

CuDATA CATALYST FOR NITRATE ELECTROREDUCTION TO GENERATE AMMONIA

BACKGROUND OF THE INVENTION

Analogous to nitrate leaching in conventional agricultural practices, excess toxic nitrate, those beyond an acceptable level (above 50 mg/L, EU standard), is often detected in wastewater.

10 Nitrate leached to neighboring marine areas cause red tides, low dissolved oxygens, and loss of aquatic lives. Nitrate-containing agricultural run-offs left untreated can further lead to downstream socioeconomical burden, and diseases, such as blue baby syndrome, methemoglobinemia, and cancers.

Presently, industrial nitrate removal is limited to physical methods to collect or
15 concentrate nitrate, which are typically treated via an energy-intensive oxygenation step in a biological system. The physical methods to isolate nitrate generally involve membrane technologies, such as reverse osmosis and electrodialysis. However, these methods only isolate nitrates from water without eliminating nitrates. Current removal process of nitrogen-containing species in centralized treatment plants include a heavily energy-intensive oxygenation step to
20 treat the trapped nitrates. Alternative biological denitrification processes require special attention and costly resources to maintain bacterial biofilm reactors, such as a strict control of dissolved oxygen, carbon sources, and/or pH. An alternative chemical method involves reduction of nitrate to nitrogen using hydrogen as the reducing agent. The arduous production and transport of hydrogen hinders industrial use.

25 Ion Exchange (IE) is the most commonly used method for the removal of nitrate in potable water treatment. IE has been widely researched and numerous full-scale installations are in operation. Optimal operation of an IE system requires disposal of waste brine, which is commonly a significant portion of operation and maintenance (O&M) costs. O&M costs include replacement of degraded resin, resin disposal, brine disposal or treatment, chemical usage (salt, anti-scalants, pH adjusters), and power. Present costs are approximately one to approximately
30 five dollars per thousand gallons of treated water.

Reverse Osmosis (RO) systems require a tradeoff between the costs of increasing water recovery through pretreatment and operational pressure and the costs of disposal by pumping, storage, and other disposal expenses. High operating pressures maximize water recovery through decreasing disposal costs, but increase energy demands and require “specialized pumps”. For small water systems, reverse osmosis is perhaps the most expensive centralized treatment and are not cost effective unless multiple contaminants needing removal. O&M costs for RO include membrane and filter replacement, membrane and filter disposal, concentrate disposal or treatment, and chemical usage (anti-scalant, pH adjustment, disinfection, etc.), and power. Present costs are approximately six to approximately twenty dollars per thousand gallons of treated water.

Electrodialysis (ED) systems are expensive though little information is available due to the limited number of full-scale systems implemented. Costs include cation and anion exchange membranes, membrane replacement, membrane disposal, concentrate disposal or treatment, chemical usage, and power.

Biological Denitrification (BD) requires the maintenance of optimal conditions for the bacteria and the balancing of the appropriate substrate and nutrient dose with managing of pre and post-treatment to achieve necessary potable water guidelines. Costs include post-treatment, sludge disposal, chemical use (pH adjustment, substrate and nutrient dosing), extensive monitoring and power. Present costs depend on post-treatment requirements but are approximately one dollar per thousand gallons of treated water.

A less examined route to nitrate control is nitrate electroreduction that chemically converts nitrate into other value-added products. One such product is ammonia. Generation of ammonia is typically an energy intensive and high carbon footprint Haber-Bosch process that occurs at 400-650 °C and elevated pressure of about 200 atm. The Haber-Bosch process has very high costs when performed in fully decentralized scales, about 4,500 per ton. A decentralized system that produces ammonia from nitrates can allow small scale production with a more even distribution of ammonia throughout densely populated cities for a well-developed society promoting green roofs and urban farming by better access to fertilizers without major infrastructure remodeling. Though nitrate conversion and released as eco-friendly nitrogen in the short run via biological method is desirable, the energy intensive and high carbon footprint Haber-Bosch process at elevated pressures and temperatures is quite expensive if used to

generate ammonia from dinitrogen at relatively small facilities requiring significant energy consumption with high carbon dioxide emissions. Presently, approximately 1.2 % of the greenhouse gas emissions worldwide and 2 % of the total global energy consumption can be attributed to the Haber-Bosch process. To this effect, a catalyst for lowering toxic nitrate levels in municipal and sanitary waste and alleviating unorthodox ecological strains on sewage and drainage systems is desirable.

Cu and Cu-based materials have been extensively investigated for nitrate reduction. This relatively low-cost metal displays a high selectivity toward ammonia production in basic and neutral media. Cu(100) reduces NO_2^- at a higher rate and a lower deactivation than does Cu(111), yet a pure Cu polycrystalline electrode only displays a Faradaic Efficiency(FE) of 35 % in the best conditions. CuO nanomaterials for NO_3^- reduction display a critical role of oxygen vacancy defects (with one free electron) for the adsorption of NO_3^- intermediates where the NH_4^+ yield has a maximum FE of 89 %. CuO nanowire arrays (NWAs) display a NO^- reduction with a reported FE of 95.8 % for NH_3 , where CuO is electrochemically converted to Cu/Cu₂O NWAs that lower the energy for *NOH formation due to an increased electron density and subsequently suppressed hydrogen evolution reaction (HER). A Cu-molecular solid catalyst, Cu-3,4,9,10-perylene tetracarboxylic dianhydride (Cu-PTCDA), was synthesized and showed a unique electronic structure of Cu that boosts H-N bond formation through proton and electron transfer between PTCDA and the Cu. To this end an improved molecular catalyst for the generation of ammonia from nitrate is desirable.

BRIEF SUMMARY OF THE INVENTION

An embodiment is directed to a system where local waste nitrate can be converted directly to the value-added product ammonia. The system includes an electrolysis cell having a working electrode that has a CuDATA molecular catalyst absorbed on carbon black. The CuDATA molecular catalyst has CuSO_4 complexed with 3,5-diamino-1,2,4-triazole (DATA). The CuDATA molecular catalyst absorbed on carbon black can be supported on glassy carbon. The working electrode can include perfluorinated acid resin. The counter electrode can be a carbon comprising electrode or any other auxiliary electrode stable in an acidic environment.

Another embodiment is directed to a method of converting nitrate to ammonia where the electrolysis system with the working electrode having a CuDATA molecular catalyst on carbon

black and a counter electrode is filled with an aqueous solution containing nitrate ions and an electrical current is applied to the working electrode and the counter electrode that reduces the nitrate ions to ammonia. The aqueous solution containing nitrate ions can be acidic and an acid can be added to any neutral or basic solution that is the nitrate source. The acid can be, but is not limited to, perchloric acid. The CuDATA molecular catalyst on carbon black is formed by absorbing copper sulfate in aqueous solution on carbon black in an aqueous suspension to form a copper sulfate on carbon black suspension and mixing the copper sulfate on carbon black suspension with a solution of 3,5-diamino-1,2,4-triazole (DATA). The solution containing nitrate can be a waste nitrate solution such that waste remediation can occur in the local medium of the waste source and provide a value-added product that can be used or transformed into a fertilizer, for example when the waste nitrate is an agricultural waste.

BRIEF DESCRIPTION OF THE DRAWINGS

Fig. 1 shows a chart of the Faradaic Efficiency (FE) of a CuDATA molecular catalyst based working electrode in an electrolysis system, according to an embodiment, for conversion of nitrate to ammonia vs catalyst cost vs other reported catalysts for the equivalent transformation.

Fig. 2 shows a schematic drawing for a flow-based denitrification electrolysis system where the working electrode can be the CuDATA molecular catalyst based working electrode, according to an embodiment.

Fig. 3 shows a scanning electron microscope image of the surface of the CuDATA molecular catalyst on carbon black.

Fig. 4 shows a plot of the nitrate consumption and the ammonia formation, where the ammonia is in the protonated form when under electrolysis with the CuDATA molecular catalyst based working electrode, according to an embodiment.

Fig. 5A shows a plot of the effective current at a potential of -1.0 V over time during the conversion of nitrate to ammonia using the electrolysis system with the CuDATA molecular catalyst containing working electrode, according to an embodiment.

Fig. 5B is a bar chart of the ammonia yield rate and the FE over time using the CuDATA molecular catalyst containing working electrode, according to an embodiment at -1.0 V.

Fig. 6A is a plot for the FE of nitrate to protonated ammonia conversion at different electrical potentials using the CuDATA molecular catalyst containing working electrode, according to an embodiment, and a state-of-the-art polycrystalline Cu electrode.

Fig. 6B is a bar chart for the conversion of nitrate to protonated ammonia at different electrical potentials using the CuDATA molecular catalyst containing working electrode, according to an embodiment, and a state-of-the-art polycrystalline Cu electrode.

Fig. 7 shows alternative pathways having a plurality of state-of-the-art processes to convert nitrate to ammonia that can be replaced by the direct conversion of nitrate to ammonia by electrolysis.

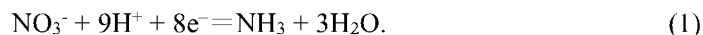
DETAILED DISCLOSURE OF THE INVENTION

An embodiment of the invention is directed to a system using a CuDATA molecular catalyst comprising a salt of copper with 3,5-diamino-1,2,4-triazole (DATA) to produce renewable ammonia from nitrate with easy and low energy-consumption synthesis and excellent catalytic activity. The CuDATA molecular catalyst is a cathode material with a Faradaic Efficiency (FE) and yield rate toward ammonia that can be as high as about 98 % with 30 g NH₃ / (g cat×h) or 1.78 mmol/(mg×h) yield rate as opposed to 0.13 mmol/(mg×h) for CuPTCDA. The synthesis of CuDATA is straightforward, low cost, energy-friendly and environmental-friendly, being conducted at room temperature under ambient pressure. CuDATA outperforms TiO₂ and TiO_{2-x} catalysts for nitrate reduction, and although CuDATA displays about three times lower ammonia production than do Ru nanoclusters display at high nitrate concentrations, the activity per price for CuDATA is about 900 times greater than that of Ru clusters.

In an embodiment, the CuDATA molecular catalyst applied as an electrocatalytic catalyst is employed in an electrolysis system for removal, treatment, and upcycling of aqueous nitrate leached from agricultural and municipal waste streams. Nitrate removal is a one-step process conducted under an ambient atmosphere with mild conditions. As ammonia is produced the product generated can be further refined and used in nitrogen-containing fertilizers.

An exemplary electrolysis system is shown in Fig. 2, where an H-cell and three electrodes are employed: a glassy carbon electrode with CuDATA catalyst appended on it, as shown in Fig. 3, working electrode; a Pt counter electrode; and an Ag/AgCl reference electrode. Electrolyte including nitrate anions is evenly distributed in the electrolytic cell.

An exemplary denitrification process can be carried out, for example, with a perchloric acid and potassium nitrate solution as the nitrate containing electrolyte. The reaction pathway is:



During electrolysis, the concentration of nitrate decreases with an increase in ammonia concentration, as indicated in Fig. 4, indicating that nitrate is converted into ammonia, indicated in its protonated form, during electrolysis. The stability of CuDATA catalyst is indicated in Figs. 5A and 5B. The ammonia yield rate and Faradaic Efficiency are maintained at a steady and superior degree for at least 240 min.

When compared with traditional Cu polycrystalline electrode systems, the exemplary CuDATA based system enhances the Faradaic Efficiency for ammonia production by over 50 %, as indicated in Fig. 6A. Cu electrode exhibits a volcano shape curve for ammonia production with increasing applied potential with a plateau at -0.8 to -1.2 V relative to the reference electrode, as indicated in Fig 6B. The generated concentration of ammonia remains approximately constant for the Cu polycrystalline electrode but increases with the CuDATA electrode when a greater negative potential is applied. The ammonia FE can be about 98 % for the CuDATA electrode while a pure Cu polycrystalline electrode has a maximum FE of about 35 % at its optimal potential. The maximum concentration of ammonia generated using the exemplary CuDATA electrode was about 33.4 ppm, while that of the otherwise equivalent system employing an exemplary Cu polycrystalline electrode was about 5.7 ppm.

The nitrate waste can be concentrated as needed before the electrolysis to ammonia. Low-level nuclear wastewater and industrial wastewater generally would not need pre-concentration treatment though acidification may be required. Textile waste and polluted ground water often require concentration, generally via a membrane technology, to achieve a nitrate concentration of about 50 mM or more and may require acidification before electrolysis.

A kilogram of the CuDATA catalyst is stable for at least 30 hours and can produce a ton of ammonia. In comparison with other modes to ultimately generate ammonia from nitrate, as shown in Fig. 7, the direct electrolysis to ammonia has significant advantages over the alternative multistage processing, ultimately through a Haber-Bosch process, where the ammonia production is performed at dispersed locations. Considering current cost of the CuDATA catalyst, electricity, and other balance of plant costs, the conversion of waste nitrate to ammonia appears to be about one third of that of the alternative multistage processes. It is assumed that this small

footprint electrolytic device, with a foot-print of about one square meter, that can be powered by solar panels or other renewable electricity, will enhance the advantages of nitrate conversion to ammonia on a local scale.

With regard to other electrolysis catalysts for direct nitrate to ammonia conversion, a FE of 98 % displayed for the CuDATA electrode exceeds that of 85 % reported for Ti (82 %), TiO_{2-x} or TiO_2 (85 and 66 %), and other copper electrodes, Cu/Cu₂O NWAs (96 %), and CuPTCDA (86 %). Hence, the CuDATA system using the low cost CuDATA molecular catalyst on the cathode is a cost-effective alternative to the higher FE systems employing much more expensive Cu/Ni alloys or strained Ru nanoclusters.

Following are examples that illustrate procedures for practicing the invention. These examples should not be construed as limiting.

MATERIALS AND METHODS

Synthesis of CuDATA catalyst

Solutions are prepared by dissolving $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ and 3,5-diamino-1,2,4-triazole (DATA) in DI water. Ultrasonication the CuSO_4 solution and adding Vulcan carbon black to form a suspension at ambient temperature and pressure. Adding the DATA solution dropwise to the CuSO_4 /Vulcan suspension under sonication. Centrifuging the solid supported catalyst from the solution. Drying the solids under vacuum at 60 °C for 24 h and grinding the solid. A 10 mg portion of the solid powder is suspended in 1 mL of absolute EtOH and 6 μL of Nafion perfluorinated resin solution to form the ink that forms the amorphous morphology of CuDATA on Vulcan carbon catalyst shown in Fig. 3.

Denitrification Process

An electrolyte solution is prepared with perchloric acid as electrolyte and potassium nitrate to yield concentrations of perchloric acid and potassium nitrate of is 0.1 M and 0.05 M, respectively. The CuDATA on Vulcan carbon black catalyst is appended on a glassy carbon electrode and dried under a stream of nitrogen. The CuDATA comprising cathode, Pt counter electrode and an Ag/AgCl reference electrode are constructed in a cell. This denitrification system is connected to an electrochemical workstation and a constant potential of -1.0 V vs Ag/AgCl is applied for 30 min. With nearly a single reduction product of ammonia in its protonated form where the yield rate of ammonia and FE is nearly constant for 240 min.

All patents, patent applications, provisional applications, and publications referred to or cited herein are incorporated by reference in their entirety, including all figures and tables, to the extent they are not inconsistent with the explicit teachings of this specification.

5 It should be understood that the examples and embodiments described herein are for illustrative purposes only and that various modifications or changes in light thereof will be suggested to persons skilled in the art and are to be included within the spirit and purview of this application and the scope of the appended claims. In addition, any elements or limitations of any invention or embodiment thereof disclosed herein can be combined with any and/or all other elements or limitations (individually or in any combination) or any other invention or
10 embodiment thereof disclosed herein, and all such combinations are contemplated with the scope of the invention without limitation thereto.

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CLAIMS

We claim:

1. A system for conversion of nitrate to ammonia, comprising an electrolysis cell wherein the working electrode comprises a CuDATA molecular catalyst on carbon black.

2. The system for conversion of nitrate to ammonia according to claim 1, wherein the CuDATA molecular catalyst comprises CuSO_4 complexed with 3,5-diamino-1,2,4-triazole (DATA).

3. The system for conversion of nitrate to ammonia according to claim 1, wherein the CuDATA molecular catalyst on carbon black is supported on a glassy carbon.

4. The system for conversion of nitrate to ammonia according to claim 1, further comprising a perfluorinated acid resin.

5. The system for conversion of nitrate to ammonia according to claim 1, further comprising a carbon comprising counter electrode.

6. A method of converting nitrate to ammonia, comprising:
providing an electrolysis cell comprising a working electrode comprising a CuDATA molecular catalyst on carbon black and a counter electrode;
providing an aqueous solution comprising nitrate ions;
applying an electric current to the working electrode and the counter electrode;
and
reducing the nitrate ions to ammonia.

7. The method of converting nitrate to ammonia according to claim 6, wherein the aqueous solution further comprises an acid and the ammonia is in a protonated form.

8. The method of converting nitrate to ammonia according to claim 7, wherein the acid is perchloric acid.

9. The method of converting nitrate to ammonia according to claim 6, wherein the CuDATA molecular catalyst on carbon black is formed by absorbing copper sulfate in aqueous solution on carbon black in an aqueous suspension to form a copper sulfate on carbon black suspension and mixing the copper sulfate on carbon black suspension with a solution of 3,5-diamino-1,2,4-triazole (DATA).

10. The method of converting nitrate to ammonia according to claim 6, wherein the solution comprising nitrate is an acidic solution.

11. The method of converting nitrate to ammonia according to claim 6, wherein the solution comprising nitrate is a waste nitrate solution.

12. The method of converting nitrate to ammonia according to claim 6, wherein the electric current is supplied at a constant potential.

13. The method of converting nitrate to ammonia according to claim 6, wherein the constant potential is at least -1.0 V.