Electrochemically Induced Conversion of Urea to Ammonia

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A novel electrochemically induced method for ammonia synthesis (eU2A) on demand from urea in alkaline media was demonstrated. A Nickel based electrode was employed as the active catalyst. The effective rate of ammonia generation of the eU2A process at 70°C is ∼28 times higher than the thermal hydrolysis (THU) of urea. The eU2A operates at lower temperature (55% lower) and pressure (6 times lower) than the THU; this could lead to significant energy savings. The process finds applications on selective catalytic reduction (SCR) for the removal of nitride oxide from combustion systems (e.g., diesel vehicles, power plants, etc.).

Ammonia is an important chemical used in many fields such as the fertilizer industry,[1] and food industry.[2] One popular application of ammonia is to control nitrogen oxide (NOx) emissions, this technology is known as selective catalytic reduction (SCR). SCR systems are typically found on utility boilers, industrial boilers, etc. The technology has shown to reduce NOx by 70–95%. Recent applications include diesel engines, such as those found on large ships, diesel locomotives, and even automobiles.[3–5] However, ammonia is considered a hazardous chemical.[6] Therefore, instead of using ammonia, most SCR systems use urea (nontoxic). Urea can be thermally hydrolyzed into ammonia on demand as shown in Eq. 1[7]

$$CO(NH_2)_{2(aq)} + H_2O \rightarrow 2NH_3 + CO_2 \qquad [1]$$
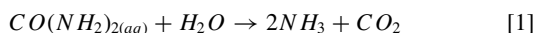
The thermal conversion of urea to ammonia processes used in power plants -such as urea pyrolysis (540°C)[8] and urea hydrolysis (150°C, 5–6 atm)[9]- are not suitable for mobile engines since the reaction conditions are inaccessible. Current thermal hydrolysis of urea (THU) processes employed in diesel engine vehicles dose urea by injecting urea-water solutions (this mixture is known as diesel effluent fluid, DEF, 32.5% weight urea in deionized water) and use the exhaust temperature to convert urea to ammonia. However, in low-load urban driving, the exhaust temperature goes from 300°C to lower than 130°C. The overall NOx conversion effectiveness in the system is low due to the curtailed urea dosing caused by insufficient conversion of urea.[10] In addition, the quality of the DEF needs to be high since the SCR catalyst can be damaged if there is contamination in DEF (e.g., due to minerals in water used for making DEF[11]).

In this paper, we demonstrate a new technology that allows the electrochemical conversion of urea to ammonia, the eU2A process.[12,13] The process allows the production of ammonia on demand by applying a cell voltage as depicted in Fig. 1a.[12,13] This technology could enable decoupling the ammonia production from the exhaust system in diesel engine vehicle SCR applications, as well as portable urea to ammonia reactors.

Experimental

The eU2A reactor was built at the Center for Electrochemical Engineering Research and presented schematically in Fig. 1b. A heat jacket with a controller (Econo 12125-14) was used to heat and maintain the temperature of the reagent in the reactor. The eU2A process was performed in a two electrodes system and the cell voltage was controlled by an Arbin BT2000 potentiostat. The anode (working electrode) of the reactor was made by Ni beads and a Ni mesh was used as cathode, refer to Section S1 of supplementary information (SI) for details. Part of the ammonia produced was dissolved in the solution in the reactor, while the rest in vapor phase was captured in a glass vessel containing

1 L of 1 M sulfuric acid solution (Fig. 1b). An ammonia ion selective electrode (ISE) (Orion 710A+, Thermo Electron Corporation) was used to measure the concentration of ammonia in both the reactor and the acid trap (SI Section S3).

The ammonia production rate in the eU2A process was measured at different applied voltages and temperatures. The eU2A process was compared with the thermal hydrolysis of urea (THU) in the same reactor (without applying a cell voltage). The volume of solution in the reactor was kept constant in all the experiments (250 mL). All the experiments were performed with DEF solution containing 7M KOH. Urea concentration was measured by UV-vis spectroscopy using a Hewlett Packard Spectrophotometer HP 8452A (SI Section S4). The gases other than ammonia and CO_2 generated in the eU2A process were collected (exhibited in Fig. 1c) and analyzed by gas chromatography (GC) -SRI 8610C Gas Chromatograph equipped with a Mole Sieve 5A column and a thermal conductivity detector. Argon gas was used as the carrier gas (SI Section S5).

Results and Discussion

The effect of temperature in the eU2A process at constant voltage (1.65 V) is shown in Fig. 2a. The ammonia production rate is a function of temperature as expected since the working electrode volume was only 18.8% of the volume of the reactor (Section S1 of SI). The maximum operating temperature was set to 70°C to limit the evaporation of water from the reactor. Fig. 2b shows the experimental results of the eU2A conducted at different voltages ranging from 1.35 V to 1.65 V. At short times, the effect of cell voltage in the moles of ammonia generated is negligible. After 45 minutes, there is a clear difference between 1.65 V and other voltages. At this voltage, there is some N_2 evolution from the working electrode due to urea electrolysis according to Eq. 2:[14]

$$CO(NH_2)_{2(aq)} + 6OH^- \rightarrow N_2 + CO_2 + 5H_2O + 6e^- \qquad [2]$$
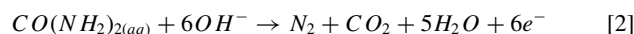
The N_2 gas evolving may refresh the electrode surface making the catalyst available for urea conversion while at other applied voltages, the effect is negligible. As shown in Figure S2, a cell voltage of at least 1.545 V should be applied to maximize the formation of NiOOH in 7 M KOH. This indicates that the ammonia generation is associated with the formation of NiOOH. This enhancement may also be due to inherent mixing caused by the gas evolution. Therefore, 1.65 V was chosen as the applied voltage for long time experiments (24 hours experiments) of the eU2A process.

Fig. 2c shows a comparison of the ammonia generated at 70°C during 24-hour experiments in the eU2A process (at 1.65 V) and the THU process. A dramatic increase in the ammonia generation is observed in the eU2A when compared to the THU. In a period of 24 hours, 1.609 moles of ammonia were generated in the eU2A process, while 0.256 moles were generated in the THU process. The rate of ammonia generation per effective volume (volume of the catalyst,

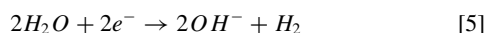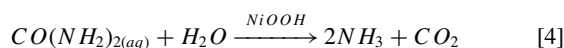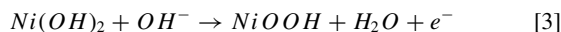*Electrochemical Society Student Member.
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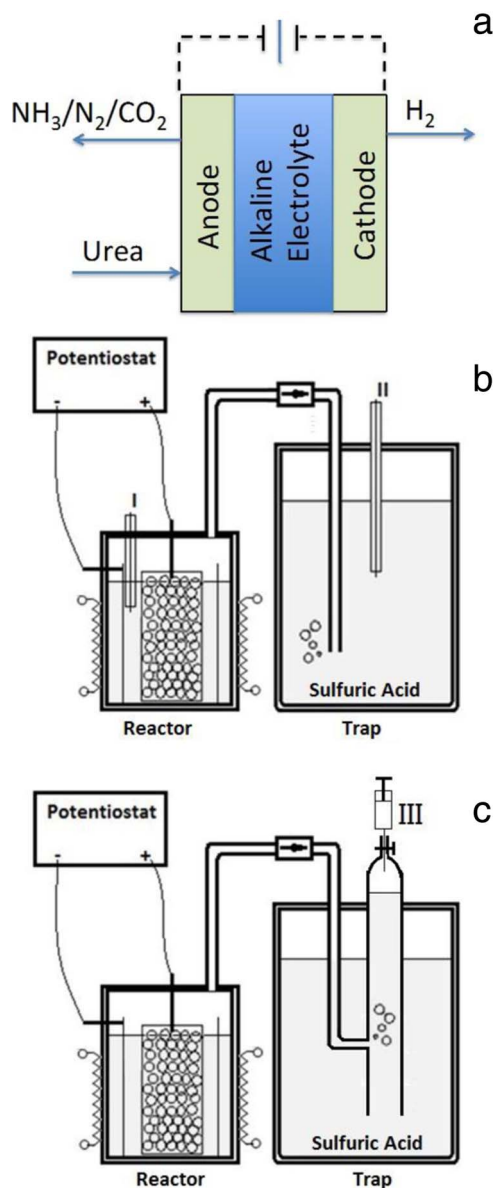
Figure 1. (a) Schematic representation of the eU2A process; (b) Schematic of the eU2A reactor (I and II are sample ports); (c) Schematic of the gas collection system for the gas analysis (III is the sample port for collecting gas for GC analysis).

47 cm^3) for the eU2A process is 20.39 g h^{-1} L^{-1} after subtracting the ammonia generated from the thermal contribution, 0.256 moles. The rate for the THU process is 0.73 g h^{-1} L^{-1} per effective volume (volume of the reagent, 250 mL). That is, the effective rate of ammonia generation of the eU2A process is ∼28 times higher than for the THU process. Accordingly, the amount of urea decreases more rapidly in the eU2A process as shown in Fig. 2d.

Our results demonstrate that urea hydrolysis can be electrochemically induced using an inexpensive transition metal, nickel. In basic solution, Ni^{+2} is oxidized to Ni^{+3} forming nickel oxyhydroxide according to reaction 3. It is proposed that the NiOOH serves as a catalyst for the hydrolysis of urea according to reaction 4 (SI section S2). At the cathode of the reactor, hydrogen evolves according to reaction 5.

$$Ni(OH)_2 + OH^- \rightarrow NiOOH + H_2O + e^- \qquad [3]$$

$$CO(NH_2)_{2(aq)} + H_2O \xrightarrow{NiOOH} 2NH_3 + CO_2 \qquad [4]$$

$$2H_2O + 2e^- \rightarrow 2OH^- + H_2 \qquad [5]$$

However, the eU2A process can compete with the urea electrolysis in alkaline media (Eq. 2) to produce nitrogen.[14–16] It has recently been proved by in-situ electrochemical X-ray diffraction that NiOOH reacts quickly with urea.[17] It has also been shown that urea electrolysis can be enhanced by adding Rh into the Ni catalyst.[18] The hydrolysis of urea (Eq. 4) could be favored by operating the electrochemical cell at voltages that enable the formation of NiOOH with minimum direct oxidation of urea to nitrogen. This cell voltage can be estimated by cyclic voltammetry analysis (SI section S2); however, it has to be confirmed experimentally due to the overpotential caused by the hydrodynamics of the reactor.

Warner postulated that urea hydrolysis -THU summarized by reaction 1- consists of two steps. The first step is the decomposition of urea to ammonia and isocyanic ion (Eq. 6) which is irreversible at pH less than 5 and greater than 12.[19] The second step is the hydrolysis of isocyanic ion to produce ammonia and CO$_2$ (Eq. 7).[19]

$$CO(NH_2)_2 \rightleftharpoons NH_3 + H^+ + CNO^- \qquad [6]$$

$$CNO^- + H^+ + H_2O \rightarrow NH_3 + CO_2 \qquad [7]$$
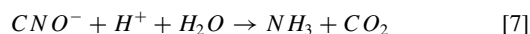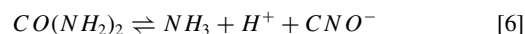
In acid solution, reaction 7 is too fast, and no isocyanic ion has been reported. In alkaline medium, reaction 7 is slow and the presence of isocyanic ion is favored.[19] When the pH increases, the rate constant of the first step increases remarkably while the one of the second step decreases (e.g., at pH of 14.5, the rate constant of the first step is about 5 times the rate constant of the second[19]). As a consequence, in alkaline solution, the stoichiometric ratio of produced ammonia and decomposed urea is less than 2 -e.g., 1.38 at pH of 12.78 and 100°C.[19] During the 24-hour experiments, the ratio of produced ammonia and decomposed urea in the THU was 1.19, much lower than the ratio in the eU2A, which was 1.96 (the subtle loss of urea in urea electrolysis is included, SI Section S6). The oxidation state of nickel in NiOOH is Ni^{+3}, which is considered a hard acid (Lewis acid).[20] Therefore, it is hypothesized that the NiOOH layer catalyst formed in the eU2A process provides acid sites that promote the reaction in the second step (Eq. 7) minimizing the formation of isocyanic ions.

No CO$_2$ and ammonia gases were detected in the gas chromatograph (SI Fig. S4), since CO$_2$ was absorbed in the reactor by the KOH and ammonia was trapped in both the reactor and the acid trap. H$_2$, O$_2$, and N$_2$ were observed in the gas sample and the volumetric ratio H$_2$: O$_2$: N$_2$ was 61.9%: 7.2%: 30.9% (SI Table S3.1). It is hypothesized that air was present in the dead volume of the system -such as headspace and connecting hoses- when the reactor was assembled. However, there was extra N$_2$ in the gas, see SI Table S3.2, which indicates that the urea electrolysis (Eq. 2) occurs in parallel to the eU2A reactions (Eqs. 3 and 4). The production of H$_2$ could offer additional advantages to the eU2A since it could assist the NH$_3$ SCR by reducing the reaction temperature and increasing the activity of the catalyst in the SCR reactor.[21]

The average current in the eU2A process, during the 24-hours experiments, is 0.364 A (SI Fig. S5), therefore, the consumed electrical energy for ammonia production is 0.63 Wh g^{-1}. The electrical energy is low, because, it is only needed to produce the catalyst (NiOOH), which requires one electron transferred. On the other hand, the hydrogen production rate is 0.0136 g h^{-1} (SI Section S6).

Previous research established that no rapid urea hydrolysis reaction takes place at temperatures lower than 140°C.[22] The concentration change of urea in the reactor was used to estimate overall reaction rate constants, *k*, for Eqs. 1 and 4 in the presence of KOH assuming first order reaction.[19] In the THU process, *k* = 0.00039 min^{-1}, which is in agreement with the results reported in the literature.[19] On the other hand, in the eU2A process, *k* = 0.00140 min^{-1}, which is ∼30% of that of the urea hydrolysis process[22] at 140°C and 100 kg cm^{-2} (SI Table S5). That is, the eU2A process enables significant ammonia production at lower operating pressure and temperature (atmospheric pressure, 70°C) compare to the urea hydrolysis (100 kg cm^{-2}, 140°C). These findings could result in significant energy savings as well as
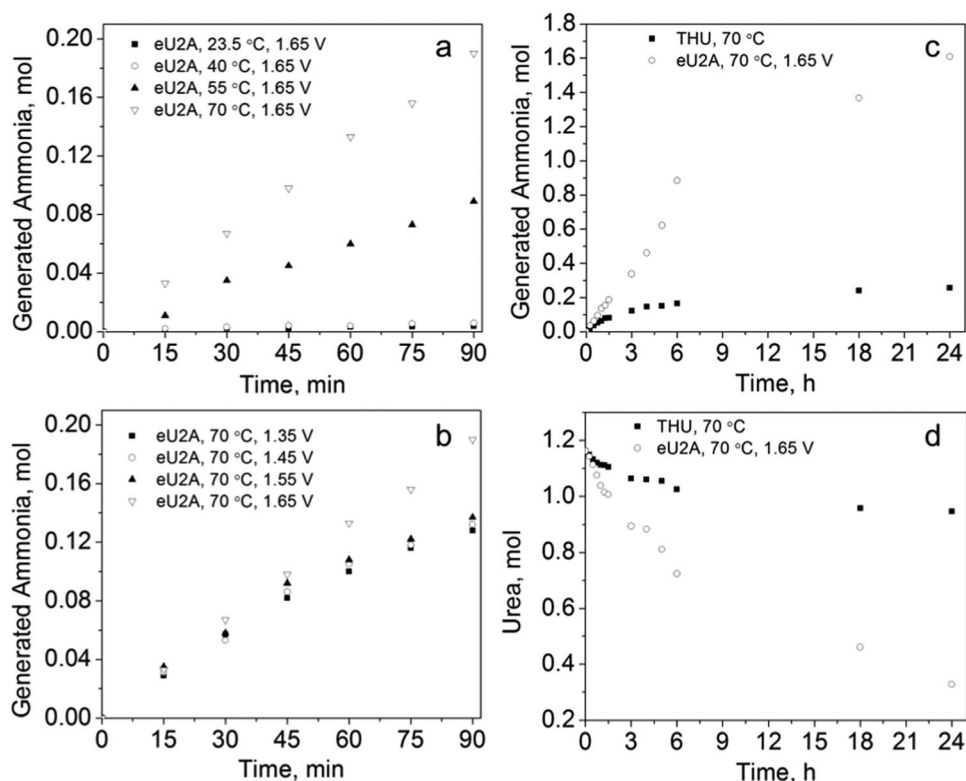
Figure 2. Ammonia generation in the eU2A process at (a) different temperatures (a) and (b) different applied potentials using DEF in the presence of 7.0 M KOH in 90 minutes experiment; (c) Ammonia generation and (d) residual urea in the eU2A (70°C, 1.65 V) process and its comparison with the THU (70°C) in a period of 24 hours using DEF in the presence of 7.0 M KOH.

less expensive reactors (the eU2A process could avoid the use of high pressure vessels).

Conclusions

A new electrochemical process for the conversion of urea to ammonia, the eU2A process, was demonstrated. The eU2A process enables the optimum conversion of urea to ammonia preventing the formation of isocyanic ions in alkaline media. The process enables higher reaction rates than the thermal hydrolysis at lower operating temperature and pressure. The new process could offer several advantages for SCR systems in vehicles. It could enable decoupling the ammonia generation from the exhaust system, preventing curtailed urea dosing while reducing the amount of water (steam) from the SCR reactor/catalyst -which is considered one of the reasons lowering the conversion of NO.[23] The hydrogen produced could potentially lead to mileage extender in vehicles and a better optimization of the SCR reactor.

Since the eU2A is an electrochemically induced process, electrodes with larger surface areas- such as finer Ni beads, Ni foams, Ni nanocomposites, among others- could also be utilized to enable higher ammonia generation rates and better packing. Moreover, the use of flow reactors could enable better exposure of the catalyst surface to the reagent solution, which would lead to higher ammonia generation rates in the eU2A process.

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