, Hyungjun Kim³ & Chang Hyuck Choi¹

Electrocatalytic conversion of nitrogen oxides to value-added chemicals is a promising strategy for mitigating the human-caused unbalance of the global nitrogen-cycle, but controlling product selectivity remains a great challenge. Here we show iron-nitrogen-doped carbon as an efficient and durable electrocatalyst for selective nitric oxide reduction into hydroxylamine. Using in operando spectroscopic techniques, the catalytic site is identified as isolated ferrous moieties, at which the rate for hydroxylamine production increases in a super-Nernstian way upon pH decrease. Computational multiscale modelling attributes the origin of unconventional pH dependence to the redox active (non-innocent) property of NO. This makes the rate-limiting NO adsorbate state more sensitive to surface charge which varies with the pH-dependent overpotential. Guided by these fundamental insights, we achieve a Faradaic efficiency of 71% and an unprecedented production rate of 215 μmol cm⁻² h⁻¹ at a short-circuit mode in a flow-type fuel cell without significant catalytic deactivation over 50 h operation.
The nitrogen-cycle is vital for sustainability of the terrestrial, marine, and atmospheric ecosystems on Earth, and comprises the key stages of nitrogen fixation-nitrification-denitrification. However, the large-scale intensification of a fertiliser-dependent agriculture and the massive combustion of fossil fuels have significantly unbalanced Nature's nitrogen-cycle. The anthropogenic inflow of nitrogen oxides (NOx) leads to its fast accumulation, causing serious environmental and health problems. Therefore, the electrocatalytic reduction of NOx from renewable energy is a promising strategy to bring the nitrogen-cycle back into balance, alleviating NOx accumulation and at the same time producing useful chemicals. In particular, hydroxylamine (NH2OH) is an interesting compound, involved in the production of caprolactam (the base chemicals for the nylon industry) as well as a potential hydrogen-carrier for the renewable energy society.

In the series of nitrogen reduction steps starting from nitrate, the catalytic reduction of nitric oxide (NO) is a key step to allow for the further reduction of nitrogen, determining the nature of the further-reduced nitrogen products (e.g., N2O, NO, NH2OH, and NH3). Noble metal electrocatalysts such as Pt and Pd typically produce N2O/N2 (low overpotential region) and NH2OH/NH3 (high overpotential region) from the NO reduction reaction (NORR). Meanwhile, some non-noble organometallic complexes (e.g., metallo-porphyrin/phthalocyanine (Pc) complexes, vitamin B12, and Prussian blue) catalyse the NORR primarily to NH2OH and NH3. In contrast, heme proteins (e.g., myoglobin and haemoglobin) mainly produce N2O, in spite of their structurally similar active sites (i.e., Fe–N3 core). This astounding difference in NORR selectivity despite similar core active site structure was also observed in biological systems. For instance, enzymatic NO reduction by cytochrome P450nor (single-heme) and nitrite reduction by cytochrome ε nitrite reductase (multi-heme), despite identical NO–FeII(N) intermediate adduct structures, lead to N2O and NH3, respectively.

Much effort has thus been devoted to identifying the physicochemical parameters that govern the NORR selectivity on single-site and metallic surfaces. Improved understanding on the NORR electrocatalysis by heme (iron protoporphyrin IX) has been reached via its controlled immobilisation on a graphite surface. Two different NORR pathways were identified: pH-dependent (NH2OH formation) and pH-independent (N2O formation) pathways, the selectivity of which is affected by electrolyte pH, NO concentration, and electrode potential. By controlling these experimental parameters, highly selective NO-to-NH2OH conversion was also achieved with a rotating disk electrode (RDE) setup. Along with the fundamental backgrounds, electrochemical NH2OH synthesis has also been demonstrated at device-level with catalysts incorporating heme-like moieties. Further progress is however still needed to improve its productivity and to secure operational durability for practical applications. For instance, unlike the broad range pH (2–12) typically applicable for half-cell studies, NH2OH production at device-level (e.g., the H2–NO fuel cells) requires strongly acidic electrolytes (3–5 M, pH < 0) to suppress a competitive N2O production. Although rapid catalytic deactivation would be expected due to the dissolution of the coordinated metal ion in such highly corrosive conditions, catalytic stability for NORR has hitherto been underinvestigated. Therefore, the development of new catalytic materials with high activity, selectivity, and stability is the next challenge for the success of NH2OH production from the artificial electrochemical denitrification.

Herein, we have studied the NORR electrocatalysis of a single-atom Fe catalyst, in which the heme-like active FeNCx moieties covalently bonded to the carbonaceous substrate (i.e., Fe–N–C catalyst). Because the FeNCx moieties in this catalyst were shown to not suffer from strong Fe demetallation in the acidic electrolytes, this well-defined catalyst has provided a suitable platform for both fundamental understandings and device-level operations of FeNCx moieties under highly corrosive reaction conditions. The NORR selectivity and the nature of catalytic sites have been investigated by advanced ex/in situ analytical approaches combined with computational electrolyte-aware density functional theory (DFT) calculations and micro-kinetic modelling. Finally, we achieved effective and durable NH2OH production on the single-atom Fe catalyst in a prototypical H2–NO fuel cell reactor.
conversion is the main NORR pathway on FeNC-dry-0.5 in the 1st reduction region. Below 0.2 \( V_{\text{RHE}} \), however, the NORR current density \( j_d \) further increases on FeNC-dry-0.5 and the polarisation curve shows a well-defined plateau at \(<0.05 \ V_{\text{RHE}} \) (Fig. 1a). The \( j_d \) value is ca. 5.2 (±0.2) mA cm\(^{-2}\), which is approximately three times the \( j_d \) value observed for Pt. This suggests that the main NORR product in this region is a three-electron reduction of NO (Supplementary Note 2), corresponding to NH\(_2\)OH. To confirm this, rotating ring disk electrode (RRDE) experiments were carried out. The Pt ring oxidises both NH\(_2\)OH and NO at \( >0.9 \ V_{\text{RHE}} \) (Supplementary Fig. 10), while NH\(_3\) oxidation is almost inactive, in agreement with previous studies\(^{21,22,38}\). During LSV of the FeNC-dry-0.5 disk in the NO-saturated electrolyte, the Pt ring current \( i \) was recorded at a constant potential of 1.4 \( V_{\text{RHE}} \) (Supplementary Fig. 1c). The plateau of Pt ring current of ca. 0.55 mA at disk potentials \( >0.6 \ V_{\text{RHE}} \) (no NORR on FeNC-dry-0.5), is attributed to NO oxidation on the Pt ring. The ring current decreases when the disk potential is polarised within the 1st reduction region, due to NO consumption on the disk (i.e., NO-to-N\(_2\)O conversion). When the disk potential is set within the 2nd reduction region, however, the Pt ring current increases again, reaching an absolute value even surpassing that observed when the NO concentration in the electrolyte is maximum (i.e., no NORR, \( >0.6 \ V_{\text{RHE}} \)). This indicates that the NORR products formed on FeNC-dry-0.5 in the 2nd reduction region are oxidisable on the Pt ring, which according to the potential window should be associated with NH\(_2\)OH rather than H\(_2\) or N\(_2\)O. Here, NO-to-N\(_2\)H\(_4\) conversion and its subsequent oxidation on the Pt ring could also be ruled out because of no considerable Pt ring current during the RRDE study performed at a Pt ring potential of 0.8 \( V_{\text{RHE}} \), at which only N\(_2\)H\(_4\) (not NO, NH\(_3\), and NH\(_2\)OH) can be oxidised (Supplementary Fig. 10).

However, these analytical approaches failed to provide quantitative information in NORR selectivity because of the unknown number of electrons transferred during NH\(_2\)OH oxidation on Pt. Thus, we compared LSV responses of the Pt ring with and without concurrent NORR on the FeNC-dry-0.5 disk (Fig. 1d)\(^{21}\). On the Pt ring, NO is reduced to N\(_2\)O in 0.8–0.25 \( V_{\text{RHE}} \), but reductions of other species (i.e., NH\(_2\)OH and NH\(_3\)) are inactive (Supplementary Fig. 10). When the disk is polarised at 0.05 \( V_{\text{RHE}} \) and consumes the NO, NO reduction current on the Pt ring decreases by ca. 0.08 mA due to consequent decrease in local concentration of NO at the ring electrode. Assuming 100% NH\(_2\)OH selectivity on the FeNC-dry-0.5 disk, the current decrement corresponds to a collection efficiency of ca. 0.42 (Supplementary Note 3), which is in agreement with the value we calibrated (Supplementary Fig. 10). Therefore, a series of SFC/DEMS and R(R)DE studies confirm that N\(_2\)O and NH\(_2\)OH are main products on the FeNC-dry-0.5 at the 1st and 2nd NORR regions, respectively.

**Confirmation of the nature of the active site.** To understand the nature of catalytic sites in NORR, we introduced a set of Fe–N–C catalysts comprising different contents of Fe\(_n\)N\(_x\)C\(_y\) moieties and bulk Fe particles. The control catalysts were named ‘FeNC-dry-1’ and ‘FeNC-wet-1’, which were prepared as FeNC-dry-0.5 but with a two-fold higher Fe content in the precursor mixture and, for FeNC-wet-1, addition of a step for the aqueous complexation of Fe and phen, before milling the dried catalyst precursor (see details in Methods section)\(^{35}\). A distinct property of the control catalysts compared to FeNC-dry-0.5 is the presence of metallic iron and Fe\(_3\)C (Supplementary Note 1). The quantitative analysis of their \(^{57}\)Fe Mössbauer spectra identified that FeNC-dry-1 contains only ca. 0.2 wt% Fe particles and 2.8 wt% Fe\(_n\)N\(_x\)C\(_y\),
moieties while FeNC-wet-1 contains ca 1.2 wt% Fe particles and 2.2 wt% FeNₓCₓ moieties (Supplementary Table 1). Due to the ability of Fe particles to catalyse graphitisation at the pyrolysis temperature, such Fe particles are surrounded by graphene shells (Supplementary Fig. 1), partially protecting them from immediate dissolution in acid medium. A N-doped carbon without any Fe intentionally added during synthesis (named ‘NC’) was also investigated as a third control.

LSV measurements for all the Fe–N–C catalysts revealed considerable NORR activity, while the NC produced a significantly lower current which did not reach the j₀ for N₂O formation (i.e., ca. 1.8 mA cm⁻²) even at −0.2 V RHE (Fig. 2a). In addition, SFC/DEMS analysis showed N₂O production on NC over the whole potential range, while it was limited to the 1st reduction region on all the Fe–N–C catalysts (Fig. 2b and Supplementary Fig. 8). Overall, this reveals that Fe plays a pivotal role in critically enhancing the NORR activity, enabling also the formation of highly reduced products such as NH₂OH. Otherwise, comparable NORR polarisation curves among the all Fe–N–C catalysts suggest an insignificant catalytic role of Fe particles. From the high NORR activity of FeNC-dry-0.5 (solely consisted with FeNₓCₓ moieties) and its significant deactivation in the presence of cyanide anion (Fig. 2a), the isolated Fe moieties were thus indicated as the main catalytic sites in NORR.

In addition, a potential-dependent shift in the Fe K-edge X-ray absorption near edge structure (XANES) spectra of FeNC-dry-0.5 was identified (Fig. 2c), similar to previous findings on other Fe–N–C catalysts in oxygen reduction reaction (ORR)⁴⁰. Coupled with voltammetric signals of electrochemical redox transition at ca. 0.6 V RHE (Supplementary Fig. 12), the spectral change refers to an average modification of the oxidation state from FeIIINₓCₓ (for surface located moieties) to FeIIINₓCₓ under NORR conditions, evidencing that the latter is the NORR active sites, similar as for molecular Fe catalysts²¹,²²,²³,²⁸.

pH-dependence and product selectivity. Motivated from the pH-dependent NORR selectivity of heme-immobilised electrode²¹–²³, NORR electrocatalysis of FeNC-dry-0.5 under various pH conditions was investigated. At an electrolyte pH 0, the NORR polarisation is highly suppressed in the 1st reduction region (Fig. 2d). As the electrolyte pH increases, however, NORR in the 1st reduction region becomes magnified with a substantial activity decay in the 2nd reduction region. For a quantitative comparison, we depicted the NORR activity in each reduction region by the half-wave potentials (E₁/₂; Supplementary Fig. 13), which were then plotted as a function of the electrolyte pH (Fig. 2e). On an RHE scale, a linear change of the E₁/₂ value can be seen for the 1st reduction region with a slope of ca. 50 mV pH⁻¹, corresponding to a pH-independence of the NO-to-N₂O pathway. In contrast, we found almost identical E₁/₂ values in the 2nd reduction region (NO-to-NH₂OH pathway) at pH 0 and 1, suggesting a Nernstian behaviour with a proton transfer (PT) to be limiting the conversion. This trend is qualitatively consistent with that of heme-based electrocatalysts²¹–²³, showing pH-dependent/independent NORR to NH₂OH/N₂O, respectively.

Interestingly, however, the pH-E₁/₂ correlation in the 2nd reduction region reveals an unusual negative slope at pH > 1. Along with the LSV data showing significant decrement of j₀ in the 2nd reduction region as the pH increases (pH 2 and 3 in particular; Fig. 2d), the negative slope suggests that decreased proton concentration significantly slows down the NO-to-NH₂OH pathway beyond the expected Nernstian behaviour. This is supported by the SFC/DEMS study, showing almost no N₂O signal at pH 0 throughout the entire potential range, but significant N₂O signal over a broad potential range (even at −0.2 V RHE at pH 3) as the pH increases (Fig. 2f and Supplementary Fig. 14). This indicates unfavourable NH₂OH formation at high pH. Therefore, it can be concluded that N₂O and NH₂OH productions compete in NORR electrocatalysis by FeNC-dry-0.5,
and their selectivity is strongly influenced by both the electrode potential and the electrolyte pH.

**NORR mechanism and the origin of non-Nernstian behaviour.** To understand the NORR mechanism, we performed advanced DFT calculations. For details, the reader is referred to Supplementary Note 4. In short, we relaxed several adsorbate geometries on the Generalised Gradient Approximation level using the revised Perdew–Burke–Ernzerhof (RPBE) functional\(^{11}\), where the effect of double-layer charging was included by means of an implicit solvent and a planar counter charge description for the Helmholtz layer (see Supplementary Fig. 15 for the optimised structures). This provided intermediate binding free energies as a function of surface charge density/potential (Supplementary Table 2 and Supplementary Figs. 16 and 17). Adsorption energies were further corrected by use of the hybrid Heyd–Scuseria–Ernzerhof (HSE06) functional (see Supplementary Note 4 including Supplementary Figs. 17–20 for a full sensitivity analysis of the functional choice\(^{12}\), which were then employed to develop a micro-kinetic model for the prediction of polarisation curves as a function of pH (see details in Methods and Supplementary Note 4). The calculated partial current densities for producing \(\text{NH}_2\text{OH}, \text{NH}_3\), and \(\text{N}_2\text{O}_2\) at pH 0 and 3 are shown in Fig. 3a as a function of applied potential on an RHE scale (see also Supplementary Note 4 for a discussion of the kinetic model sensitivity including Supplementary Figs. 21 and 22). Also, the corresponding reaction mechanism with rate-limiting steps is shown in Fig. 3b as obtained from the following analysis of the micro-kinetic modelling results and the free energy diagram in Fig. 3c (see also free energy diagram and rate-limiting step analysis in Supplementary Fig. 19).

Using the electrochemical DFT approach and Bader charge analysis, we first found all adsorbates despite \(\text{NH}_3\) and \(\text{NH}_2\text{OH}\) to exhibit a partially negative charge under negative electrode polarisation which we indicate by the superscript \(\delta^–\) (see Supplementary Fig. 23 for the Bader charge analysis).\(^{43}\) In addition, the in situ XANES measurement (Fig. 2c) indicated an oxidation state of 2+ for the Fe centre. Bader charge calculations showed that the partial charge of the Fe centre marginally varies upon charging the surface (Supplementary Fig. 24). We thus conclude that Fe is always in the oxidation state 2+ throughout the reaction and denote e.g. the adsorption state of NO with Fe\(^{11}\)-NO\(^{\delta^–}\).

From micro-kinetic modelling and a degree of rate-control analysis (Supplementary Fig. 19), we found \(\text{N}_2\text{O}\) production to be limited by Fe\(^{11}\)-\(\text{N}_2\text{O}_2\)\(^\delta^–\) formation. Previously, a decoupled electron transfer step to form NO\(^–\) was suggested as rate-determining step (RDS) for \(\text{N}_2\text{O}\) production\(^{22}\). Electron transfer on conducting materials is, however, likely too fast to resemble a RDS\(^{44}\). Instead, we suggest here a modified scenario based on charge redistribution driven by double layer electric field interaction. At the potential of zero charge (PZC), we find the NO adsorbed to the iron centre is nearly neutral judging based on the Fe–N–O angle of 150° (Supplementary Fig. 24). In going to more negative potentials, however, the additional charge yields to a partially reduced NO (Supplementary Figs. 23 and 24). In consistence with the previous understanding that NO\(^–\) can easily form an N–N bond with another NO molecule\(^{45}\), NO coupling becomes energetically favourable when the system and consequently also the NO is more negatively charged\(^{46}–48\). This leads to an inversion of relative energies of the Fe\(^{11}\)-NO\(^{\delta^–}\) state and the Fe\(^{11}\)-\(\text{N}_2\text{O}_2\)\(^\delta^–\) state (Supplementary Fig. 16).

To support this mechanism, we performed in situ attenuated total reflection-surface enhanced infrared absorption spectroscopy (ATR-SEIRAS) studies (Fig. 3e–g and Supplementary Fig. 25). The ATR-SEIRAS spectra identified two main bands at ca. 1723 (the high frequency NO; NO\(^{\text{High}}\)) and 1685 cm\(^–1\) (the low frequency NO; NO\(^{\text{Low}}\)) at \(–0.2\) V\(_\text{RHE}\) (Fig. 3e), both of which showed a Stark effect with the slope of ca. 50 cm\(^–1\)V\(^–1\). In addition, the positions of both bands were unchanged by solvent isotope labelling (in \(\text{H}_2\text{O}\) and \(\text{D}_2\text{O}\) solutions; Fig. 3f), indicating that these bands are associated with nonprotonated species. IR bands of organometallic Fe-porphyrin complexes observed at ca. 1700 cm\(^–1\) have usually been assigned to the Fe(\(\eta^1\)-NO), where NO is bonded to Fe via nitrogen\(^{49,50}\). Thus, we assigned these to the adsorbed NO species on the Fe centre, i.e., Fe\(^{11}\)-NO\(^{–}\). Also, considering the high sensitivity of the NO vibration frequency to the local chemical environment\(^{13–15,53}\), the presence of two separate bands implies that there exist (at least) two chemically inequivalent Fe\(^{11}\)-NO\(^{\delta^–}\) species. However, these bands are separated by only ca. 40 cm\(^–1\), and no appreciable signal was shown below 1600 cm\(^–1\). Thus, the possibility of different binding modes such as \(n^1\)-ON and \(n^2\)-NO could reasonably be excluded\(^{51}\). Instead, slightly more reduced NO forming a more bent Fe–N–O geometry may explain the band at the lower frequency (NO\(^{\text{low}}\)). Furthermore, the integrated peak intensities of both bands increased with decreasing an applied bias, inferring the increase of more Fe\(^{11}\)-NO\(^{\delta^–}\) species at lower potential (Fig. 3g). The super immediate Fe\(^{11}\)-NO\(^{\delta^–}\), which is predicted to exist with a high coverage below \(0.2\) V\(_\text{RHE}\) (Supplementary Fig. 19), is spectroscopically confirmed.

Since the formation of Fe\(^{11}\)-\(\text{N}_2\text{O}_2\)\(^\delta^–\) does not involve a PT, it is pH-independent on a SHE scale (Supplementary Fig. 21). On an RHE scale, we thus saw the expected Nernstian overpotential shift of ca. 59 mV \(\times \Delta\text{pH} = 178\) mV when going from pH 0 to 3 (Fig. 3a), in agreement with the experimental results in the 1st reduction region (Fig. 2e). The production of \(\text{NH}_2\text{OH}\) and \(\text{NH}_3\), however, is limited by a proton-coupled electron transfer (PCET) step to Fe\(^{11}\)-NO\(^{\delta^–}\) (Supplementary Fig. 19), and thus showed a strong pH-dependence on an SHE scale (Supplementary Fig. 21). Interestingly, however, we found the pH-induced overpotential shift to be larger than the expected 178 mV. In consequence, even after correcting for this shift by plotting the data on an RHE scale (Fig. 3a), we still observed a decrease of the reaction rate with increasing pH.

Such a non-Nernstian behaviour is originated from differences in the surface charge dependence of intermediate binding energies (Supplementary Fig. 16). At a higher pH (for a fixed potential on RHE scale), the corresponding potential in the SHE scale is more negative, which increases the surface charge. The stronger stabilisation of Fe\(^{11}\)-NO\(^{\delta^–}\) with negative charge relative to the following Fe\(^{11}\)-\(\text{NHO}\)\(^{\delta^–}\) state (Supplementary Fig. 16), increases the overall reaction barrier at fixed RHE potential (Fig. 3c). This super-Nernstian decrease of the reaction rate with increasing pH explains the experimentally observed pH dependence (Fig. 2e) and underlines the role of surface charge in controlling product selectivity.

We further elucidate that the redox non-innocent property of nitrosyl ligand originates the particularly strong surface charge stabilisation of the NO\(^*\) intermediate. With changing the redox state of nitrosyl ligand from NO\(^+\) to NO\(^–\), the metal–N–O angle is known to vary from the linear geometry (as stabilised by the \(\pi\)-back bond; Supplementary Fig. 26) to the bent geometry (as stabilised by the \(\sigma\)-forward bond; Fig. 3d (RPBE) and Supplementary Fig. 27 (HSE06)).\(^{55}\) When the surface is negatively charged, the Fermi energy increases and the occupation of the NO \(\pi^*\) orbital also increases, yielding an enhanced NO\(^–\) character as evidenced from the decrease in Fe–N–O angle (Supplementary Fig. 24). At higher cathodic overpotential, thus, the nitrosyl ligand becomes more reduced, and thus more effectively stabilised by forming the stronger Fe–N \(\sigma\)-forward bond. This results in the surface charge dependence of the
FeII–NOδ− intermediate, yielding the super-Nernstian behaviour during NH₂OH production.

Additionally, it is important to mention that the presence of a finite surface charge does not always stabilise the adsorbate states (Supplementary Fig. 16). As an example, unlike to the FeII–NOδ− state, the FeII–NH3 state has an anti-bonding singly occupied (highest) MO (SOMO) (Supplementary Fig. 28). Filling of this SOMO results in a destabilisation at more negative potentials. This indicates that charge stabilisation is a complex function of the electronic structure of adsorption states, and thus a quantum-
mechanical level of simulation reflecting the finite bias potential effect is a necessity for a comprehensive understanding of the electrochemical reaction mechanism.

**NH$_2$OH production in a flow-type H$_2$-NO fuel cell.** To confirm the NH$_2$OH production in a fuel cell with FeNC-dry-0.5, a H-type flow cell with gas-diffusion electrode (GDE) was employed as a prototype reactor (Supplementary Fig. 29). An Ar-saturated 1 M HClO$_4$ electrolyte was introduced into the cathode compartment, directly connected to ion chromatography (IC) for online monitoring of NH$_3$ and NH$_2$OH production. NH$_2$OH production is detected at a cell voltage ($V_{\text{cell}}$) below 0.17 V ($E_{\text{cathode}} = 0.2$ V$_{\text{RHE}}$), and its Faradaic efficiency ($\text{FE}_{\text{NH2OH}}$) reaches 60–70% as $V_{\text{cell}}$ further decreases (Fig. 4a, b and Supplementary Fig. 30). NH$_3$ production is also found at $V_{\text{cell}}$ below 0.06 V ($E_{\text{cathode}} = 0.1$ V$_{\text{RHE}}$), while $\text{FE}_{\text{NH3}}$ is as low as <7%, verifying highly selective NO-to-NH$_2$OH conversion on FeNC-dry-0.5 over NO-to-NH$_3$.

However, the overall FE of NH$_2$OH and NH$_3$ is lower than 75%. The remainder is consequently assigned to N$_2$O production, which becomes magnified or diminished as the electrolyte acidity decreases (0.1 M; Supplementary Fig. 31) or increases (3 M; Supplementary Fig. 32), respectively. This result is qualitatively in accordance with the data measured in the half-cell setup (Fig. 2d–f). Despite the enhanced $N_2$O formation, FeNC-dry-0.5 demonstrates a successful NH$_2$OH production of ca. 105 μmol h$^{-1}$ cm$^{-2}$ at a short-circuit condition (i.e., $V_{\text{cell}} = 0$ V), which is one of the highest values reported in literature (Fig. 4c and Supplementary Table 3), although much milder condition (1 M HClO$_4$) was employed in this work. Notably, the cell operation with a strong acid electrolyte of 3 M HClO$_4$, i.e., similar condition with that in literature, verifies remarkable NH$_2$OH production rates of ca. 215 and 519 μmol h$^{-1}$ cm$^{-2}$ at short-circuit and electrolysis ($V_{\text{cell}} = -0.24$ V) modes, respectively.

A durability test at the short-circuit condition reveals an initial current density of ca. $-16$ mA cm$^{-2}$ (Fig. 4d), while it rapidly declines by ca. 25% for the first 5 h operation and the decay is mitigated afterward. However, NORR selectivity is almost untouched throughout the 50 h period, showing a stable $\text{FE}_{\text{NH2OH}}$ of ca. 61%. Considering a fact that a destruction of active FeN$_x$Cy moieties or nearby carbon surface significantly alters reaction selectivity as well-exemplified in ORR and CO$_2$ reduction cases$^{36,37}$, catalytic degradation could be ruled out as a major cause of the current density decay. The good catalytic stability of FeNC-dry-0.5 was also corroborated by the RDE studies (Supplementary Fig. 33), showing stable NORR over 10 h measurement. Meanwhile, a fully wetted catalyst layer (i.e., decrement in its hydrophobicity) and small leakage of electrolyte through the GDE were found after the durability test (Supplementary Fig. 34). This suggests that the initial current density decay may be attributed to partial electrolyte flooding into the GDE, leading to the blockage of diffusion path for NO gas and consequently to the partial loss of the triple-phase-boundary. However, the single-cell operation with this prototype reactor successfully validates the potential of practical NO-to-NH$_2$OH conversion on FeNC-dry-0.5 over FeN$_x$Cy moieties with high selectivity and catalytic stability, and brings hope for durable operation in a device-level if rational systematic strategies minimising the electrolyte flooding in GDE are developed$^{38,39}$.

**Discussion**

In summary, we presented a novel single-atom Fe catalyst for efficient NH$_2$OH production from electrochemical NO reduction. By performing detailed electrochemical analysis, we identified the catalytic site to be electrogernated Fe$^{3+}$/N$_x$Cy moieties. From a combination of in operando spectroscopy and electrochemical hybrid-level DFT-based multiscale modelling, we further obtained full mechanistic details about the NH$_2$OH and N$_2$O production mechanism.
production pathways and their pH dependence. Further, we revealed an intriguing super-Nernstian pH dependence of the NH₃-NO₃ pathway which originates from the redox non-innocent character of NO. The resulting surface charge sensitivity of the Fe₃⁺–NO₃⁻ state leads to an increased sensitivity to the over-potential changes that occur by varying the pH conditions. We then finally validated the potential of practical NO-to-NH₃ conversion on the isolated FeNₓCₙ moieties also in a fuel cell device showing unprecedented long-term stability and performance. Along with the obtained detailed mechanistic insights, which will be invaluable for the development of future NO reduction catalysts, the presented excellent performance metrics in device-level will provide an important stepping stone towards the technological development of fully sustainable electro-synthesis of valuable nitrogen products from electrochemical nitrate/nitrite denitrisation, which is environmentally vital for balancing the disturbed global nitrogen-cycle.

**Methods**

**Catalyst synthesis.** FeNC-dry-0.5 and FeNC-dry-1 catalysts were prepared from the Fe(ac)₂ acetate (95%, Sigma-Aldrich), phen (≥99%, Sigma-Aldrich), and ZIF-8 (≥99%, Sigma-Aldrich). Based on the precursor mixture containing 0.5 and 1.0 wt% Fe with a mass ratio phen/ZIF-8 of 20/80, the precursor mixture was pyrolysed at 1323 K in Ar (5N, Daedeok) for 1 h, leading to FeNC-dry-0.5 and FeNC-wet-1, respectively. Active site density of FeNC-dry-0.5 estimated with the Fourier transforms of the EXAFS signals were finally validated the potential of practical NO-to-NH₃ catalysts was deposited on a Ni mesh grid coated with a carbon–polytetrafluoroethylene (PTFE) membrane, which was positioned ca. 100 μm away from the electrode, and introduced into the vacuum system of the mass spectrometer. Working electrode was prepared by depositing the catalyst inks onto GC electrode (0.07 cm², 011169, ALS) with a catalyst loading of 200 μg cm⁻². During the measurements, the ion currents from NO, N₂O, H₂, and N₂ were monitored at a potential range of 0.6 to 0.2 V Ag/AgCl in a potential of the Pt ring electrode (10 mV s⁻¹ 1600 μA) was collected during a cathodic scan of FeNC-dry-0.5 disk electrode from 0.8 to −0.2 VAg/AgCl in NO-saturated 0.1 M HClO₄. Otherwise, LSV polarisation of the Pt ring from 0.8 to 0.25 VAg/AgCl was gathered with potential hold of the disk electrode at 0.05 VAg/AgCl or OCP. A collection efficiency of the RRDE electrode was estimated with 2 mM KCl (≥99%, Sigma-Aldrich) dissolved in an Ar-saturated 0.1 M KNO₃ (≥99%, Sigma-Aldrich) electrolyte at rotation speeds of 100, 400, 900, 1600, and 2500 rpm. CV of the disk was measured in a potential range of 0.6 to −0.2 VAg/AgCl with a potential hold of the Pt ring at 0.6 VAg/AgCl. The square-wave voltammogram was measured in a potential range of 0.05 to −1.2 VRHE with a step potential of 10 mV, a scan frequency of 50 mHz in an Ar-saturated 0.1 M HClO₄ containing 0.5 mM NaF electrolyte. Chronoamperometry of the NC catalysts was performed at fixed current density of −3.5 mA cm⁻² for 10 h. For stability comparison with typical molecular catalysts, heme (95%, TCI) and iron phthalocyanine (FePc, 90%, Sigma-Aldrich) was grafted on multi-walled carbon nanotube (Carbon Nanomaterial Technology Co.) with a 1.5 wt% Fe loading (i.e., identical to the Fe content of the FeNC-dry-0.5), and their NORR polarisation was measured. The PZC of FeNC-dry-0.5 was measured using staircase potentiostatic electrochemical impedance spectroscopy. The measurement was performed in an Ar-saturated 10 mM NaFe electrolyte from −1.2 to 0.8 VAg/AgCl at 10 mHz frequency and with a 10 mV potential amplitude.

**In situ and operando spectroscopic analyses.** The online DEMS studies were carried out with the SFC directly connected to mass spectroscopy (Max 300 LG, ExCell). The SFC had an U-shaped channel with an opening diameter of 1 cm at the bottom of the cell, where electrochemical contact was made with the working electrode. After a 30 min purge with Ar gas, low boiling point products evaporated through a hydrophobic polytetrafluoroethylene (PTFE) membrane, which was positioned ca. 100 μm away from the electrode, and introduced into the vacuum system of the mass spectrometer. Working electrode was prepared by depositing the catalyst ink onto GC electrode (0.07 cm², 011169, ALS) with a catalyst loading of 200 μg cm⁻². During the measurements, the ion currents from NO, N₂O, H₂, and N₂ were monitored at a potential range of 0.6 to −0.2 VAg/AgCl and a CV at a 1 mV s⁻¹ scan rate in a potential range of −0.2 to 0.8 VAg/AgCl. For a comparison, a commercial polycrystalline Pt electrode (0.07 cm²) was employed. After the beam calibration with a Pt foil. During the XAS measurements, the ion currents from NO, N₂O, and N₂ were monitored at m/z = 30, 44, 2, and 28, respectively. The NO signal was shown after correction of the initial signal at m/z = 30 by subtraction of 27% signal from m/z = 44 to remove NO₂ contributions at m/z = 30.

The in situ XANES measurements were performed at RIST-PAL beamline (1D) at Pohang Accelerator Laboratory (PAL). A flow-through X-ray spectroscopy (XAS) cell was equipped with an electrolyte flow channel and a window for X-ray radiation. The window was a carbon-coated Kapton film (200μRS100, DuPont, t = 0.05 mm, A = 0.138 cm²), which was directly used as a working electrode after a loading of the FeNC-dry-0.5 (3 mg cm⁻²). Pt wire and Ag/AgCl reference electrodes were connected to the electrolyte outlet. Due to safety issues in PAL, Ar-saturated 0.1 M HClO₄ + 1.5 mM KNO₃ (≥96%, Sigma-Aldrich) solution was used as an electrolyte (no direct NO-bubbling), in which nitrite can be chemically decomposed to NO at such highly acidic conditions⁹⁸. The XAS spectra were collected at a fluorescence mode after the beam calibration with a Pt foil. During the XAS measurements, the FeNC-dry-0.5 catalysts was polarized at constant potentials of 0.1, 0.4, 0.7 VAg/AgCl and OCP with a SP-150 portable potentiostat (Bio-Logic).

The in situ ATR-SEIRAS measurements were performed with an Au thin film-coated Si prism working electrode (Veermax, 2 cm in diameter), which was placed in a quartz cuvette. After the electrochemical activation of the thin film was prepared by an electrolec plating procedure⁹⁸. The working electrode, on which FeNC-dry-0.5 catalyst was deposited, and the Ag/AgCl (Basi, 3 M NaCl)
reference electrode were separated from the Pt wire counter electrode using a Nafion 117 membrane. The cell was integrated into a Fourier transform infrared spectrophotometer (FTIR, VERTEX 70v, Bruker) equipped with a mercury cadmium telluride detector and a variable angle specular reflectance accessory (VeCoaxIII, Pike Technologies). All spectroscopic measurements were conducted at a 4 cm⁻¹ spectral resolution, and the spectra were presented in absorbance mode. NO-saturated 1 mM HClO₄ or 0.1 M KClO₄/H₂O and 1 mM DCOO⁻ + 0.1 M KClO₄/D₂O solutions were used as electrolytes. Potential-dependent IR measurements were carried out during chronoamperometry polarisations between 0.8 and −2.0 V_RHE. The spectrum collected at 0.8 V_RHE was used as the baseline.

H₂–NO single-cell operations. The H-type flow cell was operated with Ar-saturated 0.1, 1, or 3 M HClO₄ solution as both anolyte and a catholyte, which were separated by a Nafion 115 membrane (1.5 x 1.5 cm², DuPont). Flow rate of the electrolyte was ca. 7.3 ± 0.2 μL⁻¹ for each compartment (inner volume = ca. 1.9 cm³ each). On a carbon paper with a 20 wt% PTFE content (3×3 cm², TGP-H, Nippon Carbon), the catholyte outlet was directly connected to online IC (ICS-930, Merck) eluent. Before the single-cell operations, retention time and concentration of H₂ and NH₄⁺ were measured using an HPLC system. Retention time and concentration of NH₄⁺ were measured using an HPLC system.

Before and after the durability test, contact angle on the cathode electrode was measured. A water droplet was placed on the cathode surface, and the contact angle was measured using contact angle measurement software (Labview). Contact angle measurements were carried out at least three times for each sample.

The single-cell operation was performed at room temperature for 1 h at a constant cathode potential, screened from 0.4 to 1.6 V_RHE. The single-cell operation was performed at room temperature for 1 h at a constant cathode potential, screened from 0.4 to 1.6 V_RHE.

Computational methods. DFT calculations of reaction energetics were carried out with a periodic plane-wave implementation and ultra-soft pseudo-potentials using the QUANTUM ESPRESSO version 6.1 on a single Fe–N₄ moiety embedded into a graphene unit cell. The self-consistent continuum solution implicit solvation model as implemented in the Environ QUANTUM ESPRESSO module was used to model the presence of implicit water. The surface charge density was modulated by changing the total charge of the system and a planar counter charge was introduced above the slab to compensate the charge. The relaxed surface states were also re-calculated using the Vienna Abinitio Simulation Package as spin-polarised single point calculations using the PBE+U and HSE06 functionals. Assuming a constant double layer capacitance C₀ (ca. 20 μF cm⁻² for graphene), the surface charge density σ is generated according to σ = C₀(E – PZC), where E is the applied electrode potential and PZC is the PZC which we measured here to characterize the graphene layer.

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

Code availability. The QUANTUM ESPRESSO DFT program package is available from the website https://www.quantum-espresso.org/, the CatMAP micro-kinetic modeling program package from https://github.com/SUNCAT-Center/catmap. Input and output files for both simulation techniques are available from the corresponding authors upon reasonable request.

Received: 5 July 2020; Accepted: 19 February 2021
Published online: 25 March 2021

References

1. Hermann Bothe, Stuart Ferguson & Newton, W. E. Biology of the Nitrogen Cycle 5th Edition. (Elsevier Science, 2006).

2. Delwiche, C. C. The nitrogen cycle. Sci. Am. 223, 137–146 (1970).

3. Battye, W., Aneja, V. P. & Schlesinger, W. H. Is nitrogen the next carbon? Earth’s Future 5, 894–904 (2017).

4. Rockström, J. et al. A safe operating space for humanity. Nature 461, 472–475 (2009).

5. Vitousek, P. M. et al. Human alteration of the global nitrogen cycle: sources and consequences. Ecol. Appl. 7, 737–750 (1997).

6. Langer, S. H. & Pate, K. T. Electrogenerative reduction of nitric oxide. Nature 284, 434–435 (1980).

7. Otsuka, K., Savada, H. & Yamanaka, J. A hydrogen-nitric oxide cell for the synthesis of hydroxylamine. J. Electrochem. Soc. 143, 3491–3497 (1996).

8. Rosca, V., Duca, M., de Groot, M. T. & Koper, M. T. M. Nitrogen cycle electrocatalysis. Chem. Rev. 109, 2209–2244 (2009).

9. Colucci, J. A., Foral, M. J. & Langer, S. H. Nitric oxide reduction at noble metal electrodes: a voltammetric study in acid solution. Electrochim. Acta 30, 1673–1685 (1985).

10. Jansen, L. J. J., Pieterse, M. M. J. & Barendrecht, E. Reduction of nitric oxide at a platinum cathode in an acidic solution. Electrochim. Acta 22, 27–30 (1977).

11. de Vooys, A. C. A., Koper, M. T. M., van Santen, R. A. & van Veen, J. A. R. Mechanistic study on the electrocatalytic reduction of nitric oxide on transition-metal electrodes. J. Catal. 202, 387–394 (2001).

12. Ogura, K. & Yamasaki, S. Electroreduction of nitric oxide to ammonia at chemically modified electrodes. J. Appl. Electrochem. 15, 279–284 (1985).

13. Vilakazi, S. L. & Nyokong, T. Electrocatalytic properties of vitamin B₉ towards oxidation and reduction of nitric oxide. Electrochem. Acta 46, 453–461 (2000).

14. Pan, K. C., Chiang, C.-S., Cheng, S. H. & Su, Y. O. Electrocatalytic reactions of nitric oxide on Prussian blue film modified electrodes. J. Electroanal. Chem. 501, 160–165 (2001).

15. Cheng, S. H. & Su, Y. O. Electroreduction of nitric oxide by water-soluble cobalt porphyrin. Spectr. Electrochim. Stud. Inorg. Chem. 33, 5847–5854 (1994).

16. Bayachou, M., Lin, R., Cho, W. & Farmer, P. J. Electrochemical reduction of NO by myoglobin in surfactant film: characterization and reactivity of the nitrosyl (NO⁻) adduct. J. Am. Chem. Soc. 120, 9888–9893 (1998).

17. Mimica, D., Zagal, J. H. & Bediou, F. Electroreduction of nitric oxide by hemoglobin entrapped in surfactant films. Electrochem. Commun. 3, 435–438 (2001).

18. Nakahara, K., Tanimoto, T., Hatano, K., Usuda, K. & Shoun, H. Cytochrome P-450 55A1 (P450NRD) acts as nitric oxide reductase employing NADH as the direct electron donor. J. Biol. Chem. 268, 8350–8355 (1993).

19. Daiber, A. et al. Isotope effects and intermediates in the reduction of NO by F430, J. Inorg. Biochem. 88, 343–352 (2002).

20. Einsle, O., Messerschmidt, A., Huber, R., Kromeck, P. M. H. & Neese, F. Mechanism of the six-electron reduction of nitrite to ammonia by cytochrome c nitrite reductase. J. Am. Chem. Soc. 124, 11737–11745 (2002).

21. de Groot, M. T., Merkx, M., Wonders, A. H. & Koper, M. T. M. Electrochemical reduction of NO by hemin adsorbed at pyrolic graphite. J. Am. Chem. Soc. 127, 7579–7586 (2005).

22. de Groot, M. T., Merkx, M. & Koper, M. T. M. Heme release in myoglobin–DDAB films and its role in electrochemical NO reduction. J. Am. Chem. Soc. 127, 16224–16232 (2005).

23. de Groot, M. T., Merkx, M. & Koper, M. T. M. Bioinspired electrocatalytic reduction of nitric oxide by immobilized heme groups. C. R. Chim. 10, 414–420 (2007).

24. Katoumaros, I., Figueiredo, M. C., Chen, X., Calle-Vallejo, F. & Koper, M. T. M. Structure- and coverage-sensitive mechanism of NO reduction on platinum electrodes. ACS Catal. 7, 4660–4667 (2017).

25. de Vooys, A. C. A., Koper, M. T. M., van Santen, R. A. & van Veen, J. A. R. Mechanistic study of the nitric oxide reduction on a polycrystalline platinum electrode. Electrochim. Acta 46, 923–930 (2001).

26. Alvarez-Gallego, Y. et al. Development of gas diffusion electrodes for cogeneration of chemicals and electricity. Electrochim. Acta 82, 415–426 (2012).

27. Daems, N., Sheng, X., Alvarez-Gallego, Y., Vankelecom, I. F. J. & Pescarmona, P. P. Iron-containing N-doped carbon electrocatalysts for the cogeneration of hydroxylamine and electricity in a H₂–NO fuel cell. Green. Chem. 18, 1547–1559 (2016).

28. Sheng, X. et al. Carbon-supported iron complexes as electrocatalysts for the cogeneration of hydroxylamine and electricity in a NO–H₂ fuel cell: A combined electrochemical and density functional theory study. J. Power Sources 390, 249–260 (2018).

29. Bediou, F. et al. Design and characterization of chemically modified electrodes with iron(III) porphyrinic-based polymers: Study of their reactivity
toward nitrites and nitric oxide in aqueous solution. Anal. Chem. Acta 341, 172–185 (1997).

30. Immno, C. E. et al. Electrocatatytic reductions of nitrite, nitric oxide, and nitrous oxide by thermophilic cytochrome P450 CYP119 in film-modified electrodes and an analytical comparison of its catalytic activities with myoglobin. J. Am. Chem. Soc. 126, 4934–4942 (2004).

31. Meier, H., Tschirwitz, U., Zimmerhackl, E., Albrecht, W. & Zeitler, G. Application of electrode techniques for the study of phthalocyanine-catalyzed electrochemical processes in fuel cells. J. Phys. Chem. 81, 712–718 (1977).

32. Baranton, S., Coutanceau, C., Roux, C., Hahn, F. & Léger, J. M. Oxygen reduction reaction in acid medium at iron phthalocyanine dispersed on high surface area carbon substrate: tolerance to methanol, stability and kinetics. J. Electroanal. Chem. 577, 223–234 (2005).

33. Espenson, J. H. & Christensen, R. J. Kinetics and mechanism of the demetallation of iron(III) porphyrins catalyzed by iron(II). Inorg. Chem. 16, 2561–2564 (1977).

34. Choi, C. H. et al. Stability of Fe-N-C catalysts in acidic medium studied by operando. Spectrosc. Angew. Chem. Int. Ed. 54, 12753–12757 (2015).

35. Choi, C. H. et al. Unraveling the nature of sites active toward hydrogen peroxide reduction in Fe-N-C catalysts. Angew. Chem. Int. Ed. 56, 8809–8812 (2017).

36. Zito, A. et al. Identification of catalytic sites for oxygen reduction in iron- and nitrogen-doped graphene materials. Nat. Mater. 14, 957–962 (2015).

37. de Vooy, A. C. A., Beltramino, G. L. L., van Veen, J. A. R. & Koper, M. T. M. Mechanisms of electrochemical reduction and oxidation of nitric oxide. Electrochim. Acta 49, 1307–1304 (2004).

38. Halseid, R., Wainright, J. S., Savinell, R. F. & Tunold, R. Oxidation of myoglobin. J. Am. Chem. Soc. 138, 11359–11365 (2016).

39. Hammer, B., Hansen, L. B. & Nørskov, J. K. Improved adsorption energetics of CO and NO in CO-Ni catalysts. J. Phys. Chem. Lett. 4, 354–360 (2013).

40. Zitolo, A. et al. Identification of catalytic sites in cobalt-nitrogen-carbon materials for the oxygen reduction reaction. Nat. Commun. 8, 957 (2017).

41. Hammer, B., Hansen, L. B. & Nørskov, J. K. Improved adsorption energetics within density-functional theory using revised Perdew-Burke-Ernzerhof functionals. Phys. Rev. B 95, 7413–7421 (2019).

42. Heyd, J., Scuseria, G. E. & Ernzerhof, M. Hybrid functionals based on a screened Coulomb potential. J. Chem. Phys. 118, 8207–8215 (2003).

43. Henkelman, G., Arnaldsson, A. & Jónsson, H. A fast and robust algorithm for Bader decomposition of charge density. Comput. Mater. Sci. 36, 354–360 (2006).

44. Gauthier, J. A. et al. Facile electron transfer to CO2 during adsorption at the metal|solution interface. J. Phys. Chem. C 123, 29278–29283 (2019).

45. Shafirovich, V. & Lymar, S. V. Nitroxyl and its anion in aqueous solutions: Spin states, protic equilibria, and reactivities toward oxygen and nitric oxide. Proc. Natl. Acad. Sci. U.S.A. 270 (2007).

46. Sandberg, R. B., Montoya, J. H., Chan, K. & Nørskov, J. K. Electric field effects in electrochemical CO2 reduction. ACS Catal. 6, 7133–7139 (2016).

47. Ringo, S. et al. Understanding cation effects in electrochemical CO2 reduction. Energy Environ. Sci. 12, 3001–3014 (2019).

48. Lin, R. & Farmer, P. J. O atom transfer from nitric oxide catalyzed by Fe(TPP). J. Am. Chem. Soc. 123, 1143–1150 (2001).

49. Cheng, L. et al. First observation of photoinduced nitrosyl linkage isomers of iron nitrosyl porphyrins. J. Am. Chem. Soc. 122, 7142–7143 (2000).

50. Ellison, M. K., Schulz, C. E. & Scheidt, W. R. Structural and electronic characterization of nitrosyl(oc-tacthylylporphinato)iron(III) perchlorate derivatives. Inorg. Chem. 39, 5102–5110 (2000).

51. Ellison, M. K., Schulz, C. E. & Scheidt, W. R. Syntheses, characterization, and structural studies of several (nitro)nitrosyl(iron(III)) porphyrinates: [Fe (Porph)(NO)(N)](NO). Inorg. Chem. 38, 100–108 (1999).

52. Speelman, A. L. et al. Non-heme high-spin [FeNO]6–8 complexes: One ligand platform can do it all. J. Am. Chem. Soc. 140, 11341–11359 (2018).

53. Awasabash, D. & Richter-Addo, G. B. Chapter one - NO, linkage isomerization in metal complexes, in Advances in Inorganic Chemistry Vol. 67 (eds. Rudi van Eldik & José A. Olabe) 1–86 (Academic Press, 2015).

54. Coppen, P., Nowożwiłowa, I. & Kovalyavsky, A. Photoinduced linkage isomers of transition-metal nitrosyl compounds and related complexes. Chem. Rev. 102, 861–884 (2002).

55. Choi, C. H. et al. The Achilles’ heel of iron-based catalysts during oxygen reduction in an acidic medium. Energy Environ. Sci. 11, 3176–3182 (2018).
