

SLUTRAPPORT

1 (13)

Datum
2024-02-28

Dnr
2018-004320

Projekt nr
46551-1

Energimyndighetens titel på projektet – svenska Ammoniak skapat från Luft, Vatten och Solljus - det ideala förnyelsebara bränslet	
Energimyndighetens titel på projektet – engelska Ammonia made from Air, Water and Sunshine – the ideal renewable fuel	
Universitet/högskola/företag Uppsala University	Avdelning/institution Department of Chemistry – Ångström Laboratory
Adress Box 256, 751 05 Uppsala	
Namn på projektledare Johannes Messinger	
Namn på ev övriga projektdeltagare Thomas Wågberg, Wai Ling Kwong, Petko Chernev, Eduardo Gracia-Espino, Christian Larsen	
Nyckelord: 5-7 st Electrochemical ammonia production, dinitrogen reduction under ambient conditions, sustainable fuels, green catalysis, catalysts made of earth abundant elements	

Förord

The project was financed by Energimyndigheten with co-financing of both Uppsala and Umeå Universities.

Innehållsförteckning

Sammanfattning.....	1
Summary.....	2
Inledning/Bakgrund.....	3
Genomförande.....	4
Resultat.....	4
Diskussion.....	12
Publikationslista.....	13
Referenser, källor.....	13
Bilagor.....	13

Sammanfattning

Den nuvarande användningen av fossila bränslen är ohållbar eftersom den leder till en ökning av växthusgaser i atmosfären, särskilt av CO₂. En stor del av förbrukningen av fossila bränslen orsakas av transportsektorn. Medan elektrifiering av bilar är den mest effektiva lösningen för personbilar och andra lätta transporter, är det svårare att driva tunga transporter med batterier på

grund av deras höga energibehov. Här krävs alternativa bränslen som produceras med hållbara metoder och som har en energidensitet som är jämförbar med fossila bränslen. Ett alternativ som diskuterats mycket är vätgas (H_2). H_2 har många fördelar, såsom en relativt enkel produktion genom vattenkatalys och en hög gravimetrisk energidensitet, men också egenskaper som begränsar dess tillämpning för långväga tunga transporter, till exempel inom den marina sektorn: H_2 har en låg volymetrisk energitäthet och långtidslagring är en utmaning.

Ett mindre diskuterat alternativ är ammoniak (NH_3), som är en vätgasbärare som lätt kan förvätskas för transport och lagring vid rumstemperatur. För användning som bränsle kan ammoniak antingen omvandlas tillbaka till N_2 och H_2 eller omvandlas med O_2 från luften till N_2 och vatten (H_2O), till exempel i en bränslecell. För att förverkliga NH_3 's potential som hållbart transportbränsle måste det produceras på ett energieffektivt sätt från rikligt förekommande råvaror med hjälp av katalysatorer tillverkade av grundämnen som finns rikligt på jorden. Utvecklingen av en effektiv elektrokemisk process för att producera NH_3 från luft- N_2 , vatten och förnybar el under omgivande temperatur och tryck skulle innebära ett paradigmskifte och möjliggöra en hållbar produktion av ammoniak både i stor skala, vilket är viktigt för industrin och den marina sektorn, samt i liten skala, vilket t.ex. skulle vara relevant för lokal produktion av gödselmedel och transportbränsle inom jordbrukssektorn.

Den största utmaningen för att realisera elektrokemisk reduktion av N_2 till ammoniak är den höga energi som krävs för att bryta en av naturens starkaste bindningar, trippelbindningen mellan de två kväveatomerna. Detta är problematiskt eftersom andra molekyler, såsom di-syre (O_2), karbondioxid (CO_2) och protoner i vatten, kan reduceras elektrokemiskt vid mycket lägre elektriska potentialer. Därför krävs antingen selektiva katalysatorer eller processförhållanden som gynnar N_2 -reduktion framför konkurrerande processer.

Huvudresultatet av projektet är således utvecklingen av en elektrokemisk cell som gör det möjligt att reducera N_2 till ammoniak med en specificitet på över 70%, om än med låg katalytisk hastighet. Dessutom undersöktes och karakteriserades flera potentiella katalysatorer, tillverkade av grundämnen som finns rikligt på jorden. Som ett nästa steg ska dessa resultat kombineras för att optimera processen i laboratorieskala. Betydande framsteg eller eventuellt alternativa koncept kommer att krävas innan förnybar, elektrokemisk ammoniakproduktion kan ge praktiska bidrag till ett förnybart och flexibelt energisystem.

Summary

The present use of fossil fuels is unsustainable as it leads to an increase in greenhouse gases in the atmosphere, especially of CO_2 . A large fraction of fossil fuel consumption is caused by the transport sector. While electrification of cars is the most efficient solution for person vehicles and other light transport, heavy transport is more difficult to run on batteries due to its high energy demand. Here, alternative fuels, produced by sustainable methods, are required that have energy densities comparable to fossil fuels. One much discussed option is hydrogen (H_2). H_2 has many advantages, such as a comparatively simple production by water catalysis and a high gravimetric energy density, but also limitations that restrict its application for long distance heavy transport, such as in the marine sector: H_2 has a low volumetric energy density and long-term storage is challenging.

A less discussed alternative is ammonia (NH_3), which is a hydrogen carrier that can be easily liquified for transport and storage at room temperature. For use as fuel, ammonia may either be converted back to N_2 and H_2 or converted with O_2 from the air to N_2 and water (H_2O), for

example in a fuel cell. To realize the potential of NH₃ as sustainable transportation fuel, it needs to be produced in an energy efficient manner from abundant feedstocks employing catalysts made of earth-abundant elements. Thus, the development of an efficient electrochemical process to produce NH₃ from air-N₂, water and renewable electricity under ambient temperature and pressure would allow a paradigm shift and enable a sustainable production of ammonia both at large scale, important for industry and the marine sector, as well as at small scale, which would be relevant, *e.g.*, for the local production of fertilizer and transport fuel in the agricultural sector.

The main challenge for realizing electrochemical N₂ reduction to ammonia is the high energy required for breaking one of Nature's strongest bonds, the triple bond between the two nitrogen atoms. This is problematic, since other molecules, such as di-oxygen (O₂), carbon dioxide (CO₂) and protons in water can be electrochemically reduced at much lower electrical potentials. Therefore, either selective catalysts or process conditions are required that favor N₂ reduction over the competing processes.

The main result of the project is thus the development of an electrochemical cell that allows reducing N₂ to ammonia with a specificity of over 70%, albeit at low catalytic rate. In addition, several prospective catalysts, made from earth-abundant elements, were explored and characterized. As a next step, these results shall be combined to optimize the process at lab scale. Significant progress or possibly alternative concepts will be required before renewable, electrochemical ammonia production can make practical contributions towards a renewable and flexible energy system.

Inledning/Bakgrund

Ammonia (NH₃) is well known to be essential for producing fertilizers. Presently, half the human population depends on food produced using NH₃ made by the industrial Haber-Bosch (HB) process. It may be less appreciated that NH₃ is also an excellent alternative fuel. In contrast to H₂, ammonia has both a high gravimetric (18.6 MJ kg⁻¹) and a high volumetric (11.5 MJ L⁻¹) energy density. Importantly, it can be easily liquefied for storage and transport at room temperature. Thus, green ammonia may be especially suitable for heavy-duty, long-distance transports in the marine sector or heavy trucks. However, it may also be ideal for local storage of surplus renewable energy from wind and solar, to be used, for example, in agricultural settings for transportation or for producing fertilizers.

Containing 17% hydrogen by weight, NH₃ can act as hydrogen carrier that releases H₂ upon catalytic decomposition ($2\text{NH}_3 \rightarrow \text{N}_2 + 3\text{H}_2$). Alternatively, it can be oxidized directly in a fuel cell to generate electricity, N₂ and H₂O ($4\text{NH}_3 + 3\text{O}_2 \rightarrow 2\text{N}_2 + 6\text{H}_2\text{O}$). Currently, research is being conducted actively at developing NH₃ fuel cells, which operate at efficiencies that are reportedly higher than those of the equivalent H₂-based fuel cells. Being the second most produced chemical, NH₃ is one of the most transported chemicals worldwide. That is, infrastructure and safety policy for NH₃ distribution already exist, thus minimize the establishment cost. Compared to the hydrogenation of CO₂ to form hydrocarbon products, hydrogenation of N₂ to form NH₃ has a clear advantage, since with its nearly 80% abundance in the air, N₂ is readily available without prior concentration. To realize the potential of NH₃ as transportation fuel, NH₃ needs to be produced in an energy-efficient manner from the abundant resources such as N₂ (from air), water and sunlight.

Presently, NH₃ is produced solely by HB process ($\text{N}_2 + 3\text{H}_2 \rightarrow 2\text{NH}_3$), which consumes fossil fuels to create H₂ feedstock (via steam-reforming) and suitable reaction condition (temperature

400-500°C and pressure 150-300 atm) in large, centralized facilities. The development of an efficient electrochemical process that produces NH₃ using air-N₂, H₂O and renewable electricity under ambient temperature and pressure, would enable a paradigm-shifting sustainable production of NH₃ as agricultural ingredient as well as energy fuel, contributing to largely reducing CO₂ emissions. The inherent flexibility of electrochemical systems would allow NH₃ production in both large-scale centralized and small-scale distributed manners.

The aim of this 4-year project, which was led by Prof. Johannes Messinger (Uppsala University) and was financed by Energimyndigheten with co-financing by Uppsala and Umeå Universities, was to lay the foundation for such a renewable NH₃ production technology by developing, from earth-abundant elements, catalysts for electrochemical N₂ fixation at ambient condition and understanding the essential factors governing the NH₃ production efficiency from individual perspectives of operational parameters and catalytic properties.

Genomförande

The main challenge for realizing electrochemical N₂ reduction to ammonia is the high energy required for breaking the triple bond between the two nitrogen atoms. This is problematic, since other molecules, such as di-oxygen (O₂), carbon dioxide (CO₂) and protons in water can be electrochemically reduced at much lower electrical potentials. To circumvent this, either selective catalysts and/or process conditions are required that favor N₂ reduction over the competing processes.

The present project thus had two main research directions:

1. Synthesis and characterization of various earth-abundant catalyst candidates.
2. Assembly and testing of a lab-scale electrochemical cell that allows optimization of process parameters for selective ammonia synthesis.

The project was a collaboration between the groups of Thomas Wågberg and Ludvig Edman at Umeå University, and the team of Johannes Messinger at Uppsala University. In the project, various methods for synthesis, characterization of the synthesized materials and their catalytic performance have been employed. These will be described, in the context with the results obtained, in the next section.

Resultat

1. Synthesis and characterization of various earth-abundant catalyst candidates for N₂ reduction

1.1 *Fe-Ti and Fe-Mo metal powders*

Inspired by the Fe-Mo-S containing active site of Nitrogenase, which is Nature's catalyst for N₂ reduction, we developed a set of metallic Fe-Ti and Fe-Mo powders with varying Fe:X (X = Ti or Mo) molar composition using a scalable hydrothermal synthesis method, followed by a low-temperature annealing in H₂ atmosphere. The Fe-Ti powders displayed a non-uniform agglomerate morphology, irrespective of the Fe:Ti metallic composition (see Figure 1a), while the Fe-Mo powders are particles with sizes <1.5 μm. Addition of small amounts of Mo resulted in a smaller Fe-Mo particle size as compared to that of pure Fe powders, owing to the inhibited grain growth caused by the Mo dopant. The nanoparticulate morphology is expected to be beneficial in providing plentiful surface-active sites for the electrocatalytic N₂-reduction reaction (NRR) to form NH₃. An

elemental examination using energy dispersive spectroscopy (EDS) shows that the Fe:Ti and Fe:Mo compositions of our catalysts agree well with that of the precursor solutions (see Table 1), demonstrating the effectiveness of our synthesis protocol in compositional control of the catalysts.

Table 1. Summary of elemental analysis of Fe-Ti catalysts.

Precursor	EDS
Fe : Ti	
0.80 : 0.20	0.82 : 0.18
0.60 : 0.40	0.59 : 0.41
0.40 : 0.60	0.43 : 0.57
0.20 : 0.80	0.20 : 0.80
Fe : Mo	
0.875 : 0.125	0.870 : 0.130

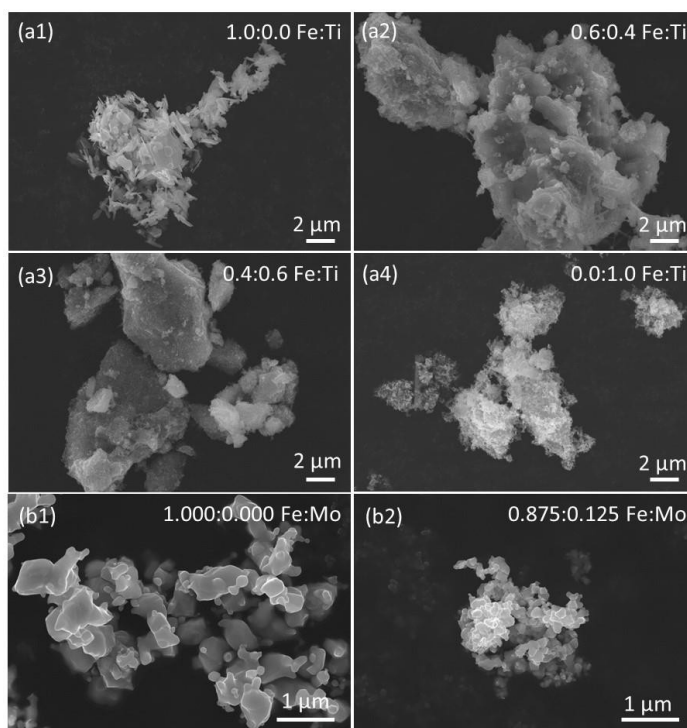


Figure 1. Scanning electron microscopy images of (a) Fe-Ti and (b) Fe-Mo powders.

1.2 Prussian Blue derivatives

In the experiments described in section 2, we show that strict control of proton availability favors ammonia product over competing hydrogen formation. Careful optimization of operating conditions led to a high Faradaic efficiency of 70%, however the rate of ammonia production is very low (about $3 \times 10^{-11} \text{ mol s}^{-1} \text{ cm}^{-2}$).

Following this, we decide to develop a more specific nitrogen reduction catalyst. To this end, we examined transition metal nitroprussides as potential nitrogen reduction catalysts. The rationale for selecting these materials for examination is that both the NO and CN groups are isoelectronic with the N₂ molecule. We hypothesize that the redox active NO group can be reduced and released, thus leaving a vacant site for N₂ to bind and be activated for further reduction.

Transition metal nitroprussides (NP) were synthesized by chemical precipitation with the parent sodium nitroprusside complex and the corresponding 1st row transition metals ions such as Fe²⁺ or Cu²⁺. The precipitates were collected by centrifugation and washed extensively by resuspension in pure water and additional centrifugation and discarding the supernatant. The samples were dried under N₂ stream and stored in air. In our first attempt, the materials were placed onto the glassy carbon (GC) electrode by drop casting from suspensions in ethanol or dichloromethane (DCM).

The thus prepared Fe based transition metal nitroprussides were examined for their reduction chemistry under Ar and N₂ atmosphere employing cyclic voltammetry experiments. We observed that the voltammograms collected under N₂ are different relative to those collected under Ar, a possible sign for N₂ activation by these materials.

Therefore, we conducted a more detailed screening of N₂ activation activity using various mixed metal (Mn, Fe, Co, Ni, Cu) nitroprusside based cyanometallates complexes.

During the screening, we encounter a major problem related to loading and stability of the deposited cyanometallate complexes on the electrode surface. Irreproducible material loading and detachment of the complexes during experiment precludes meaning comparison of the voltammetry response under Ar and N₂ atmosphere. To this solve this, we examined various means of immobilization of cyanometallates onto electrode surfaces, including direct synthesis of cyanometallates on electrode surfaces and drop casting of cyanometallates on electrode surface with or without binding agents. After extensive testing, we concluded that a two-step drop casting procedure where cyanometallates are first drop cast onto electrodes followed by drop cast of bind agent to give the most reproducible results.

Using this two-step procedure, we then screened different mixed metal (Mn, Fe, Co, Ni, Cu) nitroprusside based cyanometallates complexes for N₂ activation or catalytic N₂ reduction. For Fe and Cu complexes, noticeable difference between voltammetry response under N₂ and Ar atmosphere suggest possible N₂ activation. However, we did not observe any catalytic behavior in the in the voltammetry response. Additionally, we noted an electrochemical behavior that is consistent with the reduction of Cu²⁺ ions to metallic Cu. It is likely that during chemical synthesis of CuNP cyanometallates, Cu²⁺ ions are trapped as counter cations within the lattice.

To circumvent this, we developed an electrodeposition method where a thin layer of metallic copper is deposited onto a glassy carbon electrode, which is subsequently oxidized in the presence of sodium nitroprusside to form CuNP cyanometallate on the electrode surface. Using this electrodeposition method, the formation of CuNP cyanometallate was performed under conditions in which the concentration of Cu²⁺ is limited and by the presence of a 100-fold excess of Na⁺ counterions in the electrolyte to suppress the entrapment of free Cu²⁺ ions.

The voltammetry response of such electrodeposited CuNP films no longer showed the Cu^{2+} reduction feature in the voltammogram. Thus, this procedure allowed deposition of CuNP with a higher level of homogeneity compared to our initial drop cast method. Reduction under N_2 showed a reduction wave at -0.59 V vs. Ag/AgCl that is not present under analogous experiments under Ar. However, the reduction wave does not exhibit catalytic behavior. At present, we hypothesize that during formation of CuNP under N_2 , either (i) N_2 is reductively incorporated into the structure of CuNP but is not catalytically reduced to NH_3 or (ii) the morphology of CuNP formed under N_2 is different compared to that obtained in presence of Ar, so that the different coordination environments of Cu lead to different redox behaviors. The second option may be supported by reports in the literature that CuNP has at least three different structural composition depending on the hydration level.

To study the catalytic properties of these materials further, we also carried out investigations into the reaction of NO with CuNP and its precursor sodium nitroprusside. Such experiments allow exploring the possibility of NO reduction to ammonia or ammonium. Our preliminary investigation by CV shows that NO does react strongly with sodium nitroprusside. We will follow up this interesting observation in a future project.

In summary, our investigation on using transition metal nitroprusside reduction revealed that these materials have very rich redox properties and we observed redox behavior that may indicate N_2 reaction, although not catalytic reduction to NH_3 . Thus, we conclude based on our studies that cyanometallate materials are not viable candidates for the direct electrochemical NH_3 production from N_2 . The suitability of these materials for multi-step processes involving, for example, NO as intermediate should be investigated further.

1.3 Carbon Dots

In search for alternative electrocatalysts for the reduction of N_2 to ammonia that are made of earth-abundant elements and allow scalable synthesis we decided to investigate Carbon Dots (CDs). CDs are metal-free and quasi-zero-dimensional carbon-based nanostructures, typically composed of a carbon core and a number of functional groups on the surface. The electronic properties of CDs can be manipulated via, for example, introducing structural defects in the carbon core via heteroatom doping, or by altering functional groups on the surface. These structure variations enable the effective regulation of both photocatalytic and electrocatalytic activities. Another important advantage of CDs is that, unlike traditional functional materials, CDs can be synthesized from various biomass-derived starting materials and crude biomass, therefore being free from precious and heavy metals and critical raw materials.

The potential application of CDs for the reduction of N_2 to ammonia is a new research direction with some initial promising reports in the literature. For example, CDs prepared from glucose via a simple hydrothermal reaction, are reported to exhibit excellent catalytic performance in 0.1 M HCl with a Faradaic efficiency of 17.59% , under ambient conditions.[1] CDs can also serve as a surface modification on metal oxide catalyst materials and improve their catalytic efficiency. [2-3]

We thus, recently, synthesized CDs from the bio-derivable starting material phloroglucinol. The cyclic voltammetry measurement demonstrated that these CDs present good electrochemical activity. With these results in hand, we will next study the catalytic conversion of N_2 to NH_3 under ambient conditions.

References

¹Nanoscale, 2022, 14, 9893.

²Cell Reports Physical Science, 2022 3, 100961.

³J. Mater. Chem. A, 2022, 10, 12713.

2. Assembly and testing of a lab-scale electrochemical cell that allows optimization of process parameters for selective ammonia synthesis

The nitrogen reduction reaction (NRR) has been reported at ambient temperature and pressure using heterogeneous catalysts, albeit with low NH_3 production rate and selectivity. This is because most of the reactants, i.e., electrons and protons (produced from water oxidation as the anodic half-reaction), were consumed preferably in a competing side-reaction, i.e. in the this case undesired hydrogen-evolution reaction (HER). NRR is limited also by the extremely low solubility of N_2 in liquid media commonly used as the electrolyte solution in a cathodic compartment that houses the NRR catalysts. To promote NRR by suppressing HER, we employed in this project a custom-made gas-diffusion electrochemical cell (see **Figure 2**) that allows facile control of availabilities of electrons and protons, as well as supply of gaseous N_2 .

In this cell, a membrane-electrode assembly (MEA) was used as cathode for NRR. For preparing the MEA, the catalyst powder was deposited onto a carbon paper that formed the gas diffusion layer. This structure was subsequently hot-pressed with a Nafion membrane (see Figure 2b). To minimize HER, we employed a polar aprotic solvent such as ethyl acetate (EA), which is miscible with water, in the anodic compartment that houses a Pt counter electrode for water oxidation, in order to restrain the availability of protons as well as electrons. LiClO_4 was used as the electrolyte and thus determines the ionic conductivity of the solvent, and its concentration provides an additional means to control the effective concentration of protons and electrons near the catalyst surface.

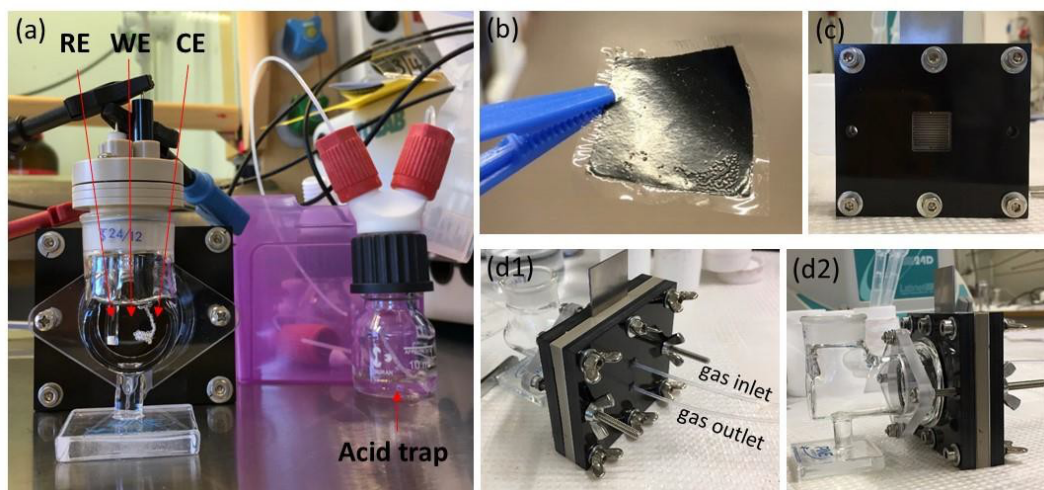


Figure 2. Photos of a custom-made electrochemical cell used for NRR measurement. (a) Electrochemical cell with electrode holder and electrolyte solution in the anodic compartment. Gaseous N_2 is flown through the cathodic compartment that houses the catalyst-coated carbon paper as working electrode (WE). The anodic and cathodic compartments are electrically separated by a Nafion membrane. Pt and Ag wires are used as counter (CE) and reference electrodes (RE), respectively. An acid trap consisting of 0.1 M HCl is connected to the gas outlet to trap the gaseous NH_3 product. (b) MEA consisting of a Nafion membrane hot-pressed to a catalyst-coated carbon paper. The active geometric area of the electrode is $1.5 \times 1.5 \text{ cm}^2$. (c) Cathodic compartment without the MEA. (d) Electrochemical cell without the electrode holder.

For the detection of NH_3 product on daily basis, we employed two complementary low-cost techniques such as indophenol blue (**IB**) and ammonia ion-selective electrode (**ISE**) measurements. The hydrophobic membrane at the tip of ISE allows only the permeation of NH_3 from the sample for detection by the electrode sensor, while for IB, the reaction of NH_3 with salicylic acid and hypochlorite reagents generates a blue-colored indophenol product that exhibits a characteristic optical absorbance at 655 nm wavelength. Both techniques yield a linear response in the system calibration using ammonia standard solutions (see **Figure 3**), with the limit of detection being 0.01 ppm.

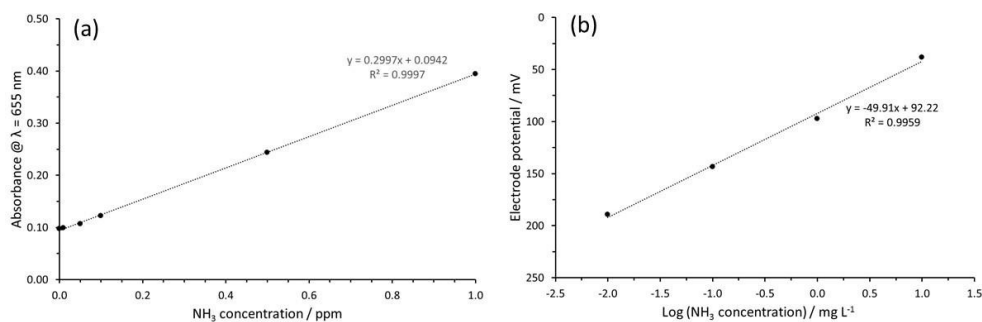


Figure 3. Calibrations using ammonia standard solutions and measured by (a) IB and (b) ISE methods.

Prior to the NRR measurement of the catalysts, we tested the gas tightness of the electrochemical cell by gradually injecting NH_3 gas into the cathodic compartment of the cell under a flowing N_2 . Our test shows that most of the injected NH_3 is absorbed on the Nafion membrane and permeates into the anodic electrolyte solution. This means that NH_3 produced from NRR would need to be quantified by summing up the NH_3 trapped in the acid trap and in the anodic electrolyte solution.

We noted, however, that most of the low-cost NH_3 quantification techniques including IB and ISE are effective only for aqueous-based samples. That addition of organic solvents such as EA to ammonia standard solutions affects the optical spectra and thus causes false negative signals (**Figure 4a**). This is also observed in our tests using ISE in the presence of EA, owing to the undesired wettability of the ISE membrane by organic solvents. To overcome such technical issue, we developed a pre-quantification protocol that firstly converts the NH_3 product to NH_4Cl by adding HCl to the samples extracted from the acid trap and anodic electrolyte solution. This is followed by a low-temperature heating overnight to evaporate the EA, water and excess HCl from the samples, leaving NH_4Cl and LiClO_4 salts, which are then dissolved in water for NH_3 quantification. **Figure 4b** shows the IB results of the ammonia standard solutions that had been processed using the pre-quantification protocol. The overlapping spectra with that of ammonia standard solution that did not undergo the pre-quantification protocol demonstrate that our protocol is effective for NH_3 measurement involving organic solvents and that the presence of LiClO_4 does not affect the measurement results.

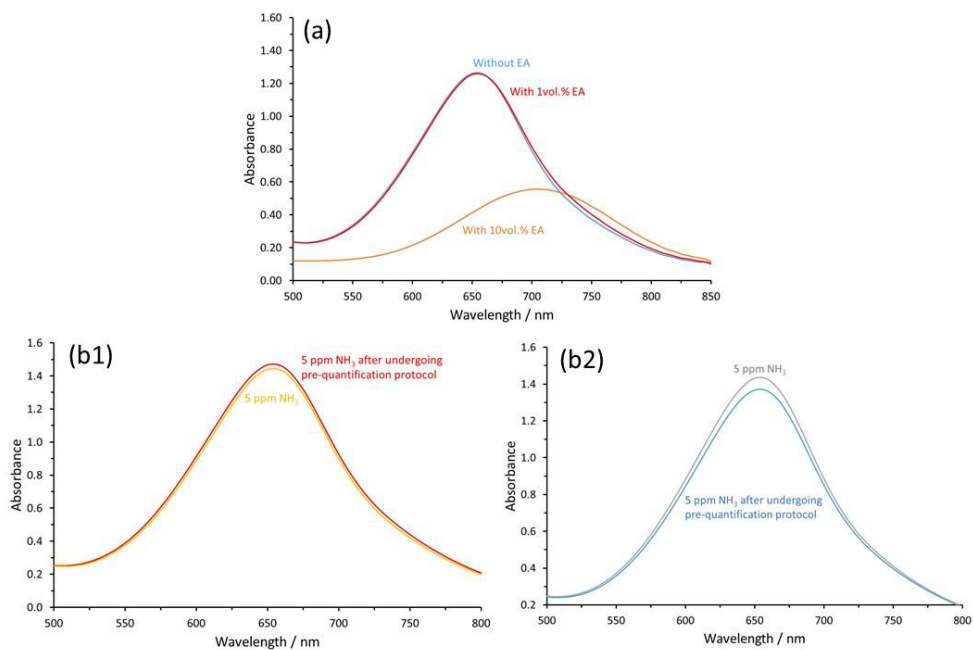


Figure 4. IB results of (a) sample containing 4.5 ppm NH₃ in water with or without EA, and sample containing 5 ppm NH₃ in (b1) EA or (b2) 0.1 M HCl and treated with pre-quantification protocol. Absorbance spectrum of 5 ppm NH₃ in water also is shown in (b). Samples in 0.1 M HCl acid trap is treated using the protocol to remove the trapped EA that originates from the anodic compartment due to the high volatility of EA.

Using our custom-made electrochemical cell and above-mentioned NH₃ detection protocol, we measured the electrocatalytic performance of our Fe catalyst in 25 mL EA containing 0.2 M LiClO₄ as well as 0.04-0.60 vol.% (10-150 μL) water, using a flowing gaseous N₂ as the N source. The polarization curves in **Figure 5a** show that EA that contains a higher amount of water, thus the availability of protons, leads to a higher current due to NRR or HER. To determine the Faradaic efficiency (FE) and the catalytic rate for NRR, a series of fixed potentials are applied for 1 h (see **Figure 5b**) and the accumulated NH₃ product is quantified and compared to the theoretical quantity of NH₃ calculated from the measured current.

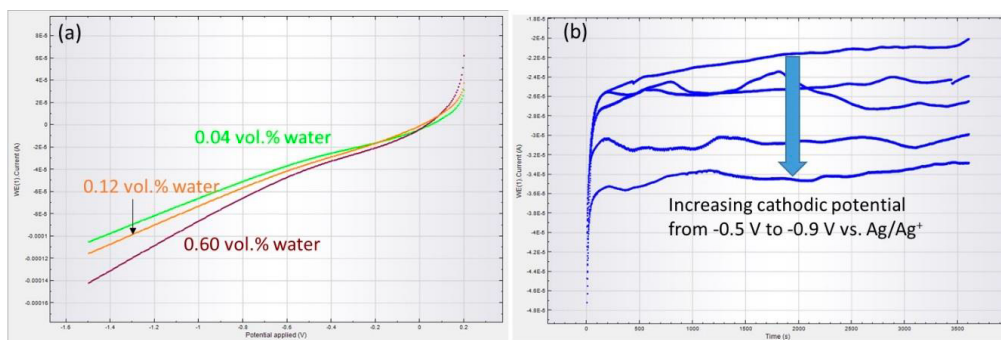


Figure 5. (a) Polarization curves measured in EA containing 0.04-0.60 vol.% water. (b) Typical chronoamperometries at different applied potentials measured in EA containing 0.12 vol.% water.

By optimizing the water content at 0.12 vol.% in EA, a FE for NRR as high as 77% and a NRR rate of $3 \times 10^{-11} \text{ mol s}^{-1} \text{ cm}^{-2}$ were achieved. The FE for NRR of our catalyst is much higher than that ($\text{FE} < 10\%$)² of heterogeneous catalysts reported in the literature, where aqueous electrolyte solution is commonly used in their measurements at ambient

temperature and pressure. An exceptionally high FE for NRR at 57% has been reported,³ however, in an aqueous-based electrolyte using single-atomic Fe grown on N-doped carbon as the catalyst, indicating the importance of downsizing catalyst materials to improve their catalytic properties. Our results agree with the recently proposed theoretical strategy that the FE for NRR can be improved by (1) thermodynamically hindering proton and electron transfer via a substantial reduce of proton source from water and (2) substantially increasing the concentration of N source,⁴ which can be easily implemented in our custom-made electrochemical system.

In addition to FeOx/CFP electrodes, several mono-(Co, Mo, Ti, Fe) and bimetallic phosphide, sulfide and nitrides were synthesized and tested for ammonia production under various conditions using the same approach as described above. None of these catalysts showed any appreciable ammonia production, despite reports to the contrary in the literature.

Finally, we made a first attempt adapting the Li-mediated NRR approach to our system, in which metallic Li reacts first with N₂ to Li₃N (step 1), then Li₃N and protons (generated from anodic oxidation reaction) form ammonia and Li⁺ (step 2), and finally Li⁺ is recycled to metallic Li by electrodeposition (step 3). Already upon the first attempt, ammonia production was observed that exceeded the best results obtained above. A large potential for improvements was noted.

References

1. Kyriakou, V.; Garagounis, I.; Vasileiou, E.; Vourros, A.; Stoukides, M., Progress in the Electrochemical Synthesis of Ammonia. *Catal. Today* **2017**, *286* 2–13.
2. Greenlee, L. F.; Renner, J. N.; Foster, S. L., The Use of Controls for Consistent and Accurate Measurements of Electrocatalytic Ammonia Synthesis from Dinitrogen. *ACS Catal.* **2018**, *8*, 7820-7827.
3. Wang, M.; Liu, S.; Qian, T.; Liu, J.; Zhou, J.; Ji, H.; Xiong, J.; Zhong, J.; Yan, C., Over 56.55% Faradaic Efficiency of Ambient Ammonia Synthesis Enabled by Positively Shifting The Reaction Potential. *Nat. Commun.* **2019**, *10*, 341
4. Singh, A. R.; Rohr, B. A.; Schwalbe, J. A.; Cargnello, M.; Chan, K.; Jaramillo, T. F.; Chorkendorff, I.; Nørskov, J. K., Electrochemical Ammonia Synthesis The Selectivity Challenge. *ACS Catal.* **2017**, *7*, 706–709.
5. Skúlason, E.; Bligaard, T.; Gudmundsdóttir, S.; Studt, F.; Rossmeisl, J.; Abild-Pedersen, F.; Vegge, T.; Jónsson, H.; Nørskov, J. K., A theoretical evaluation of possible transition metal electro-catalysts for N₂ reduction. *Phys. Chem. Chem. Phys.* **2012**, *14*, 1235–1245.

Diskussion

The data obtained in this project confirm the hypothesis that it is crucial to control both the proton and the N₂ availabilities in order to favor ammonia production over the competing hydrogen formation. Optimizing the potential range and other operating conditions for the FeO_x/CFP electrode led to a high Faradaic efficiency of 70% for NH₃ production, but the rate of ammonia production remained low (about $3 \times 10^{-11} \text{ mol s}^{-1} \text{ cm}^{-2}$) as compared to the benchmark for commercial processes ($10^{-7} \text{ mol s}^{-1} \text{ cm}^{-2}$). On that basis, we conclude that in addition to optimal operation conditions, the catalysts must have a strong intrinsic preference for N₂ reduction over H⁺ reduction to allow for higher rates of electrochemical ammonia production from N₂.

We thus synthesized and tested a number of NRR catalysts described in the literature, however, none led to a measurable ammonia formation under our carefully controlled conditions. This indicates that it may be very difficult to achieve the required specificity for NRR with simple material catalysts.

We thus turned to transition metal nitroprussides as new materials that have many options for tuning and may thus be developed into efficient N₂ reduction catalysts. While promising, based on the initial differences in electrochemical properties under N₂ and Ar, our further tests indicated that mixed metal nitroprusside based cyanometallates are not viable as catalysts for N₂ reduction to ammonia, because the voltammetry response does not exhibit features that are typically attributed to catalysis.

Our approach of limiting proton availability to minimize hydrogen production is a form of kinetic control of proton reduction. However, in future it may be important to also examine the hydricity, a thermodynamic concept, of these materials in relation to ammonia production and hydrogen production.

Hydricity measures the ability to donate a hydride anion (H⁻) from a metal-hydride bond. Hydride transfer to the N₂ molecule is a first critical step in the nitrogen reduction reaction. Using insights from theoretical simulations, it may be possible to tune the hydricity of transition metal complexes to facilitate ammonia production while suppressing hydrogen production by varying parameters such as transition metals ratio (eg. Fe/Co or Fe/Ni) and incorporating additional ligands.

One additional new approach may be the utilization of carbon dots as NRR catalysts, either alone or in combination with other materials.

Overall, we were able to test and advance a number of concepts towards increasing the specificity for nitrogen reduction, which form the basis for subsequent projects. However, at present, the direct electrochemical reduction of N₂ from air remains far from any practical application.

Publikationslista

Electrochemical N₂ reduction at ambient condition – Overcoming the selectivity issue via control of reactants' availabilities

Wai Ling Kwong, Thomas Wågberg and Johannes Messinger (2021) Intern. J.

Hydrogen Energy 46, 30366-30372

DOI: 10.1016/j.ijhydene.2021.06.184

Referenser, källor

See above.

Bilagor

Administrativ bilaga