Towards Higher NH_3 Faradaic Efficiency
Selective-Poisoning of HER Active Sites by Co-Feeding CO in NO Electroreduction**

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DOI
10.1002/cssc.202300949

Publication date
2023

Document Version
Final published version

Published in
ChemSusChem

Citation (APA)
Li, M., Verkuil, J., Bunea, S., Kortlever, R., & Urakawa, A. (2023). Towards Higher NH_3 Faradaic Efficiency: Selective-Poisoning of HER Active Sites by Co-Feeding CO in NO Electroreduction**. *ChemSusChem*, *16*(22), Article e202300949. https://doi.org/10.1002/cssc.202300949

ChemSusChem
Research Article
doi.org/10.1002/cssc.202300949
Chemistry Europe
European Chemical Societies Publishing
www.chemsuschem.org

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Towards Higher NH_3 Faradaic Efficiency: Selective-Poisoning of HER Active Sites by Co-Feeding CO in NO Electroreduction**

Min Li,[a] Jarco Verkuil,[a] Sorin Bunea,[a] Ruud Kortlever,[b] and Atsushi Urakawa*[a]

Direct electroreduction of nitric oxide offers a promising avenue to produce valuable chemicals, such as ammonia, which is an essential chemical to produce fertilizers. Direct ammonia synthesis from NO in a polymer electrolyte membrane (PEM) electrolyzer is advantageous for its continuous operation and excellent mass transport characteristics. However, at a high current density, the faradaic efficiency of NO electroreduction reaction is limited by the competing hydrogen evolution reaction (HER). Herein, we report a CO-mediated selective poisoning strategy to enhance the faradaic efficiency (FE) towards ammonia by suppressing the HER. In the presence of only NO at the cathode, Pt/C and Pd/C catalysts showed a lower FE towards NH_3 than to H_2 due to the dominating HER. Cu/C catalyst showed a 78% FE towards NH_3 at 2.0 V due to the stronger binding affinity to NO* compared to H*. By co-feeding CO, the FE of Cu/C catalyst towards NH_3 was improved by 12%. More strikingly, for Pd/C, the FE towards NH_3 was enhanced by 95% with CO co-feeding, by effectively suppressing HER. This is attributed to the change of the favorable surface coverage resulting from the selective and competitive binding of CO* to H* binding sites, thereby improving NH_3 selectivity.

Introduction

Ammonia (NH_3) is essential to human society and is one of the most produced inorganic compounds in the world. The annual production of synthetic ammonia in 2021 is over 230 million tons, of which about 80% is applied to chemical fertilizers.[1] NH_3 has also gained great global interest in its use as hydrogen carrier and thus a chemical fuel.[2] Currently, ammonia is mainly synthesized by the Haber-Bosch process in which atmospheric nitrogen reacts with hydrogen at high temperatures (400–500 °C) and high pressure (200–300 atm).[3] This widely employed process is energy intensive and causes massive CO_2 emissions mainly due to the hydrogen source commonly derived from natural gas. Therefore, it is important to explore other alternatives for obtaining green ammonia (carbon-neutral ammonia) at moderate conditions, ideally driven by green electricity.

Meanwhile, nitric oxide (NO) removal has been widely investigated in environmental catalysis.[4,5] To date, the most established approach for NO removal is selective catalytic reduction (SCR) technology which can convert NO to harmless N_2.[6,7] However, those techniques require a constant supply of reductants such as ammonia or hydrogen.[8] While great efforts have been committed to the thermocatalytic NO_x removal process, converting NO_x to useful chemicals like ammonia (NH_3) would be preferable due to the growing demand for nitrogen-based fertilizers for crops.

Electrochemical denitrification is an alternative strategy to remove NO_x species and produce value-added chemicals such as NH_3. Here, electrochemical NO reduction (NORR) is implemented in a polymer electrolyte membrane (PEM) flow cell, where water (H_2O) is employed as the proton source at the anode side. This process can driven by renewable energy, eliminating the drawbacks of grey hydrogen production from fossil fuels and reducing the overall CO_2 emissions. Recently, Feng Jiao and co-workers have investigated the NO electroreduction in flow cell systems and found that ammonia synthesis is more favourable under acidic conditions.[9] This finding indicates that a PEM electrolyzer is ideal for electrochemical ammonia synthesis from NO due to its acidic nature at the cathode side.[10]

However, when operating at high cell potentials, the coverage of H* which is an intermediate of the hydrogen evolution reaction (HER) increases.[11,12] This enhances the HER that occurs in the same potential window as the NORR, resulting in a loss of selectivity towards NH_3 synthesis. It has been reported that increasing the CO* coverage on the surface can block H* active sites by weakening the H* binding energy,

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[**] HER: hydrogen evolution reaction

Supporting information for this article is available on the WWW under https://doi.org/10.1002/cssc.202300949

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thereby suppressing the HER.[13–15] Herein, we propose a strategy to co-feed CO together with NO to moderate the local CO* coverage on different electrocatalysts to selectively inhibit the HER active sites, which can decrease the H* coverage and suppress the HER. Five catalysts (Cu/C, Ru/C, Pt/C, Pd/C and Ag/C) were prepared and tested for their performance during NO electroreduction in the absence or presence of CO in a PEM electrolyzer. Notably, in the case of Pd/C, the FE towards NH_3 improved by 95 %, while the FE towards H_2 decreased by 56 % which suggest that CO* preferentially and selectivity adsorbs on HER active sites, resulting in enhancement of the FE towards NH_3.

Results and Discussion

Electrochemical reduction of NO and NO + CO was performed in a PEM electrolyzer (Figure S1), where gaseous NO (2.5 vol % NO in He) or NO + CO (2.5 vol % NO and 2.5 vol % CO in He) is fed directly to the cathode chamber and can be reduced to ammonia or other products. The cathode catalysts (Cu/C, Ru/C, Pt/C, Pd/C, and Ag/C) were prepared by a sodium borohydride reduction method with 40 wt% metal loading on Vulcan XC72 carbon black. XRD results (Figure S2) show that all the catalysts are present in their metallic form, except for Cu/C which formed CuO and is further reduced to metallic Cu during the reaction. Transmission electron microscope (TEM) images (Figure S3) indicated that all catalysts are highly dispersed on the carbon support.

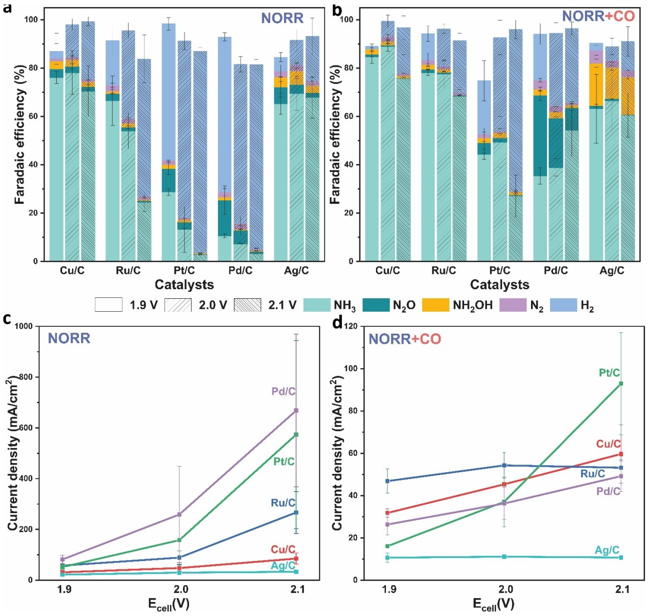

Figure 1. Faradaic efficiency at 1.9 V, 2.0 V, and 2.1 V of various catalysts in (a) NO electroreduction, and (b) NO electroreduction + CO. Total current density vs cell voltage of various catalysts in (c) NO electroreduction, and (d) NO electroreduction + CO.

NO and NO + CO electrolysis performance

First, the electrochemical reduction of NO was conducted in the PEM electrolyzer. The FE towards different NO reduction products of various catalysts at a cell voltage from 1.9 to 2.1 V is presented in Figure 1a and the total current density is shown in Figure 1c. Blank experiments with only carbon support were evaluated in our previous work for the conversion of nitrate to ammonia in a PEM system, which behaves similar to NORR. It showed low current density and less than 1 % FE towards NH_3 which indicates the carbon black has barely no activity in our reaction.[16] NH_3, N_2O, N_2, and NH_2OH were the detected nitrogen-containing products from NO electroreduction. As is shown in Figure 1a, among the five catalysts evaluated, Cu/C exhibits the highest selectivity for electrochemical NO reduction to NH_3. The FE over a wide range of cell potentials of Cu/C is shown in Figure S4a, where the FE towards NH_3 reached 62 % at a low cell potential of 1.7 V. While increasing the cell voltage, the FE towards NH_3 increased and achieved the highest value of 78 % at 2.0 V, at a current density of 48 mA/cm^2. Upon further increasing the cell voltage, the H_2 FE increased. Jianping Xiao et al. reported that copper is the most selective catalyst for NH_3 synthesis from the NORR.[17] Compared to other catalysts, Cu has a stronger binding affinity to NO* against H*, resulting in a well-balanced surface coverage of NO* and H*, which promotes higher selectivity towards NH_3 than other nitrogen-containing products.[18] For Ru/C and Ag/C catalysts, the FE towards NH_3 dominates for all studied cell potentials. In contrast, Pt/C and Pd/C were more efficient for HER than NH_3 synthesis. The FE of all the measured products during the NORR over the studied cell voltages of Ru/C, Pt/C, Pd/C and Ag/C are shown in Figures S5a, S6a, S7a and S8a. We observe that at low cell potentials, the FE towards N_2O was higher than at higher cell voltages for all catalysts. Feng Jiao et al. proposed that NO* coverage on the surface of the catalyst significantly affects the distribution of N-containing products. At high NO* coverages, N–N coupling products like N_2O or N_2 are more likely to form, in contrast, low (or balanced) NO* coverages result in N products like NH_3 or NH_2OH.[9] However, most of the protons and electrons are heading toward the HER upon operating the reaction at high cell potentials. These results indicate that at a high voltage, the surface coverage of H* significantly exceeds that of NO* and therefore we have directed our research effort towards decreasing the H* coverage to enhance the selectivity and FE towards NH_3.

With CO co-feeding, the FE towards different products of various catalysts in NORR + CO at cell potentials from 1.9 to 2.1 V is shown in Figure 1b. With respect to the current density, it is obvious that the current density significantly decreased in the presence of CO, especially for Pt/C and Pd/C (Figure 1d). Interestingly at 2.1 V, the current density decreased by 91 % and 86 % for Pd/C and Pt/C, respectively. The adsorbed CO* on the surface seems to affect the binding of H* and decreases the H* coverage which is directly related to the decrease in the FE towards H_2, especially under high cell potential conditions. The tendency of HER suppresion is general. At 2.1 V, the FE towards H_2 decreased by 21 %, 62 %, 20 %, 46 % and 35 % for Cu/C, Ru/C, Pt/C, Pd/C and Ag/C, respectively. Notably, NORR is not or less affected by the presence of CO. The FE towards NH_3 for all the catalysts improved, except for Ag/C. For Cu/C, at 2.0 V, the FE towards NH_3 improved by 12 % and achieved 89 %, which is the highest among all the catalysts. More strikingly, the FE towards NH_3 was enhanced by 95 %, 90 % and 54 % for Pd/C, Pt/C and Ru/C.

To further understand the CO poisoning effect on the electrochemical NO reduction of different catalysts, partial current densities of NH_3 and H_2 in NORR and NORR + CO reactions were plotted for both Pt/C and Pd/C (Figure 2a and 2b). In the case of Pd/C, the partial current density towards NH_3 was enhanced while that of Pt/C decreased. Despite the difference in the effects of CO on the NH_3 selectivity using Pd/C and Pt/C, H_2 formation was greatly suppressed for both catalysts which can be seen from the drastically decreased H_2 partial current density (Figure 2b). Based on these results, we propose a selective CO poisoning effect on Pt/C and Pd/C (Figures 2c and 2d). For both catalysts, NO is known to favourably bind to the atop site on the surface of the catalysts.[19] In the case of Pt/C in the absence of CO, the HER is dominating during NO electroreduction. When CO is introduced, we observe that the partial current density of NH_3 also decreased, which suggests that the adsorption of CO* is competitive with NO* on the surface lowering the NH_3 formation rate (Figure 2c). It is well documented that CO can bind on both the atop sites and bridge sites on Pt, while atop sites CO* dominate on Pt surfaces.[20] However, while increasing the surface charge, the preference of CO binding sites can change from atop to bridge sites.[21,22] These results are consistent with our results. At lower cell potentials, NO conversion decreased significantly (Figure S11a) because the atop NO* adsorption is inhibited by atop CO*. With increasing cell potentials, the adsorption of CO* is weakened; hence the NO* coverage on the surface increases, leading to the enhancement of NH_3 partial current density at high cell potentials. For the HER active sites, since the binding affinity towards CO* is stronger than H*, which is well-known for Pt, the adsorption of CO* can block the active bridge sites and is also competing with the atop H* active sites, lowering the partial current density towards H_2 production.

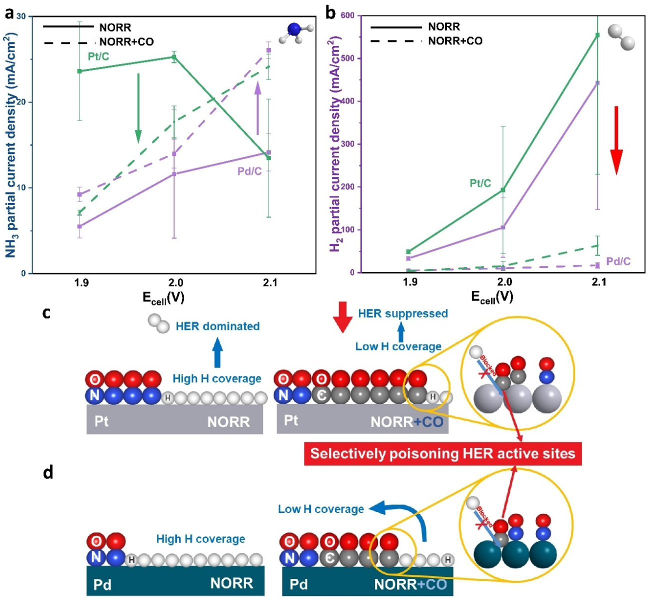

Figure 2. (a) NH_3 partial current density and (b) H_2 partial current density at 1.9 V, 2.0 V, and 2.1 V of Pt/C and Pd/C. Schematics of surface coverage of NO*, CO* and H* on (c) Pt/C and (d) Pd/C.

For Pd/C, in the presence of only NO, the high coverage of H* on the surface leads to a dominating HER and low FE towards NH_3. After introducing CO in the NO feed, which is more likely to bind to the bridge site of the Pd surface,[23] CO* is selectivity binding to, thus blocking, the active bridge sites for the HER, resulting in the decreased of FE towards H_2 and current density. NO* which adsorbs on the atop sites is not affected by bridge-bonded CO* (Figure 2d). Therefore, the FE towards NH_3 increases (Figure S12).

For the other catalysts, the NO conversion, NH_3 and H_2 partial current density of Cu/C, Ru/C and Ag/C are presented in Figures S9, S10 and S13, respectively. For Cu/C, the partial current density towards NH_3 increased in the presence of CO (Figure S13b). It has been reported that Cu has a stronger affinity to NO* compared to CO*;[24] therefore, the high FE towards NH_3 can be explained by the preferential NO coverage. However, for Ru/C and Ag/C, the partial current density towards NH_3 decreased in the presence of CO. Analogous to Pt/C, on the surface of Ru/C, NO* also competes with CO*, but the binding affinity to NO* is likely stronger than Pt/C, resulting in the observed higher partial current density toward NH_3. In the case of Ag/C, It has been suggested that NO*, H* and CO* bind on Ag weakly, which is in good accordance with our experiments. The current density and NO conversion on Ag/C (Figure S13a) was therefore much lower than with the other catalysts. Regarding NH_2OH formation, in the presence of CO*, the coverage of H* decreased so that there was not enough H* provided to reduce NH_2OH which is regards as an intermediate product[25] in the pathway toward NH_3 production (Figure S13b). As a consequence, the FE towards NH_2OH increased.

A comparison of the NH_3 production rate on various catalysts of NORR and NORR + CO over a range of cell voltages is presented in Figure S14. Among all the catalysts, Ru/C exhibited the highest NH_3 production rate in NORR, reaching 376 $\mu mol\,cm^{-2}\,h^{-1}$ at 2.0 V. Following closely, Cu/C demonstrated a production rate of 301 $\mu mol\,cm^{-2}\,h^{-1}$ at 2.1 V. In contrast, Pd/C displayed the lowest NH_3 production rate, yielding only 63 $\mu mol\,cm^{-2}\,h^{-1}$, even at 2.1 V (Figure S14a). Upon co-feeding CO (Figure S14b), notably the NH_3 production rates for Pd/C and Cu/C increased significantly, while for the other catalysts, the values decreased. For Cu/C at 2.1 V, the NH_3 production rate increased to 325 $\mu mol\,cm^{-2}\,h^{-1}$. However, the most striking result was observed with Pd/C, where the NH_3 production rate increased to 198 $\mu mol\,cm^{-2}\,h^{-1}$ in NORR + CO, which is 3 times higher than the value in NORR. This indicates that the poisoning and suppression of HER can promote NH_3 production in case of Pd/C. A similar tendency was observed for Pt/C at 2.1 V to a lesser extent. In comparison to other electrochemical NH_3 production studies utilizing different cells (batch cell, H cell, etc.) with liquid electrolytes (Table S1), which naturally suffers from mass-transport limitations for NORR, our results are promising for continuous NH_3 production from NO.

Conclusions

We report a strategy of CO-mediated selective poisoning of hydrogen evolution reaction (HER) active sites to enhance the faradaic efficiency (FE) towards ammonia in NO electroreduction. Cu/C is the most active catalyst for NO electroreduction to NH_3, exbiting the highest FE of 78 % at 2.0 V among all the catalysts. Pd/C and Pt/C show high FE towards H_2. In general, the competing HER dominates when operating at high cell potentials. With co-feeding CO, the current density and FE towards H_2 of all the catalysts drastically decreased, which can be ascribed to the increased the coverage CO* that competitively and selectively binds to HER active sites. Such effects are most pronouced for Pd/C and also clearly observed for Pt/C. This results in the enhanced NO* coverage on the surface, while poisoning HER sites, thus enabling a higher FE towards NH_3.

Experimental Section

Chemicals

Vulcan XC72 carbon black was bought from Cabot Corporation. $Cu(NO_3)_2$ trihydrate (99.5 %), $RuCl_3$ hydrate (99.9 %), $PdCl_2$ (99.9 %), $PtCl_2$ (98 %), $AgNO_3$ (99.5 %), $NaBH_4$, H_2O_2, H_2SO_4 were purchased from Sigma Aldrich.

Catalyst preparation

All catalysts (Cu/C, Ru/C, Pd/C, Pt/C, Ag/C) with 40 wt.% metal loading on a Vulcan XC72 carbon black support were synthesized using the sodium borohydride reduction method.[26] Briefly, 120 mg Vulcan XC72 carbon black was first suspended in 200 mL MilliQ water. An amount of metal precursor that corresponded with the final metal loading of 40 wt% was added to the solution. The solution was stirred with a stirring bar for 1 h at room temperature and then transferred to an ultrasonic bath for another 30 min. Subsequently, $NaBH_4$ was added dropwise as a reducing agent in sixfold excess with respect to the stoichiometric amount of different catalyst precursors. After reduction, the sample centrifuged and washed with MilliQ water several times. The obtained catalyst powder was dried at 90 °C for 12 h.

Membrane electrode assembly (MEA) preparation

Nafion™ 115 membranes from Ion power were pre-treated according to the procedure of 1 h in 3 wt.% hydrogen peroxide (H_2O_2) solution at 80 °C, 1 h in 1 M H_2SO_4 solution at 80 °C and 1 h in boiling MilliQ water. 10 mg of the prepared cathode catalyst and 30 wt.% Nafion ionomer were ultrasonically dispersed in 2 mL of isopropanol for 30 min to generate a homogenous ink. Then, the catalyst ink was spray-coating onto a Nafion membrane with an active area of $2\times2\ cm^2$ at 60 °C to obtain $2.5\ mg\cdot cm^{-2}$ catalyst loading. The anode ink was prepared via the same method consisting of 8 mg commercial IrO_2 ($2\ mg\cdot cm^{-2}$ catalyst loading), 20 wt.% Nafion ionomer and 2 mL isopropanol. After spray coating, the catalyst-coated membranes (CCMs) were hot-pressed at 120 °C and 1 MPa for 3 min using an automatic press (Speca Press). The MEA was prepared by pressing two porous sintered titanium gas diffusion layers ($2\times2\ cm^2$) (GDL, Bekaert) on both sides of the membrane. The PEM cell was assembled by sandwiching the MEA, two titanium bipolar plates with flow channels, and two aluminium cartridge-heated end plates with 5 N·m screw torque.

Electrochemical experiments

The electrochemical experiments were conducted in the PEM electrolyser (Figure S1) on an AUTOLAB PGSTAT302 N potentiostat equipped with a 20 A booster. The PEM electrolyser was operating at 80 °C. For electrochemical NO reduction, at the cathode chamber, the mixture of 2.5 % NO and 4 % CH_4 in He flowed at $26\ mL\cdot min^{-1}$. CH_4 was acting as the internal standard to correct the volume changes during reactions. For NORR + CO reactions, the mixture of 2.5 % NO, 2.5 % CO and 4 % CH_4 in He flowed at $26\ mL\cdot min^{-1}$ at the cathode side. For both reactions, at the anode chamber, MilliQ water was supplied at the flow rate of $1\ mL\cdot min^{-1}$ by a peristaltic pump (Ismatec). After the reaction, the cathode chamber outlet was connected to an acid trap with 0.2 M H_2SO_4 solution to trap the produced ammonia (NH_3) and hydrolymine (NH_2OH). After the acid trap, the gas flowed to the connected Alpha infrared spectrometer and gas chromatography (GC).

Product quantification

The outlet gas products (NO, N_2O, CO, and CH_4) were analysed via a Bruker Alpha infrared spectrometer. And the other gaseous products (N_2 and H_2) were quantified on a CompactGC from Global Analyser Solutions with a thermal conductivity detector (TCD).

Ammonium cations (NH_4^+) from the acid trap were executed by Metrohm 883 Basic ion chromatography with a Metrosep C6 separation column. Hydrolymine (NH_2OH) was quantified by UV-Vis spectroscopy (Unicam UV 500), measuring absorbance at 525 nm. In detail, 200 μL of the sample was diluted to 6 mL with MilliQ water. Then, 1 mL of $0.047\ mol\cdot L^{-1}$ KIO_3 and 1 mL of $3\ mol\cdot L^{-1}$ H_2SO_4 were added in turn; the mixed solution stayed for 5 min at room temperature. Lastly, 2 mL of $3.46\times10^{-4}\ mol\cdot L^{-1}$neutral red was added, and the absorbance at 525 nm was measured. The calibration curve of the natural red method for quantifying NH_2OH is shown in Figure S15.

Catalyst characterization

The powder X-ray diffraction (XRD) was measured on Bruker D8 ADVANCE X-ray diffractometer with Cu K-α radiation source in a range of 5° to 90° with a step of 0.05. The surface morphology of the catalysts was characterized by a Transmission electron microscope (TEM, Jeol JEM-1400 plus).

Acknowledgements

M. L. acknowledges funding from China Scholarship Council for this work.

Conflict of Interests

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.

Keywords: electrochemical NO reduction · direct ammonia synthesis · selective poisoning · hydrogen evolution suppression · co-feeding CO

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Manuscript received: June 30, 2023
Revised manuscript received: July 29, 2023
Accepted manuscript online: August 2, 2023
Version of record online: ■■, ■■

RESEARCH ARTICLE

*M. Li, J. Verkuil, Dr. S. Bunea, Dr. R. Kortlever, Prof. Dr. A. Urakawa**

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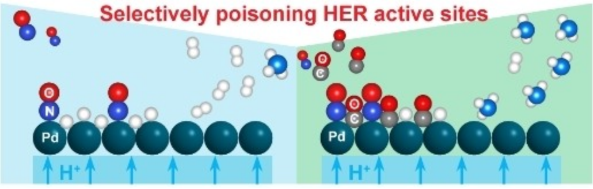
Towards Higher NH_3 Faradaic Efficiency: Selective-Poisoning of HER Active Sites by Co-Feeding CO in NO Electroreduction



Poisoning to promote? Poisoning of cathode catalyst surface by CO induces suppression of hydrogen evolution reaction (HER) and drastically boosts the Faradaic efficiency of NO reduction to NH_3 in a polymer electrolyte membrane (PEM) cell. The promotional effects towards selective ammonia formation is dependent on the type of metals which uniquely interact with CO with specific surface sites driving HER and/or NO reduction.