Enhanced Activity of Titanocene Complex for Electrocatalytic Nitrogen Reduction Reaction

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Abstract: Enhanced titanocene (Cp2TiCl2) based electrocatalytic system for nitrogen reduction was shown, comprising glassy carbon electrode, high level of the catechol redox mediator, optimized binary THF/MeOH solvent and unique design of the reactor having ammonia permeable membrane at the outlet, which allowed constant nitrogen flow through the working solution during entire electrolysis without risk of evaporation of the solvent. Catalytic activity was observed in the potential range of (−1.5)−(−2.3) V, reaching TON of 2.83%, corresponding to the production of 0.566 µmol NH3 (9.64 µg) in 24 h hydrolysis at −2.3 V using 0.02 mmol TiCp2Cl2 (5 mg).

Keywords: nitrogen reduction; electrocatalysis; titanocene complex

1. Introduction

Dinitrogen (N2) is the most stable and inert homoatomic molecule (bond enthalpy of −945 kJ/mol, dissociation energy of 9.79 eV); however, its reduction is crucial for sustaining life on Earth since nitrogen-containing organic compounds (e.g., amino acids, proteins, etc.) are utilized by all organisms. Naturally, reduction of N2 is carried out by diazotrophs (bacteria and archaea) in biosynthetic processes involving nitrogenase enzymes upon production of ammonia [1], which is further converted by bacteria to various organic compounds within the nitrogen cycle. Industrially, ammonia is being produced in the Haber−Bosch process (designed in 1908–1913; awarded the Nobel prize in 1918 and 1931) and further utilized to produce synthetic fertilizers. The Haber–Bosch process comprises a direct exothermic reaction between N2 and H2 over iron or ruthenium catalysts (Equation (1)), which requires high temperature (500–600 °C) and high pressure (200–500 bar) to overcome the kinetic barrier [2–4]:

\[ \text{N}_2 + 3\text{H}_2 \rightarrow 2\text{NH}_3 \] (1)

Due to large energy consumption, the Haber–Bosch process consumes 1−2% of world energy production, accounting for 1.44% of the world’s CO2 emission [5] and consuming 42.6% of the world’s H2 production [6], but still is the only method known for the industrial production of ammonia. Currently, food fertilized by the products of Haber–Bosch process is consumed by ca. 33% of the world’s population; thus, it is believed that. Thus, it crucial to investigate more sustainable methods of ammonia production, allowing for a low-energy ammonia fabrication in off-grid setups.

The natural process of nitrogen reduction has been intensively studied to determine the mechanism of nitrogenase catalyzed reaction, which utilizes 16 equivalents of ATP upon production of two ammonia molecules [1,7]:

\[ \text{N}_2 + 10\text{H}^+ + 8\text{e}^- + 16\text{ATP} \rightarrow 2\text{NH}_4^+ + 2\text{H}_2 + 16\text{ADP} + 16\text{P}_i \] (2)
Three categories of nitrogenases can be distinguished depending on the composition of the cofactor, i.e., a Mo-dependent cofactor (FeMo-co), a V-dependent cofactor (VFe-co), or an all-iron cofactor (FeFe-co) [1]. Due to the high energy demand of the reaction, a sustainable process of ATP recycling would be needed for the enhanced design of a nitrogenase-based nitrogen fixation system [8,9].

Semiartificial nitrogen reduction systems utilizing nitrogenase have been demonstrated. Electrocatalytic or photocatalytic systems use immobilized nitrogenase enzymes (e.g., deposited on CdS nanorods) operating in ATP-free conditions [10]. A bioelectrochemical ammonia fuel cell has been constructed having a cathodic nitrogenase compartment, and an anodic hydrogenase compartment separated by PEM membrane was shown to operate with 59% efficiency [11,12]. Systems utilizing fragile enzymes normally are being deactivated within several hours of operation.

Transition metal complexes have been synthesized and tested towards nitrogen reduction in the presence of strong chemical reductants already in the 1960s [13,14]. Multistep ammonia generation cycle using [W(N\textsubscript{2})\textsubscript{2}(PMe\textsubscript{2}Ph)\textsubscript{4}] complex comprising two nitrogen molecules has been shown [15,16]. A biomimetic complex [Mo(HIPTN\textsubscript{3}N)] with an active molybdenum center has been shown to produce ammonia with 66% efficiency [17]. Various biomimetic iron complexes have been designed to mimic nitrogenase active center using tripodal phosphene ligands, known to catalytically reduce nitrogen at $-78^\circ$C when using an excess of strong reductants and strong acids, such as KC\textsubscript{8} or HBA\textsubscript{F}\textsubscript{4}·2Et\textsubscript{2}O [18–22]. The highest turn-over-number of ammonia production using complexes of this type reached 84% per iron atom [23]. An osmium-containing complex [(NH\textsubscript{3})\textsubscript{5}Os\textsuperscript{II}(N\textsubscript{2})Os\textsuperscript{III}(NH\textsubscript{3})\textsubscript{5}]\textsuperscript{5+} is known to split and reduce N\textsubscript{2} molecules when irradiated with UV light under a mercury lamp [24]. A chalcogel system comprising biomimetic [Mo\textsubscript{2}Fe\textsubscript{6}S\textsubscript{8}]\textsuperscript{3+} clusters can produce ammonia under visible light irradiation [25]. Unfortunately, the use of most complexes of molecular nitrogen needs rigorous exclusion of oxygen and water while operating, which makes their large-scale use challenging.

Recently, simple photocatalytic and electrocatalytic systems of nitrogen fixation have been shown. Robust crystalline TiO\textsubscript{2} powder was reported to be able to catalytically reduce nitrogen under UV irradiation due to the presence of Ti\textsuperscript{3+} species and oxygen vacancies on surface defects [26]. A similar effect has been observed when using TiO\textsubscript{2}/Au electrodes where oxygen vacancies promote nitrogen absorption and activation towards its reduction to ammonia [27]. Nafion-containing carbon electrodes with an active layer of Bi\textsubscript{4}V\textsubscript{2}O\textsubscript{11}/CeO\textsubscript{2} have been used for electrocatalytic reduction of nitrogen with a faradaic efficiency of 10.16% and ammonia production yield of 23.21 µg/h/mg\textsubscript{CAT} [28]. A similar system with an active layer of defected polymeric carbon nitride has been shown to produce ammonia with a yield of 8.09 µg/h/mg\textsubscript{CAT} and faradaic efficiency of 11.59% [29].

Titanium-based molecular complexes have also been investigated as catalysts for nitrogen reduction. Already the first reports showed that titanocene derivatives could be adapted as catalysts towards ammonia production [13,30–32]. Further studies showed an electrochemical system using titanocene dichloride complex (C\textsubscript{p}\textsubscript{2}TiCl\textsubscript{2}) for nitrogen fixation, operating in organic solvents yielding TON of 1.45% [33].

Here, is presented a successful enhancement of the well-known titanocene-based system for ammonia generation [33]. Optimization of the system, considering simplification of the design, use of more robust, cheap and eco-friendly materials, resulted in an enhanced TON of ammonia production. This opens possibilities towards immobilization of the titanocene complex on the surface of carbon electrodes for further development of the system.

2. Results and Discussion

The first reports on titanium complexes as catalysts for selective nitrogen reduction were published in 1966 by Vol’pin and Shur, who investigated the use of a variety of transition metal compounds (e.g., TiCl\textsubscript{4}) for stoichiometric reduction of nitrogen to ammonia [13]. Further studies have shown that the activity of titanocene dichloride can be
improved using a variety of alkali metals as reductants [30]. Mechanistic studies suggested that titanium dimer may be an intermediate in the nitrogen reduction process. This dimer is in equilibrium with the monomer, which can then react with dinitrogen to a titanium dinitrogen complex, which promotes the reduction of the coordinated N₂ to ammonia molecule [31,32].

In 1987, Becker et al. reported an electrochemical system for the reduction of molecular dinitrogen to ammonia using titanocene dichloride as a catalyst [33]. Reduction of dinitrogen to ammonia was achieved in polar solvents, such as methanol and THF using catechol as an additive, n-Bu₄NClO₄ or LiClO₄ as electrolytes and platinum or mercury as working electrodes. The optimized conditions considered the use of a platinum working electrode, 0.05 M Cp₂TiCl₂, 0.25 M catechol, 0.1 M LiClO₄ in 60 mL methanol, carried out at −2.2 V against silver pseudo-reference electrode, to give 20.1 µmol NH₃ (340.6 µg) within 5 h electrolysis, which corresponds to a TON of 0.67%. The addition of magnesium salt can further enhance the performance of the system to reach 43.7 µmol NH₃ (744.3 µg) during 4.83 h electrolysis, corresponding to a TON of 1.45%.

It has been attempted to enhance the setup and optimize reaction conditions proposed by Becker et al. [33]. The total volume of the solution and catalyst concentration was reduced to minimize the possible negative environmental impact of the procedure and to decrease the amount of perchlorate waste generated. Expensive (Pt) and toxic (Hg) working electrode materials were exchanged for eco-friendly glassy carbon to decrease the overall cost of the process. However, the catechol level has been increased to reach the better performance of the system.

To enhance the yield of electrolysis, it was decided to purge the working solution with N₂ during the entire electrolysis to keep it saturated; however, this resulted in rapid evaporation of THF and drying the working solution, which leads to the deactivation of the system and a hazard of an explosion of perchlorates. In addition, I have discovered that contamination of the acid trap with THF interferes with the result of Nessler’s test (Figure 1). These issues have been overcome by separating the reactor and the acid trap by a membrane permeable for ammonia and smaller molecules. This allows a constant flow of nitrogen through the working solution during the entire electrolysis. In addition, the membrane keeps THF inside the reactor preventing its migration to the acid trap.

![Figure 1](image.png)

**Figure 1.** Influence of THF contamination on the reading of Nessler’s tests of aqueous ammonia solutions. Starting solution of 10 µg/mL diluted with portions of pristine THF.

For optimization of the reaction conditions, various solvents (THF, MeOH, MeCN) electrolytes (LiClO₄, n-BuNCIO₄, n-BuNBF₄) and the presence of an additive (catechol) were tested. Comparison of cyclic voltammograms collected for various combinations of process parameters allowed to preselect promising reaction conditions: a solvent mixture of THF and MeOH, n-BuNCIO₄ electrolyte and presence of catechol additive.
Cyclic voltammograms (CVs) collected in MeOH (selected as the best solvent by Becker et al. [33]) showed hydrogen reduction wave starting already at ca. −1.8 V. Similar measurement carried out in THF gave CVs with characteristic waves of reversible titanocene reduction/oxidation at ca. (−0.3)−(−0.6) V followed by catalytic wave of nitrogen reduction at ca. (−1.6)−(−2.4) V and hydrogen reduction wave below ca. −2.5 V. Such difference in the behavior of titanocene complex result from different properties of the solvents used. MeOH as a protic solvent promotes the evolution of gaseous hydrogen at relatively mild conditions, which compete with nitrogen reduction significantly enhanced by a large number of protons available in the solution. On the other hand, THF shifts an onset of hydrogen reduction down to ca. −2.5 V and promotes ammonia reduction at ca. −2.3 V. This encouraged us to propose a mixed electrolyte THF/MeOH 9:1, which could show benefits of both solvents: protons available for nitrogen reduction and larger overpotential for hydrogen reduction. Indeed, CVs collected at mixed electrolyte (Figure 2) showed a large nitrogen reduction wave at ca. (−1.5)−(−2.4) V followed by a hydrogen reduction wave with an onset at ca. −2.5 V.

![Figure 2. Comparison of cyclic voltammograms of Cp2TiCl2 (2 mM) working solution in a solvent mixture THF/MeOH 9:1 with 0.1 M n-Bu4NClO4 under N2 or Ar, with or without 20 mM catechol.](image)

The addition of catechol can further enhance the performance of the Cp2TiCl2 catalyst, which is clearly visible at CVs of mixed solution THF/MeOH 9:1 (Figure 2) and consistent with earlier observations of Becker et al. [33]. Catechol plays the role of redox mediator in this process, interacting with reduced titanium species promoting nitrogen reduction [33]. On one hand, catechol as a fast, one-electron reversible redox system can accelerate electron transfer to the oxidized titanocene complex enhancing overall kinetics of the process of catalyst regeneration. On the other hand, catechol may act as an auxiliary proton donor, further facilitating ammonia generation.

Qualitative tests of nitrogen reduction using titanocene catalyst working solutions at a series of preselected solvents (THF, THF/MeOH, MeOH, MeCN) with or without catechol additive, using various electrolytes (LiClO4, n-Bu4NClO4) were carried out at −2.3 V to seek for an optimum combination of reaction conditions (Table 1). The qualitative test of ammonia production was attempt using Nessler’s colorimetric method estimating the intensity of the color of formed Millon’s base iodide complex (approximate concentration in the range of 1–15 ppm according to validated Nessler’s test). Control experiments (all negative) were performed under argon atmosphere for each tested reaction setup.

The use of n-Bu4NClO4 as an electrolyte leads to higher amounts of ammonia than the use of other electrolytes (LiClO4 or n-Bu4BF4), which can be presumably attributed to the better stabilization of reactive intermediates. In addition, n-Bu4BF4 can react with organometallic Ti species having a high affinity for fluorine, leading to catalyst decomposition.
Table 1. Results of qualitative tests of 24 h electrocatalytic ammonia generation at $-2.3 \text{ V}$ under $N_2$ (with control experiment under Ar) using 10 mL of a working solution containing 2 mM $\text{Cp}_2\text{TiCl}_2$ catalyst in various solvents (MeOH, THF, MeCN, THF/MeOH), 0.1 M of electrolyte ($n$-$\text{Bu}_4\text{NBF}_4$, LiClO$_4$, $n$-$\text{Bu}_4\text{NClO}_4$) and optionally 20 mM (10 equivalents) of catechol additive.

| Electrolyte | n-$\text{Bu}_4\text{NBF}_4$ | LiClO$_4$ | n-$\text{Bu}_4\text{NClO}_4$ |
|-------------|----------------|----------|----------------|
| Atmosphere  | Catechol | No 10 eq. | No 10 eq. | No 10 eq. |
| MeCN        | Ar | N$_2$ | Ar | N$_2$ | Ar | N$_2$ | Ar | N$_2$ | Ar | N$_2$ | Ar | N$_2$ | Ar | N$_2$ |
| MeOH        | - | - | - | - | - | - | - | - | - | - | - | - | - | - |
| THF         | - | - | - | - | - | - | - | - | - | - | - | - | - | - |
| THF/MeOH 9:1| - | - | - | - | - | - | - | - | - | - | - | - | - | - |

Results of the qualitative tests were measured in a three-point scale, where “–” represents a negative response, “+” represents a weakly positive response (pale red), “++” represents a moderately positive response (red), and “+++” represents a strong positive response (deep red).

Large solvent effects have been observed during the tests. No catalytic activity has been observed in MeCN, while some activity was recorded in pure MeOH and pure THF. Interestingly, the highest ammonia production has been observed in a solvent mixture of THF with a 10% additive of methanol. This can be attributed to a combination of two factors favoring nitrogen reduction, mainly the presence of a source of protons needed to complete the catalytic cycle (polar and protic methanol) and relatively high solubility of nitrogen (less polar and aprotic THF). Surprisingly, the activity of methanol and its dissociation ability may be higher in a mixture with THF than in a pure form. Similar effects have been reported for binary mixtures of acetonitrile and water, where the highest water activity is observed for the smallest concentrations of water in the mixture. Differences in the solubility of nitrogen in THF and methanol cannot be discussed because no reference data have been found regarding THF solution. However, higher solubility of dinitrogen in THF in comparison to solubility in MeOH can be presumed because diglyme can dissolve ca. 10 times more N$_2$ than methanol [34].

The lower performance of titanocene catalyst in pure MeOH could be ascribed to the ligand exchange of the chloride ligands to methoxy ligands in $\text{Cp}_2\text{TiCl}_2$. Due to the stronger Ti–O bond as compared to the Ti–Cl bond, the displacement of a methoxy ligand with a dinitrogen ligand becomes increasingly difficult, leading to the lower catalytic activity of $\text{Cp}_2\text{TiCl}_2$ when the reaction is carried out in pure MeOH. Similarly, if the reaction is carried out in MeCN, no NH$_3$ can be detected, which can presumably be attributed to the more difficult displacement of MeCN ligands.

The positive impact of catechol additive has been confirmed as it led to increased production of ammonia. Preliminary tests of the activity of titanocene complex catalyst showed optimal electrolysis parameters to be: 2 mM $\text{Cp}_2\text{TiCl}_2$; 0.1 M $\text{Bu}_4\text{NClO}_4$; 20 mM catechol; 9 mL THF; 1 mL MeOH; $E = -2.3 \text{ V}$; $t = 24 \text{ h}$. At more positive potentials, observed production is much smaller. At more negative potentials, the red working solution changes color to yellow, which indicates decomposition of titanocene catalyst, or when containing catechol, it tends to darken and eventually clouded with black precipitate, probably due to the reduction and decomposition of catechol.

Further tests using the preselected reaction setup resulted in the determination of optimum catalytic parameters of the process (Figure 3, Table 2). The catalytic activity of the titanocene complex $\text{Cp}_2\text{TiCl}_2$ towards the reduction of nitrogen has been studied. Yields observed here for the enhanced setup are significantly higher than those reported earlier by Becker et al. [33] (Table 2).
It has been observed that the working solution tends to deactivate upon prolonged electrolysis. The highest activity has been observed during the first 6 h of the process, which might explain why Becker et al. [32] mostly presented results of short (4–5 h) electrolyses using a similar system. The catalytic activity has been observed in the potential range of (−1.5)–(−2.3) V, however, the more negative potential, the higher ammonia production, reaching TON of 2.83%, corresponding to the production of 0.566 μmol NH₃ (9.64 μg) in 24 h hydrolysis at −2.3 V using 0.02 mmol TiCp₂Cl₂ (5 mg) and catechol.

3. Experimental

Chemicals were stored under nitrogen atmosphere inside the MBRAUN glovebox (O₂ < 1 ppm, H₂O < 1 ppm). All manipulations and reactions were carried out under a nitrogen or argon atmosphere. All the reagents and solvents were fine quality anhydrous chemicals purchased from Sigma-Aldrich (Cp₂TiCl₂, tetrahydorfurane (THF), MeOH, MeCN, toluene, catechol, n-Bu₄NClO₄, LiClO₄, NBu₄BF₄, K₂[HgI₄]) and Fisher (H₂SO₄, NH₃). Aqueous electrolytes were prepared using deionized water purified in a two-step procedure involving distillation followed by UV irradiation using Millipore Simplicity 185 (Millipore, Burlington, MA, US).
Electrochemical setup (Figure 4) comprised a three-electrode system with a glassy carbon working electrode (1 cm$^2$ surface), platinum mesh counter electrode and silver wire pseudo-reference electrode (potential values presented in this study refer to Ag reference), equipped with IVIUM COMPACTSTAT.

![Electrochemical setup](image)

**Figure 4.** Electrochemical three-electrode setup equipped with an ammonia-selective membrane.

A flamed-dried three-necked round-bottomed flask (25 mL) was charged inside a glovebox with 10 mL working solution and sealed with septa under an inert atmosphere. The reactor was purged with nitrogen or argon prior to the experiments for 20 min.

During electrolysis, the reactor was connected with an ammonia capturing acid trap through an elastic tubing equipped with an ammonia permeable PTFE membrane from Hanna Instruments (HI-4001-51, Woonsocket, RI, USA). The trap consisted of three serially connected vessels, each filled with H$_2$SO$_4$ solution (3 mL, pH = 3), with an outlet in the end. The solution was purged with N$_2$ or Ar during the entire electrolysis with a gas flow of ca. 0.07 mL/min and stirred with a magnetic bar at a rate of 500 RPM. After the electrolysis, ammonia remaining in the working solution was pushed to the trap by purging the solution with a large Ar flow for 20 min. The concentration of NH$_3$ was determined in joined trap solution.

Spectrophotometric ammonia detection. Nessler’s reagent (17% alkaline solution of potassium tetra-iodine mercurate, K$_2$[HgI$_4$]) was used as an indicator in UV-vis detection of ammonium cations in aqueous solutions. Nessler’s reagent reacts with NH$_4^+$ to form a complex of Millon’s base iodide, [Hg$_2$N]OH·H$_2$O [35]. The color of the complex (yellow to orange) depends on the concentration of NH$_4^+$. Calibration curve was constructed ($y = 0.0549x, R^2 = 0.9982$) using 1.2 mL pH = 7 ammonia standards of the concentration range of 0.075–30 μg/mL. UV-vis measurements were done at $\lambda = 500$ nm after 60 s incubation time after the addition of 0.2 mL additive of Nessler’s indicator (Figure 5).

![Spectrophotometric ammonia detection](image)

**Figure 5.** Calibration curve for Nessler’s ammonia detection method in water pH = 7: series of UV-vis spectra of standard solutions (A), curve build using reading at wavelength 500 nm (B).
4. Conclusions

In this work, it was reported enhancement of titanocene-based electrocatalytic system for nitrogen reduction studied earlier by Becker et al. [33]. More than four times higher performance was achieved by changing the electrode material into glassy carbon, optimization of catechol level and solvent composition, and major modifications in the setup by closing the outlet of the reactor by ammonia permeable membrane, which allows constant nitrogen flow through the working solution during entire electrolysis without risk of evaporation of the solvent, which was kept in the reactor by the membrane.

Change of the electrode material from platinum and mercury used by Becker et al. [33] into glassy carbon used in this study increased the rate of electron transfer towards titanocene catalyst and further formation of an active complex with nitrogen. In addition, carbon material has a lower affinity to form complexes with ammonia than platinum and mercury, which enables quick release of ammonia from the reactor.

The use of a binary solvent mixture of THF and methanol (9:1) was crucial for reaching the highest yields of the process. The mixture used allowed to benefit from both solvents: protic methanol acted as a source of protons, while aprotic THF acted as a medium providing high solubility of nitrogen. Surprisingly, the activity of methanol turned out to be higher when mixed with THF than in a pure form.

This study showed room for enhancement for the nitrogen reduction process using titanocene as a catalyst. Further modifications of reaction conditions, setup and the form of the catalyst may enable reaching the higher performance of this system.

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References
1. Hoffman, B.M.; Lukoyanov, D.; Yang, Z.Y.; Dean, D.R.; Seefeldt, L.C. Mechanism of Nitrogen Fixation by Nitrogenase: The Next Stage. *Chem. Rev.* 2014, *114*, 4041–4062. [CrossRef] [PubMed]
2. Bosch, C. Process of Producing Ammonia. U.S. Patent 990191, 18 April 1911.
3. Haber, F.; Le Rossignol, R. Über die technische Darstellung von Ammoniak aus den Elementen. *Zeitschrift für Elektrochemie und Angewandte Physikalische Chemie* 1913, 19, 53–72.
4. Van der Ham, C.J.M.; Koper, M.T.M.; Hetterscheid, D.G.H. Challenges in reduction of dinitrogen by proton and electron transfer. *Chem. Soc. Rev.* 2014, *43*, 5183–5191. [CrossRef]
5. Kyriakou, V.; Garagounis, J.; Vourros, A.; Vasileiou, E.; Stoukides, M. An Electrochemical Haber-Bosch Process. *Joule* 2020, *4*, 142–158. [CrossRef]
6. Birol, F. *The Future of Hydrogen. Seizing Today’s Opportunities. Report Prepared by the IEA for the G20, Japan*; International Energy Agency: Paris, France, 2019.
7. Dalle, K.E.; Warnan, J.; Leung, J.J.; Reuillard, B.; Karmel, I.S.; Reisner, E. Electro- and Solar-Driven Fuel Synthesis with First Row Transition Metal Complexes. *Chem. Rev.* 2019, *119*, 2752–2875. [CrossRef]
8. Milton, R.D.; Abdellaloui, S.; Khadka, N.; Dean, D.R.; Leech, D.; Seefeldt, L.C.; Minteer, S.D. Nitrogenase bioelectrocatalysis: Heterogeneous ammonia and hydrogen production by MoFe protein. *Energy Environ. Sci.* 2016, *9*, 2550–2554. [CrossRef]
9. Milton, R.D.; Minteer, S.D. Enzymatic Bioelectrosynthetic Ammonia Production: Recent Electrochemistry of Nitrogenase, Nitrate Reductase, and Nitrite Reductase. *ChemPlusChem* 2017, *82*, 513–521. [CrossRef] [PubMed]
10. Brown, K.A.; Harris, D.F.; Wilker, M.B.; Rasmussen, A.; Khadka, N.; Hamby, H.; Keable, S.; Dukovic, G.; Peters, J.W.; Seefeldt, L.C.; et al. Light-driven dinitrogen reduction catalyzed by a CdS:nitrogenase MoFe protein biohybrid. *Science* 2016, *352*, 448–450. [CrossRef] [PubMed]
11. Milton, R.D.; Cai, R.; Abdellaloui, S.; Leech, D.; De Lacey, A.L.; Pita, M.; Minteer, S.D. Bioelectrochemical Haber-Bosch Process: An Ammonia-Producing H2 /N2 Fuel Cell. *Angew. Chem. Int. Ed.* 2017, *56*, 2680–2683. [CrossRef] [PubMed]
Catalysts 2021, 11, 389

12. Fourmond, V.; Léger, C. Dinitrogen Reduction: Interfacing the Enzyme Nitrogenase with Electrodes. Angew. Chem. Int. Ed. 2017, 56, 4388–4390. [CrossRef] [PubMed]

13. Vol’pin, M.E.; Shur, V.B. Nitrogen fixation on complex catalysts. Doklady Akademii Nauk SSSR 1964, 156, 1102–1104.

14. Shilov, A.E.; Shilova, A.K.; Kvashina, E.F. Kinet. Katal. 1969, 10, 1402.

15. Chatt, J.; Pearman, A.J.; Richards, R.L. The reduction of mono-coordinated molecular nitrogen to ammonia in a protic environment. Nature 1975, 253, 39–40. [CrossRef]

16. Hidai, M.; Takahashi, T.; Yokotake, I.; Uchida, Y. Reactions Of Ligating Dinitrogen With Alcohols Or Metal Hydrides. Chem. Lett. 1980, 9, 645. [CrossRef]

17. Yandulov, D.V.; Schrock, R.R. Catalytic Reduction of Dinitrogen to Ammonia at a Single Molybdenum Center. Science 2003, 301, 76–78. [CrossRef] [PubMed]

18. Anderson, J.S.; Rittle, J.; Peters, J.C. Catalytic conversion of nitrogen to ammonia by an iron model complex. Nature 2013, 501, 84–87. [CrossRef]

19. Creutz, S.E.; Peters, J.C. Catalytic Reduction of N2 to NH3 by an Fe–N3 Complex Featuring a C-Atom Anchor. J. Am. Chem. Soc. 2014, 136, 1105–1115. [CrossRef] [PubMed]

20. Anderson, J.S.; Cutsail, G.E.; Rittle, J.; Connor, B.A.; Gunderson, W.A.; Zhang, L.; Hoffman, B.M.; Peters, J.C. Characterization of an Fe=≡N–NH2 Intermediate Relevant to Catalytic N2 Reduction to NH3. J. Am. Chem. Soc. 2015, 137, 7803–7809. [CrossRef]

21. Rittle, J.; Peters, J.C. An Fe-N2 Complex That Generates Hydrazine and Ammonia via Fe≡NNH2: Demonstrating a Hybrid Distal-to-Alternating Pathway for N2 Reduction. J. Am. Chem. Soc. 2016, 138, 4243–4248. [CrossRef]

22. Del Castillo, T.J.; Thompson, N.B.; Peters, J.C. A Synthetic Single-Site Fe Nitrogenase: High Turnover, Freeze-Quench 57Fe Mössbauer Data, and a Hydride Resting State. J. Am. Chem. Soc. 2016, 138, 5341–5350. [CrossRef]

23. Chalkley, M.J.; Del Castillo, T.J.; Matson, B.D.; Roddy, J.P.; Peters, J.C. Catalytic N2-to-NH3 Conversion by Fe at Lower Driving Force: A Proposed Role for Metallocene-Mediated PCET. ACS Cent. Sci. 2017, 3, 217–223. [CrossRef]

24. Kunkely, H.; Vogler, A. Photolysis of aqueous [Os(NH3)3(N2)]5+: Dismutation of coordinated dinitrogen. Inorganica Chim. Acta 2012, 391, 229–231. [CrossRef]

25. Banerjee, A.; Yuhas, B.D.; Margulies, E.A.; Zhang, Y.; Shim, Y.; Wasielewski, M.R.; Kanatzidis, M.G. Photochemical Nitrogen Conversion to Ammonia in Ambient Conditions with FeMoS-Chalcogels. J. Am. Chem. Soc. 2015, 137, 2030–2034. [CrossRef]

26. Hirakawa, H.; Hashimoto, M.; Shiraishi, Y.; Hirai, T. Photocatalytic Conversion of Nitrogen to Ammonia with Water on Surface Oxygen Vacancies of Titanium Dioxide. J. Am. Chem. Soc. 2017, 139, 10929–10936. [CrossRef]

27. Li, C.; Wang, T.; Zhao, Z.J.; Yang, W.; Li, J.F.; Li, A.; Yang, Z.; Ozin, G.A.; Gong, J. Promoted Fixation of Molecular Nitrogen with Surface Oxygen Vacancies on Plasmon-Enhanced TiO2 Photoelectrodes. Angew. Chem. Int. Ed. 2018, 57, 5278–5282. [CrossRef]

28. Lv, C.; Yan, C.; Chen, G.; Ding, Y.; Sun, J.; Zhou, Y.; Yu, G. An Amorphous Noble-Metal-Free Electrocatalyst that Enables Nitrogen Fixation under Ambient Conditions. Angew. Chem. Int. Ed. 2018, 57, 6073–6076. [CrossRef]

29. Lv, C.; Qian, Y.; Yan, C.; Ding, Y.; Liu, Y.; Chen, G.; Yu, G. Defect Engineering Metal-Free Polymeric Carbon Nitride Electrocatalyst for Effective Nitrogen Fixation under Ambient Conditions. Angew. Chem. Int. Ed. 2018, 57, 10246–10250. [CrossRef]

30. Bayer, E.; Schurig, V. Stickstoff-Fixierung und Reduktion zu Ammoniak mit metall-organischen Katalysatoren. Chem. Ber. 1969, 102, 3378–3390. [CrossRef]

31. Van Tamelen, E.E.; Fechter, R.B.; Schneller, S.W.; Boche, G.; Greeley, R.H.; Akermark, B. Titanium(II) in the fixation-reduction of molecular nitrogen under mild conditions. J. Am. Chem. Soc. 1969, 91, 1551–1552. [CrossRef]

32. Van Tamelen, E.E.; Seeley, D.A. The Catalytic Fixation of Molecular Nitrogen by Electronic and Chemical Reduction. J. Am. Chem. Soc. 1969, 91, 5194. [CrossRef]

33. Becker, J.Y.; Avraham, S.; Posin, B. Part I. Electrochemical reduction of titanium compounds in the presence of catechol and N2 in MeOH or THF. J. Electroanal. Chem. 1987, 230, 143–153. [CrossRef]

34. Battino, R.; Rettich, T.R.; Tominaga, T. The Solubility of Nitrogen and Air in Liquids. J. Phys. Chem. Ref. Data 1984, 13, 563. [CrossRef]

35. Panda, H. The Complete Book on Electroplating & Allied Chemicals; Asia Pacific Business Press: New Delhi, India, 2013; p. 204.