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Unconventional Catalytic Approaches to Ammonia Synthesis

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#### Keywords

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#### Abstract

Ammonia is a critically important industrial chemical and is largely responsible for sustaining the growing global population. To provide ammonia to underdeveloped regions and/or regions far from industrial production hubs, modular systems have been targeted and often involve unconventional production methodologies. These novel approaches for ammonia production can tap renewable resources at smaller scales located at the point of use, while decreasing the  $CO_2$  footprint. Plasma-assisted catalysis and electrochemical ammonia synthesis have promise owing to their atmospheric pressure and low-temperature operation conditions and the ability to construct units at scales desired for modularization. Fundamental and applied studies are underway to assess these processes, although many unknowns remain. In this review, we discuss recent developments and opportunities for unconventional ammonia synthesis with a focus on plasma-stimulated systems.

# INTRODUCTION: AMMONIA SYNTHESIS AND MOTIVATION FOR ALTERNATIVE APPROACHES

Global reliance on ammonia as a fertilizer or a precursor has fueled the growing demand for its production. The industrial ammonia synthesis (i.e., Haber–Bosch) process produces >146 million tons of ammonia annually and consumes 1–2% of global energy (1). The Haber–Bosch process converts molecular hydrogen and molecular nitrogen at temperatures in the range of 650–750 K and pressures ranging between 50 and 200 bar over an Fe-based catalyst (1–3). Fossil energy serves as the primary source of hydrogen for this process, resulting in CO<sub>2</sub> emissions that exceed 1.6% of the annual global amount (4). Industrial ammonia synthesis is a process vital to global population growth and now accounts for nearly 30% of the total nitrogen fixed by either natural or artificial routes.

With these considerations, coupled with the critical, global need for this invaluable resource, alternative processes to synthesize ammonia have been proposed or are in the early stages of development. The primary drivers for an alternative ammonia synthesis process include (*a*) use of renewable energy to reduce the CO<sub>2</sub> footprint; (*b*) implementation of modular processes that can produce ammonia in regions with limited or no access to commercial sources; and (*c*) a desire to address the rising and prohibitive transportation costs of ammonia from central processing facilities owing to safety, environmental, and security concerns. A clear example of such technology is a modular, distributed ammonia synthesis process deployed at the point of use. Taking advantage of remotely located wind energy, alternative and renewable resources can drive small-scale ammonia synthesis at farming operations for direct use (5, 6). Because the conventional high temperatures and pressures applied to ammonia production are undesired, the discovery and development of new, unconventional approaches to realize these goals are transformative.

Creative and innovative solutions for atmospheric pressure, low-temperature nitrogen fixation have been investigated in recent years, including enzyme catalysis (7), homogeneous catalysis (8), chemical looping (9), electrocatalysis (10), photocatalysis (11), and plasma-assisted catalysis (12, 13), among others (14) (**Figure 1**). This review focuses primarily on insights derived from plasma-assisted ammonia synthesis owing to the recent advances in plasma-stimulated catalytic processes. Given the growing fields of electrochemical and photocatalytic ammonia synthesis, we point the reader to multiple, recently published reviews that highlight these approaches (11, 15, 16). Near the end of the review, we highlight recent efforts on hybrid plasma-electrochemical processes (17–19) that may impact the future design of unconventional systems.

# PLASMA-ASSISTED AMMONIA SYNTHESIS

# **Plasma-Stimulated Reaction Systems**

Plasma represents the fourth state of matter, which exists as a gaseous form of ions and unbound electrons. Plasmas are generally categorized as either (*a*) thermal plasmas, in which the unbound electrons and the ions are at the same temperature, or (*b*) nonthermal plasmas, in which the electrons are hotter than the species that constitute the gas phase. Although the majority of plasmas observed in nature are thermal plasmas, plasma technology adopted in materials processing (20), pollution abatement (21), and plasma-assisted catalysis is generally based on nonthermal plasmas. Nonthermal plasmas are generated by applying high voltages across a volume of gas at (or below) atmospheric pressure, resulting in gas breakdown. The coexistence of high-energy electrons ( $T_e \approx 10,000$  K) and low-temperature ions ( $T_i \approx$  ambient) results in a weakly ionized system, in which unbound electrons and ground-state species produce a chemically active phase containing ions, radicals, and rotationally and vibrationally excited species. The ability to activate and convert



Current (red) and emerging (green) routes for nitrogen fixation, including examples of products derived from industrial ammonia production and proposed technologies using ammonia.

highly stable molecules such as  $CO_2$ ,  $CH_4$ , and  $N_2$  at lower pressures and temperatures than the corresponding thermal processes has motivated research in this area (13, 24).

In 1800, Sir Humphry Davy (25) first reported plasma activation of air through the generation of  $NO_x$  when air was passed over an electrified cable. More than a century after this discovery, the Birkeland-Eyde process was developed, which used an electric arc of air to reach gas temperatures of  $3,000^{\circ}$ C to form nitrogen oxides with yields of up to 4% (12). The NO<sub>x</sub> was subsequently cooled and mixed with water to form nitric acid (12). Although it was among the first nitrogen fixation processes implemented, it was quickly supplanted by the Haber-Bosch process owing to the low yields and high energy requirements of up to 15 MWh/ton of nitric acid (12). Despite these issues, interest in plasma nitrogen fixation techniques has continued, especially as nonthermal plasma technologies that operate at substantially lower bulk gas temperatures and higher energy efficiencies (26) have been developed for ozone production and pollution abatement (27). Yin & Venugopalan (28) published the first report of nonthermal plasma ammonia synthesis, using hydrogen-nitrogen glow discharge plasmas at low pressures. Following these initial studies, several atmospheric-pressure plasma configurations have been reported, such as gliding arcs (29), plasma jets (30), and dielectric barrier discharges (DBDs) (31, 32). DBD systems represent most of the studies owing to the ease of operation and incorporation of catalytic materials. Additionally, DBDs are atmospheric-pressure plasmas generated by applying voltage across a volume of gas between two electrodes separated by a dielectric material, such as quartz or another ceramic (33). These different plasma reactors are assessed in more detail in subsequent sections.

# Synergy Between Plasma and Catalysis

Almost immediately after the first report of plasma ammonia synthesis, Sugiyama et al. (34) discovered that catalytic materials introduced in the plasma discharge zone enhanced ammonia yields owing to the suspected synergy between the plasma species and catalyst surface. This synergistic effect has been demonstrated by numerous studies on several different metal catalysts, including Ru (31, 35), Fe (36), Ni (37), Pt (38), and Co (39), among others (40, 41). Although this synergistic effect has been reported in many plasma systems, the inherent complexity of the reactive environment has limited detailed mechanistic investigations in the presence of plasma stimulation.

Thermal catalytic processes, plasma phase reactions, and interactions between the plasma species and the catalyst can occur in parallel. Figure 2a summarizes three proposed



#### Figure 2

(*a*) Reaction pathways that may occur in plasma-assisted catalysis, as well as the interactions between the plasma and catalyst that can influence these pathways. (*b*) Measured ammonia production rates using different reactor configurations with a 5 wt % Co/Al<sub>2</sub>O<sub>3</sub> catalyst to demonstrate the synergy between the plasma and catalyst in plasma-assisted ammonia synthesis. Panel *b* modified with permission from Reference 42; copyright 2019 American Chemical Society.

plasma–catalyst interactions that are possible under plasma stimulation: (*a*) plasma-induced modification of the catalyst, (*b*) catalyst-induced modification of the plasma, and (*c*) direct interactions between the plasma phase species and the catalyst surface (22). Plasma-assisted catalysis is a broad and growing field, and many of these interactions have been investigated in other reaction systems to identify and exploit the primary mode that drives the desired chemical transformation (13, 22, 23).

As depicted in Figure 2b, we include experiments from our lab that demonstrate the plasmacatalyst synergy (42). Measured ammonia production rates are plotted with respect to the DBD plasma/catalyst configuration (Figure 2b). In each of these experiments, the bulk gas temperature, DBD power, N<sub>2</sub>:H<sub>2</sub> ratio, and pressure were maintained at 200°C, 10 W, 3:1, and 1 atm, respectively. Thermal catalytic activity (denoted as no plasma) at this temperature and pressure over a 5 wt% Co/Al<sub>2</sub>O<sub>3</sub> catalyst is negligible, as shown in Figure 2b, and is the basis for comparison (42). An empty reactor with plasma stimulation at these conditions successfully converts N2 and H2 to ammonia without added catalyst. A similar production rate of NH3 is observed when the catalyst is added but not present in the plasma discharge zone (no overlap). As overlap of the discharge zone with the catalyst is increased, ammonia production also increases, providing evidence for the synergy between the plasma phase and the Co catalyst. As observed in these experiments, the plasma phase reaction constitutes ~50% or more of the total ammonia yield under these conditions. The homogeneous plasma phase reactivity and kinetics have been measured and modeled extensively (43), and these reactions are also shown here to be an important contributor to ammonia production. Therefore, it is necessary to quantify and compare background thermal and plasma phase reactions to identify plasma-assisted catalytic effects.

Plasma-induced modification of the catalyst can occur through the creation of hot spots on the catalyst surface, resulting in increased sintering/surface migration of the catalyst particles or localized thermal ramps that could influence reaction kinetics (Figure 2a). Aihara et al. (44) reported the use of a high-surface area copper electrode as a catalyst for ammonia synthesis. During plasma exposure, the authors observed the migration of the Cu from the electrode to the walls of the reactor, which resulted in an increase in the ammonia production rates (44). In a separate study, an alumina-supported Co catalyst was used for ammonia synthesis stimulated by a DBD plasma (42). The ammonia production rate ( $\sim$ 40  $\mu$ mol NH<sub>3</sub>/g/min) remained stable for 7 h under plasma stimulation at 200°C and 10 W. Additionally, transmission electron microscopy images revealed the catalyst particle sizes were retained after reaction (42). Many factors can influence these results, including applied power, catalyst type and composition, gas composition, and bulk gas temperature, to name a few. Catalyst-stability studies with plasma stimulation for ammonia synthesis are relatively uncommon in the literature. More detailed characterization studies (including in situ/operando studies, as discussed later) could be used to elucidate operational conditions and/or desired material properties that could be targeted with accompanying plasma exposure. Alternatively, the plasma can alter catalytic activity by heating the system or by generating catalytic hot spots through electron impact, which is significantly more difficult to identify and evaluate (45). In thermal systems, thermocouples are inserted into the reaction zone to monitor the reactant or effluent temperatures. However, when metal-based thermocouples are introduced in plasmas, system discharges can occur to the thermocouple, thus preventing this method of measurement. Two relatively simple approaches to measure the bulk gas temperature involve either (a) applying infrared cameras to monitor the discharge zone or (b) placing a thermocouple downstream from the discharge and calibrating the temperature difference ex situ with standards (33, 39, 42, 46). Although these methods are useful for estimating temperature, they can underestimate the temperature of the reaction zone. Using antimony as a melting point reference, Kim et al. (46) observed a 10-K difference in the melting point in a DBD plasma at three powers (1 W, 5 W, and 10 W), indicating that a higher bulk gas temperature (and likely surface temperature) existed under plasma stimulation. The other example comes from Gibson et al. (45), who developed extended X-ray absorption fine structure experiments of plasma-stimulated methane oxidation over Pd/Al<sub>2</sub>O<sub>3</sub>. The authors did not observe structural changes in the catalyst, but temperatures higher than the measured bulk gas temperature were determined (45).

Catalyst-induced modification of the plasma can also impact the reactions occurring at or near the catalyst surface through localized changes in the electric field. The incorporation of dielectric materials, such as those used as supports for metal catalysts, in the plasma discharge zone alters plasma behavior, influencing the electric field strength and electron temperatures, which in turn alters the activity of plasma (47, 48). Similarly, the active metal could induce changes to the plasma. For example, a study on the plasma-assisted decomposition of volatile organic compounds showed that silver nanoparticles cause significant expansion to the plasma discharge area that could not be achieved with dielectric materials like BaTiO<sub>3</sub> alone (49, 50). By contrast, in a recent report, Herrera et al. (51) characterized a  $N_2/H_2$  DBD plasma exposed to three different  $\gamma$ -Al<sub>2</sub>O<sub>3</sub>-supported metal catalysts (Ni/Al<sub>2</sub>O<sub>3</sub>, Co/Al<sub>2</sub>O<sub>3</sub>, and Fe/Al<sub>2</sub>O<sub>3</sub>) and compared the plasma properties to a plasma reactor packed only with  $\gamma$ -Al<sub>2</sub>O<sub>3</sub>. Despite differences in ammonia production rates from the various materials, the authors found no statistically significant differences between the plasma current, number of plasma filaments, or plasma capacitance (51). Thus, the differences in the ammonia production rate were related to the intrinsic differences in the activity of the catalysts and not due to the alterations of the bulk plasma by the metals (51). However, owing to limitations in the spatial resolution of the macroscale measurements, it is possible that the metals influence the plasma properties at the microscale near the catalyst surface, which was not captured in these experiments and remains an important aspect of these systems to study in more detail.

As presented in Figure 2b, positioning a catalyst in direct contact with the plasma phase significantly improves ammonia production rates, which is speculated to result from the direct interactions between plasma phase species and the catalyst surface. To exploit these interactions and identify optimal catalyst compositions for ammonia production, Mizushima et al. (38) reported ammonia production rates over different metals using an alumina membrane loaded with either Fe, Ni, Pt, or Ru. Enhancement beyond the background ammonia production was observed with all materials, with measured activities for each metal (e.g., mol  $NH_3/min$ ) decreasing in the order Ru > Ni = Pt > Fe (38). Although Ru was expected to be effective, the authors noted that the high activity of Ni and Pt could indicate a change in the mechanism under plasma stimulation (38). Recently, Iwamoto et al. (41) studied the effects of different metal wools as electrodes for ammonia synthesis (Figure 3). The authors also revealed an unusual activity trend, with Au, Ag, and Pd being the most active (mol NH<sub>3</sub>/min), as opposed to Ru- or Fe-based wools (41). To understand this unusual activity trend, nitrogen adsorption energies and the energy for metal nitride formation were determined based on the assumption that the surface metal nitride was a reaction intermediate. The production rates were plotted as a function of the nitride formation energy (Figure 3*a*) or the nitrogen binding energy (Figure 3*b*) to show an inverse relationship between the stability of the metal nitride and the ammonia production rate (41). A strong correlation between reactivity and nitrogen binding energy in plasma systems is sensible due to its effectiveness as a descriptor in thermal catalysis (52). Since the initial development and deployment of the Haber-Bosch process, advances in both theoretical catalysis research and surface science have led to an enhanced understanding of the fundamental processes governing catalytic ammonia synthesis. In particular, a detailed understanding of how the reaction proceeds on metal surfaces has been developed (53). The reaction follows a Langmuir-Hinshelwood mechanism whereby both nitrogen and hydrogen dissociatively adsorb on the surface, combine, and subsequently



Measured ammonia synthesis rates using different wool-like metal electrodes as a function of (a) surface nitride energy of formation on that metal and (b) the binding energy of N on the metal. Adapted with permission from Reference 41; copyright 2017 American Chemical Society.

desorb as ammonia (54). In general, the reaction rate on metal surfaces is limited by one of two steps: the dissociative adsorption of nitrogen or the desorption of NH<sub>3</sub> from the surface (55). Furthermore, the activation barriers of both of these steps are related to the binding energy of nitrogen on the surface, such that the barriers scale inversely with one another (52). Therefore, metals that bind nitrogen strongly can easily activate and adsorb N<sub>2</sub>, but these metals struggle to desorb the products (e.g., Fe). Metals that weakly bind nitrogen can hydrogenate nitrogen on the surface, but these metals cannot effectively dissociate N<sub>2</sub> (e.g., Ni). As a result, rates as a function of nitrogen binding energy often result in a volcano curve, where the optimal catalyst, generally Ru, provides the highest rate by balancing the hydrogenation and adsorption rates (56). The activity trend in **Figure 3** appears to capture part of this relationship, in which metals with less favorable binding energies are better catalysts, which would suggest that metals that more easily desorb ammonia after hydrogenation are more active under plasma stimulation. This study highlights that correlations between nitrogen binding energy and ammonia production rate under plasma stimulation may diverge from the correlations known for thermal ammonia synthesis.

Polanyi (57) originally proposed that vibrational energy was more effective than translational energy in activating adsorption reactions with late transition states (e.g., nitrogen, methane, or water). Supersonic molecular beam studies have since shown that when water and methane are vibrationally excited, the rate of dissociative adsorption of that molecule on a metal surface is enhanced (58, 59). Owing to the significance of vibrational excitation in atmospheric pressure discharges, Bogaerts & Neyts (60) proposed that increased reactivity of vibrationally excited molecules contributes to plasma-assisted catalytic enhancement. To probe this effect, Mehta et al. (39) combined experimental rate measurements, spectroscopic plasma evaluation, and microkinetic modeling of ammonia production rates that incorporated vibrational excitations. In this study, the distribution of vibrationally excited species of  $N_2$  was estimated using optical emission spectroscopy (OES) and fit to a Treanor distribution (39, 61). **Figure 4a** shows calculated reaction rates as a function of the nitrogen binding energy of a terrace or stepped surface with and without plasma stimulation



(*a*) Calculated turnover frequencies (TOFs) for plasma-assisted ammonia synthesis on various materials on (*i*) a stepped surface site and (*ii*) a terrace site. (*b*) Experimentally measured site-time yields (STYs) for plasma-assisted ammonia synthesis on various metal catalysts. Modified from Reference 39; copyright 2018 Springer Nature.

in the form of vibrational excitation. In the plasma-off calculations, the volcano plot is consistent with previous reports (52). By contrast, plasma on shows a substantial increase in computed rates and a shift in the volcano curve to materials that bind nitrogen more weakly and are generally limited by dissociative  $N_2$  adsorption.

To compliment these calculations, laboratory experiments were conducted to measure ammonia production rates over a variety of metals supported on  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> (Fe, Ru, Co, Ni, and Pt) (39). Figure 4b shows the background-subtracted and site-normalized rates as a function of the nitrogen binding energy. A similar shift in the optimal catalyst was observed experimentally, as was predicted (39). When comparing these results to previous studies, it is apparent that multiple research groups have observed that the ideal catalyst for thermal catalysis may differ when subjected to a plasma environment. Experimental reactivity trends for plasma-enhanced catalysis are not yet well-established, as differences in the plasma properties may influence the activity trend of metals in plasma systems and may account for the disagreement in activity trends observed between Figures 3 and 4. Caution must be exercised when relating vibrational excitation as the sole contributor to reaction enhancement, as other plasma species and surface processes could dominate and/or contribute directly to the increase in ammonia yields, as noted earlier in this review. In a subsequent study, detailed rate measurements were reported for the plasma-assisted ammonia synthesis reaction on supported Ni, Ru, and Co to determine how the observed plasma phase kinetics differed from the plasma-catalytic kinetics (42). Measurements of the total ammonia production, including the homogeneous plasma phase, were first order with respect to both  $N_2$  and  $H_2$ . However, after background subtracting the plasma contributions, ammonia production rates remained first order with respect to the partial pressure of  $N_2$  but were zeroth order with respect to  $H_2$ (42). These results demonstrated a clear difference between the kinetics of the plasma phase and plasma-catalytic reaction and corroborated the assumption of the microkinetic modeling study that  $N_2$  activation is kinetically relevant (42). Together, these results indicate that if a plasma can directly facilitate dissociative adsorption of N2 on the catalyst surface, the role of the catalyst will change and should be designed accordingly.

#### **Controls and Diagnostics for Plasma-Based Reaction Systems**

An opportunity exists to develop new in situ and operando experiments/configurations to characterize the catalyst under plasma stimulation and to potentially identify differences and similarities in surface intermediates between thermal and plasma-assisted catalysis systems. These advances can lead to the development of more efficient plasma-assisted ammonia synthesis processes and provide guidance on how to control plasma–surface interactions. Plasma-assisted catalytic systems are characterized by the parameters that control thermal catalysis, such as temperature, space velocity, and pressure, as well as plasma parameters, such as specific energy input (SEI), electrode configuration, and plasma phase composition. Most reports examine the effects of these parameters at a macroscopic scale by measuring production rates and energy efficiencies. However, understanding how these parameters control or direct the molecular-level interactions between the catalyst and the plasma could lead to breakthroughs in the design of plasma-stimulated catalytic processes.

Spectroscopic techniques such as infrared spectroscopy and X-ray absorption spectroscopy are commonly used in heterogeneous catalysis, but these techniques have only recently been adapted to plasma-assisted catalysis (45, 62-64). Although no studies have reported the use of these techniques for plasma-assisted ammonia synthesis, the insights gained from other reactions demonstrate their value. Stere et al. (63) reported a plasma-incorporated, diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS) cell to evaluate the effects of a plasma environment on hydrocarbon-based selective catalytic reduction (SCR). Figure 5a-c shows the modified DRIFTS cell outfitted with a plasma jet (63). This configuration allows for gases to be introduced into the reactor cell while constantly exposing the catalyst to a He plasma. Figure 5d shows the promotional effect of the plasma on the formation of surface species during operation. Based on the increase in isocyanate species on the surface (2,265 cm<sup>-1</sup>) as opposed to cyanide (2,175 cm<sup>-1</sup>) as the voltage increased, the authors determined the plasma-assisted system drives SCR through a mechanism similar to that of thermal systems (63). This study serves as the first demonstration that a DRIFTS setup can be used to interrogate reaction intermediates and elucidate the reaction mechanisms under plasma stimulation. In a separate study, Xu et al. (62) used a plasma-modified DRIFTS cell to study the mechanism of plasma-assisted water-gas shift over a Cu-based metalorganic framework (MOF). The authors reported the plasma activated Cu sites in the MOF at low temperatures and prevented degradation of the framework, which typically occurs at higher temperatures during thermal activation of the Cu sites (62). This was concluded from apparent shifts in the CO adsorption bands under plasma stimulation and through correlation with the change in oxidation state of the active Cu sites. The development and application of similar diagnostic techniques to ammonia synthesis could also provide insight into the role of the plasma in concert with the catalyst under reaction conditions.

OES is a common technique often used to measure the radiation emitted from the relaxation of electronically excited species in the plasma. The technique can be used to estimate critical plasma characteristics, such as vibrational  $(T_v)$  (39), rotational  $(T_r)$  (65), and electron  $(T_e)$  temperature (66). Jiang et al. (67) reported experimental rotational temperatures during plasma-assisted toluene degradation over a CoO<sub>x</sub>-CeO<sub>x</sub> catalyst at different SEIs using OES. Owing to the low degree of rotational excitation that occurs in the DBD plasma, the rotational temperature served as an estimate of the bulk gas temperature (67). By monitoring the bulk temperature in situ with OES, the authors were able to show that increasing the SEI had negligible effects on the reaction temperature, meaning that the improvements in yield that occurred from increased SEI were due to plasma–catalyst interactions (67). In addition to quantifying the various temperatures relevant to plasma-assisted catalysis, OES has also been used to observe plasma phase intermediates, such



(*a*) A schematic of the plasma-modified diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS) system and photographs of (*b*) the cell and (*c*) the dome during operation. (*d*) Data collected from a plasma-modified DRIFTS cell used for hydrocarbon-based selective catalytic reduction. Data are shown at various voltages of the plasma being applied. Adapted with permission from Reference 63; copyright 2015 American Chemical Society (https://pubs.acs.org/doi/10.1021/cs5019265).

as  $NH_x$  species and  $N_2$  ions (69). Gómez-Ramírez et al. (69) described an example of this in their study of the relative intensities of the emissions from excited N,  $N_2$ ,  $N_2^+$ , and NH species in a  $N_2 + H_2$  plasma. The authors observed an increase in the intensities of all species with increasing power deposition (69). However, the intensity of  $N_2^+$  relative to the  $N_2$  peak decreased, which allowed the authors to suggest that the  $N_2^+$  ion was responsible for plasma phase reactivity (69). OES probes could be included in the design of in situ/operando techniques such that the plasma phase species detected could inform the surface intermediates observed on the catalyst surface.

# Catalyst and Reactor Development for Plasma/Ammonia Synthesis

Owing to the complexity of the plasma-catalyst interaction and the role of the plasma in facilitating ammonia synthesis, improvements to yields and efficiency of ammonia synthesis are often made through variations in plasma type, reactor configuration, and catalyst composition. As noted earlier, DBDs are commonly used for plasma catalysis owing to the ease of incorporation of this system into a traditional plug flow reactor and their atmospheric pressure operation (70). Furthermore, DBD systems have been effectively scaled up for ozone production and pollution abatement (71, 72). The downside to these systems, however, is the low efficiency and the nonuniform nature of the discharge owing to the microfilaments (60, 70). Whereas the majority of plasma nitrogen fixation has been conducted in atmospheric-pressure DBD reactors, radio frequency (36), microwave (73), gliding arcs (29, 74), and plasma jets (30) have all been used, to varying degrees of success, to facilitate nitrogen fixation in the presence of a catalyst (29, 36). In general, these systems differ from DBD reactors in terms of the operating pressure, which is often below atmospheric, the frequencies applied, and temperatures within the system (70). For example, low-pressure microwave plasmas and gliding arc plasmas are more energy efficient owing to their effectiveness at exciting vibrationally excited species (60). In addition, such configurations have been used in the presence of catalytic materials to enhance yields (29, 75). Unfortunately, many of these configurations require the use of vacuum conditions and become significantly less efficient at higher pressures (70). Improved efficiencies of a DBD system have been reported by using a pulsed power source, where a threefold improvement in ammonia production using a Ru catalyst was observed with a pulsed source compared with an A/C source at the same discharge power (31). Overall, systems are desired that (a) maximize the plasma/catalyst synergy; (b) efficiently excite critical intermediates, such as vibrationally excited species; and (c) operate at atmospheric pressure.

Opportunities also exist in the design of catalytic materials for ammonia synthesis, while also considering plasma propagation through porous media as a design constraint (38, 76). Most studies thus far have focused on Ru-based catalysts owing to their effectiveness in thermal ammonia synthesis reactions (31, 35, 77, 78). However, recently more studies have investigated nontraditional metals for ammonia synthesis, such as Ni; noble metals like Au, Ag, and Pt; and molten alloys like InGa (38, 40, 41). It is clear from recent studies that the most effective surface for plasma-assisted ammonia synthesis may differ from those that are effective thermally owing to excitation of  $N_2$ . Another aspect that may affect the optimal metal surface is the strong electric fields present in the plasma. Theoretical studies have demonstrated that strong electric fields can alter adsorbate density on metal surfaces and change the binding strength of adsorbates, which could affect the surface chemistry (79-81). Furthermore, Ardagh et al. (82, 83) recently showed that binding energy oscillation of an adsorbate through an external stimulus can serve as a catalytic pump and improve activity. The dielectric constant of the catalytic material (or support) can also have a substantial impact on the discharge properties near solid surfaces. In particular, both experimental and theoretical studies have shown that high dielectric constants can lead to elevated electron temperatures and higher number densities of high-energy electrons close to the surface of the material (47, 84, 85). In a plasma, catalyst-support materials, such as alumina and silica, provide a way to control the local plasma properties near the catalytic surface, and the support can be designed to provide the appropriate properties needed to enhance desired plasma-catalyst interactions.

Lastly, the use of high-surface area and highly porous catalysts is standard to maximize contact between the reactants and the active surface in most heterogeneous catalysis applications. By contrast, many studies involving plasma-assisted catalysis report dense, low–surface area materials with large particle sizes on the order of millimeters (86, 87). This has led to some disagreement in the data presented in the literature over the most effective catalyst structure to promote plasma–catalyst interactions, particularly over the effectiveness of porous materials incorporated within a plasma. Theoretical studies suggest that plasma-activated species have limited penetration into the micropores of the high–surface area materials (85). Experimental studies of plasma-assisted dry reforming of methane over a porous Ni/Al<sub>2</sub>O<sub>3</sub> catalyst support these results through the observation that coke deposited only on the outside surface of the catalyst and not throughout the porous structure (88). However, microporous materials (i.e., MOFs) have been reported as highly effective catalysts in controlling both activity and selectivities for plasma-assisted reactions (62, 75, 76). Therefore, the development of catalysts that exploit the unique environment of the plasma by optimizing surface chemistry, dielectric properties, and pore structure could lead to improvements in the yield and efficiency of ammonia production.

#### Hybrid Plasma/Electrochemical Approaches

Another approach to nitrogen reduction is electrocatalytic ammonia synthesis, in which nitrogen is reduced by electrons driven by an applied bias at atmospheric pressure and low temperatures (10). Although this process has been demonstrated in several studies, yields are limited by two main factors: (a) the high overpotentials required owing to the difficulty in activating the  $N_2$  bond and (b) the extremely low selectivities to nitrogen reduction as opposed to hydrogen reduction in aqueous systems (15, 16). In general, catalysts with the lowest required overpotential often have the highest affinity for hydrogen reduction as opposed to activating nitrogen. Recently, several unique strategies to overcome these limitations have been investigated. Novel electrocatalytic materials have been employed to overcome these selectivity limitations, such as metal-free catalysts based on phosphorus (89), carbon (90), and boron (91), as well as intermetallic electride materials (92). Another recent approach to improve electrocatalytic ammonia synthesis has involved pairing an electrocatalyst with a nonthermal plasma (17, 18). Kumari et al. (18) reported the first attempt to improve upon electrochemical ammonia reduction by directing a nitrogen plasma jet at the surface of the cathode of a proton exchange membrane using a Pt catalyst. By comparing plasma with no bias, bias with no plasma, and bias with plasma, the authors found that the combination of the bias with plasma results in ammonia yields beyond what either the bias or plasma can do alone (18). Another recent study demonstrated a dual plasma-electrochemical cell using a low-pressure radio-frequency plasma for driving  $N_2$  oxidation (19). The nitrogen plasma was directed at a platinum electrocatalyst on one side of the cell, and water was introduced on the other side of a solid oxide electrolyte. This setup ensured that all energy introduced by the plasma was used to excite the  $N_2$ . Without a plasma, no  $NO_x$  was produced by the cell, and only recombination of the oxygen was observed on the plasma side of the cell. Ignition of the  $N_2$  plasma immediately resulted in a drop in  $O_2$  production and the observation of substantial NO<sub>x</sub> production, even achieving faradaic efficiencies of nearly 100% at low currents. Finally, a recent study by Renner and colleagues (17) developed a plasma-electrochemical ammonia synthesis cell without the incorporation of an electrocatalyst (Figure 6a). Rather, N<sub>2</sub> plasma was directed at an aqueous solution in an electrolytic cell with the intention of using solvated electrons to drive ammonia production (17). Figure 6b shows the yield of ammonia using different combinations of gas and plasma phase components, with a nitrogen plasma being the most effective system (Figure 6b). Using this method, the authors achieved up to 100% selectivity to ammonia production at low currents, which dropped to  $\sim 25\%$ selectivity at 8 mA and is higher than the selectivities often observed using metal-based electrocatalysts. The authors propose that this drop is due to transport limitations from the depletion of  $H^+$  near the plasma-liquid interface, shown by the increased yields observed at low pH (17).



(*a*) Catalyst-free hybrid plasma electrochemical cell for selective nitrogen reduction, (*b*) ammonia productivity using various plasma compositions, and (*c*) a proposed reaction mechanism for this process. Adapted from Reference 17; copyright the authors, some rights reserved; exclusive licensee American Association for the Advancement of Science. Distributed under a Creative Commons Attribution NonCommercial License 4.0 (CC BY-NC) http://creativecommons.org/licenses/by-nc/4.0/.

# **ENERGY REQUIREMENTS AND CONSIDERATIONS**

A common point of concern with plasma-assisted approaches is the energy efficiency of the process relative to current industrial standards. A common method to calculate and compare energy efficiencies is by multiplying the reaction conversion (X%) by the ratio of the enthalpy of reaction  $(\Delta H^{\circ})$  at the bulk gas temperature) to the SEI (energy/mol of the plasma) (26, 93). It is also useful to consider the energy consumption (energy required/mol N fixed) to compare various processes in terms of the energy required to produce the desired product. Figure 7 depicts a range of energy consumption values for various nitrogen fixation processes, as well as the theoretical limits of these approaches (94). The theoretical limit calculated for the nonthermal plasma system is based on the energy losses due to (a) unproductive excitation/ionization paths, (b) vibrational-translational relaxation, and (c) chemical efficiency (95), where higher concentrations of vibrationally excited N2 are sustained to form NO (90). Based on current technology, the Haber-Bosch process remains the most economically viable method of artificial nitrogen fixation at large scales. However, both plasma-assisted and electrochemical methods of ammonia synthesis clearly have the potential to exceed current energy efficiencies of the Haber-Bosch process (94, 96). Wind and solar farms generally produce 100-200 MW, which is approximately an order of magnitude below the energy required to operate a Haber-Bosch process (97). Therefore, the use of plasma-assisted or electrochemical ammonia synthesis based on renewable energy could be a viable method of



Actual energy efficiencies and theoretical minimum energy efficiencies for nitrogen fixation by various processes. Adapted with permission from Reference 94; copyright 2015 Elsevier.

small-scale onsite ammonia production (5, 6). Despite this potential, substantial improvements in energy efficiency would be required to create a deployable process: (a) efficiencies with the use of renewable energy sources, (b) efficiencies in the power supply for plasma generation, and (c) overall process design for the modular system (98). Furthermore, effective strategies for scaling laboratory plasma reactors must be considered (99). Although larger-scale DBD reactors have been used for ozone production (71, 72), the path for scaling other configurations is unclear. In addition to improvements to ammonia production, the process would need to be paired with carbon-free hydrogen produced from electrolysis to avoid the high energy cost associated with methane reforming. Although there are many unknowns in plasma-assisted systems, especially in relation to the energy efficiencies at desired scale, process design may capitalize on the use of impure feeds for plasma-enhanced ammonia synthesis. Xie et al. (78) showed that ammonia yield over  $Ru/Al_2O_3$  is improved with the addition of water in the feed. Although similar results are scarce in the literature, this study shows the potential for plasma systems to handle feeds that are often unusable in thermal systems. As another example based on the Birkeland-Eyde process, nonthermal plasma systems have also been applied for  $NO_x$  production directly from air (100–102). Because air separation for modular ammonia synthesis presents a substantial cost, removal of the initial separation may reduce the capital investment if nitrate-based fertilizers are desired. Another creative and potentially transformative solution is the combination of methane reforming and  $N_2$  reduction in a one-pot process such that separate systems are not needed on-site. Examples exist in literature that indicate methane-nitrogen plasmas can produce ammonia directly (103, 104), as well as hydrogen cyanide (105, 106). This high potential for industrial impact alongside the fundamental scientific interest leaves significant room for further innovation.

## **CONCLUDING THOUGHTS**

Unconventional ammonia synthesis is driven by the desire to produce ammonia at remote locations using small-scale, modular systems. Among the various methods being studied,

plasma-assisted catalysis has potential for implementation at low bulk gas temperatures and atmospheric pressure. These systems can be connected with renewable energy sources to lower the  $CO_2$  footprint and provide a sustainable alternative to ammonia production. The plasmacatalyst synergy has been widely reported, in which the plasma participates in nitrogen activation (via many possible routes) and facilitates the reaction on a catalyst surface. Despite these initial insights, new tools for evaluating plasma-assisted catalytic systems are needed to better understand the underlying phenomena occurring during plasma stimulation. Opportunities also exist to improve ammonia yields through reactor and catalyst design that optimizes contact between the plasma phase and the catalyst. Although current energy efficiencies are below those of the Haber–Bosch process, substantial improvements are possible that could make unconventional routes viable as small-scale distributed production plants.

# **DISCLOSURE STATEMENT**

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