Electrochemical Nitrogen Reduction Reaction on Noble Metal Catalysts in Proton and Hydroxide Exchange Membrane Electrolyzers

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Manuscript submitted October 23, 2017; revised manuscript received December 11, 2017. Published December 29, 2017.

Ammonia synthesis is one of the foundational chemical processes to the human society, which is estimated to supported approximately 27% of the world’s population over the past century.1 The development of the Haber-Bosch process revolutionized modern agriculture,2 however, the centralized, energy and carbon intensive nature of the Haber-Bosch process3,4 leaves many aspects to be desired. Distributed and modular ammonia synthesis via the electrochemical nitrogen reduction reaction (ENRR) at or close to ambient conditions, powered by renewable electricity, is an attractive alternative because it allows as-needed production of ammonia, and in turn N-fertilizers, from ubiquitously available resources, i.e., N2 and water.5 Widespread adoption of ENRR for ammonia production could drastically reduce the carbon footprint of agricultural activities. In addition, ENRR is compatible with the intermittency of renewable energy sources, e.g., solar and wind, as the ammonia and N-fertilizers can be produced and stored when renewable electricity is available.

Electrochemical fixation of atmospheric nitrogen was first attempted in 1908 even before the establishment of the Haber-Bosch process, to make nitric acid via electric discharge.6 Further studies of ENRR have generally been focused on high temperature proton conductors at 500 °C,7 however, the high operating temperature and the stability of ammonia at such conditions make it unsuitable for distributed deployment. Proton exchange membranes (PEMs) can achieve high proton conductivity (∼100 mS cm−1 at 25 °C for Nafion) at ambient or slightly elevated temperatures, which opens the possibility for electrochemical ammonia synthesis at those mild conditions.8 Although Nafion-based low temperature electrochemical ammonia synthesis has been demonstrated in several reports,9–15 no systematic investigation of noble metal catalysts exists.16 Further, the alkaline environment of hydroxide exchange membranes (HEMs) promises the employment of non-noble metal catalysts and no acid/base reaction between the produced ammonia and the membrane is expected. The slower HER kinetics in base also could lead to an improved selectivity toward ENRR.16 However, ENRR in HEM-based electrolyzers (HEMELs) has not been extensively investigated. In particular, no reliable strategy for ammonia quantification in HEMELs has yet been developed, owing to the possible leaching of quaternary ammonium cations from HEMs (or ionomer) that could interfere with the commonly used Nessler’s method.17

In this work, we survey five noble metal catalysts (Pt/C, Ir/C, Pd/C, Ru/C, and Au/C) for ENRR in both PEM-based electrolyzers (PEMELs) and HEMELs. We establish a reliable method to evaluate the ammonia production rate for ENRR with a membrane electrode assembly (MEA) configuration. We show that the competing hydrogen evolution reaction (HER) is the dominant reaction on all noble metal catalysts in PEMELs and HEMELs. Ammonia production rates are higher in PEMELs by roughly one order of magnitude higher than those in HEMELs, however, the trend is reversed with faradaic efficiencies for ENRR.

Experimental

Chemical and materials.—Pt/C [46 weight percent (wt%) Pt supported on Ketjen Black, Tanaka Kikinzoku Kogyo], Ir/C (20 wt% Ir supported on Vulcan XC-72, Premetek Co.), Pd/C (20 wt% Pd supported on Vulcan XC-72, Premetek Co.), Ru/C (20 wt% Ru supported on Vulcan XC-72, Premetek Co.), and Au/C (20 wt% Au supported on Vulcan XC-72, Premetek Co.) were obtained commercially and used as received. Their particle sizes and distributions were examined in our previous paper under a transmission electron microscope (TEM, JEOL 2010F, 200 kV).18 Potassium hydroxide (KOH, 99.99%), potassium nitrate (KNO3, 99.0%), copper sulfate (CuSO4, 99.9%), and sulfuric acid (H2SO4, 99.99%) were purchased from Sigma-Aldrich. Ammonium sulfate ((NH4)2SO4, 99.5%) was purchased from Acros Organics. Isopropanol (IPA, 99.9%) was obtained from Fisher Chemical. Nafion (LQ-1105-1100 EW, 5 wt%), Nafion-211 membrane, and carbon paper (Sigracet 39 BC) were all purchased from Fuel Cell Store. Anion exchange membrane (fumasep FAAM-PK-75) was purchased from fumatech and the ionomer solution was obtained by dissolving the membrane in IPA. Nessler’s reagents were obtained from HANNA Instruments.

Preparation of the working electrode and electrochemical measurements.—Electrochemical measurements were performed in a three-electrode cell with a saturated calomel electrode (SCE; Princeton Applied Research) immersed in a Luggin capillary (Princeton Applied Research) filled with 2 M KNO3 as the reference electrode, a Pt wire (PINE Instrument) as the counter electrode, and a glassy carbon (5-mm diameter, PINE Instrument) as the working electrode.18 Ink solutions of Pt/C, Ir/C, Pd/C, Ru/C, and Au/C were prepared by dispersing Pt/C, Ir/C, Pd/C, Ru/C, and Au/C in 0.05 wt% Nafion IPA solution followed by ultrasonication for 1 h. The thin-film electrodes were made by pipetting 2 μL of the ink solutions one, two, or four times onto pre-polished glassy carbon electrodes with final metal loadings of 2–20 μgmetal/cm2 disk. Cyclic voltammetry (CV) measurements...
The ECSAs of noble metal catalysts in acid and base.

| Catalyst | ECSA (m² g⁻¹) in Acid | ECSA (m² g⁻¹) in Base |
|----------|------------------------|-----------------------|
| Pt       | 104                    | 58                    |
| Ir       | 18                     | 34                    |
| Pd       | 33                     | 73                    |
| Ru       | 76                     | 76                    |
| Au       | 40                     | 27                    |

for these noble metal catalysts were carried out at room temperature in Ar-saturated 0.1 M H₂SO₄ and 0.1 M KOH solution at a scanning rate of 50 mV/s, respectively. All potentials were converted to values in reference to the reversible hydrogen electrode (RHE).

**Preparation of MEA and ENRR tests.**—The ink solutions of noble metal catalysts were mixed into a mixture of H₂O:IPA (50:50) with 30 wt% Nafion ionomer and then hand-sprayed onto a carbon paper to an approximate metal loading of 0.4 mg cm⁻² to serve as the cathode. The ink solution of Pt/C was prepared in the same way and was subsequently sprayed onto a Nafion-211 membrane using a Sonotek sprayer to reach a final Pt loading of 0.4 mg cm⁻², which was used as the anode. The anode is fed with 1 atm of H₂, which turns it into a RHE. Thus, the cell potential is numerically identical to the cathode potential vs. RHE and the ENRR can be performed at well-defined potentials. The membrane was then covered with a Sigracet 39 BC carbon paper anode gas diffusion layer and assembled with the cathode into an MEA with an active geometric cross-sectional area of 5 cm². The production of ammonia was conducted with the cathode and anode fed by high-purity N₂ (99.999%) and H₂ (99.999%) under 1 atm at a constant flow rate of 0.1 L min⁻¹, respectively. The temperature of the cell is controlled to be 80 °C. The relative humidity for cathode and anode are controlled to be 85 °C to maintain 100% relative humidity in the electrolyzer. The ammonia produced on the cathode and anode were collected by 1 mM H₂SO₄. After the tests in a PEMEL, the membrane was soaked in 20 mL of 3 M H₂SO₄ for 24 h to extract the ammonia inside the membrane. At least two separate MEAs were tested to observe the reproducibility of the results.

**Quantification of ammonia.**—The amount of ammonia was determined using Nessler’s methods according to the following equation:

\[
\text{NH}_4^+ + 2[\text{HgI}_2]\text{H}_2O → \text{HgO} \cdot \text{Hg}(\text{NH}_2)\text{I} ↓ + 7\text{I}^- + 3\text{H}_2\text{O}
\]

Since the ammonia was collected in acid solution, KOH solution (3 M) was added to adjust the pH of the solution to ~12.5. A calibration curve was made by using (NH₄)₂SO₄ solutions with known concentrations using a photometer (HI 96715, HANNA).¹⁹

**Results and Discussion**

Electrochemical surface areas (ECSAs) of as-purchased noble metal catalysts, i.e., Pt/C, Ir/C, Pd/C, and Au/C, were determined via CV scans performed in 0.1 M H₂SO₄ and 0.1 M KOH (Figure 1). For the commercial Pt/C and Ir/C catalysts, ECSAs were derived from charges associated with the desorption and/or adsorption of underpotential deposited (UPD) hydrogen and normalized to the corresponding metal loading on the working electrode with a charge density of 210 μC cm⁻². The ECSAs of commercial Pd/C and Au/C catalysts were determined from the reduction peaks of PdO and AuO with a double layer correction and a charge density of 424 μC cm⁻² and 386 μC cm⁻², respectively.¹⁸,²⁰ Copper under-potential deposition (Cu UPD) was carried out in 2 mM CuSO₄ (in 0.1 M H₂SO₄) to evaluate the ECSA of the Ru/C catalyst with a charge density of 420 μC cm⁻².¹⁸ Table I summarizes the specific ECSAs of the PGM catalysts in both acidic and alkaline solutions, which were used to normalize ammonia production rates in PEMELs and HEMELs, respectively.

ENRR rates were measured using an MEA configuration due to the low solubility of N₂ in aqueous electrolytes (Figure 2). It is worth noting that Pt/C at a high loading of 0.4 mgPt/cm² was employed on the anode in 1 atm of H₂ in both, and thus the anode side functions as a RHE and the cell potential is numerically identical to the cathode potential. For the ENRR in PEMEL, the first step was to conduct a break-in procedure for 1 h at the desired applied potential, in which the cathode site was fed with H₂ rather than N₂, in order to activate the cathode catalyst. After the break-in, the cathode feed was switched to N₂ for the ENRR. The current responses for the different cathode materials were generally stable with time at both −0.2 and −0.4 V. Further, currents are significantly lower for all of
of ammonia within the membrane after testing was not demonstrated conclusively. Therefore, we conclude that quantifying amounts of ammonia in Nafion and evolved at the cathode in this work is a more accurate and reliable method. No detectable level of ammonia was observed at the effluent of anode in any of the tests. In order to extract the ammonia inside the membrane, the membranes after reaction were soaked in 3 M H₂SO₄ for 24 h in PEMELs in the current study. At both –0.2 V and –0.4 V, Ru showed the highest faradaic efficiencies (FEs), which were 0.053% and 0.015%, respectively. Notably, with the increased potential, the ammonia production rate remained essentially unchanged, but the FE decreased on average by roughly one order of magnitude, which indicates that the competing HER is more favorable at low potentials. Our results are consistent with the computational predictions that noble metals and metal alloys are unlikely to be selective for ENRR, which is attributed to the correlated binding energies of various surface intermediates in ENRR and the competing HER, known as the linear scaling relations (LSR).²

According to previous experimental and computational results, conducting ENRR in an alkaline environment could potentially be more selective toward ENRR due to the slower kinetics of the competing HER on the cathode.¹⁸,²²,²³ Inspired by this, we also investigated the ENRR performance of noble metal catalysts with HEMELs, in which commercial anion exchange membrane and ionomer were employed. Since the possible leaching of quaternary ammonium cations from the membrane and ionomer, which are the typical charge carrying groups for HEMs, could react with the Nessler reagent and interfere the quantification of ammonia from ENRR, it is critical to establish a reliable experimental protocol to separate contributions from ENRR and leaching of HEM and ionomer to the Nessler’s results. Further, it is important to investigate the stability of membrane and ionomer under operating conditions to obtain accurate ammonia production rates. To test the possibility of leached quaternary ammonium cations from the commercial HEM and ionomer interfering with ammonia quantification, we conducted a control experiment in which both the cathode and anode were fed with H₂ at −0.2 V for 4 h, and thus the only source of nitrogen is from the membrane and ionomer, rather than ENRR. The exhaust solutions were collected to quantify the amount of quaternary ammonium leached from the membrane and/or the ionomer. It was found that there was a large amount of leached quaternary ammonium in both cathode and anode exhaust during the first hour. The total amount of leached quaternary ammonium (2.3 × 10⁻⁶ mol) was around the same for all noble metal catalysts. No detectable amount of quaternary ammonium was observed in the exhaust afterwards, indicating that the leaching from membrane and ionomer after 1 h at −0.2 V is negligible. To further identify the distributions of leached quaternary ammonium, we conducted another control experiment in which no ionomer was used, and thus the only source of nitrogen is from the membrane. It was found that the total amount of leached quaternary ammonium was about 0.8 × 10⁻⁶ mol, indicating that about two thirds of leached quaternary ammonium came from the ionomer, which was about half of the total amount of ionomer employed. Therefore, a pretreatment step with both cathode and anode fed with H₂ at −0.2 V for 1 h was added to all ENRR testing in HEMELs to ensure all detected ammonia comes from ENRR. The cathode feed was switched from H₂ to N₂ after 1 h, and all ammonia detected afterwards was considered to be produced from ENRR. Ammonia was only detected in the effluent on the cathode side, over all noble metal catalysts in HEMELs, which indicates that the ammonia detected after the pretreatment is indeed from ENRR. As shown in Figure 4, ammonia production rates of all noble metal catalysts are close in alkaline environment, and are approximately one order of magnitude lower than those in acid. Again, Ir shows the highest ammonia production rate at ~0.2 V in a HEMEL at 4.3 × 10⁻¹⁵ mol cm⁻² s⁻¹. Interestingly, due to the slower kinetics of HER in basic medium, most noble metal catalysts show higher FEs in HEMELs than in PEMELs. Au showed the highest FE of 0.55% in HEMELs, which is about one order of magnitude higher than that in PEMELs, indicating that Au might be a good candidate catalyst for ENRR in HEMELs. Recent works reported high faradaic efficiencies

Figure 2. Schematic illustration of the MEA configuration used in this work.

Figure 3. The ammonia production rate and faradaic efficiency (FE) on noble metal catalysts tested in PEMELs for 1 h at –0.2 V and –0.4 V. The production rate is normalized by the ECSA.
for Au sub-nanoclusters (8.11%2) and tetrahedrally Au nanorods (4.02%), which were attributed to their unique nanostructures, 3,4,25

In addition to their catalytic activity and selectivity, we also investigated the durability of commercial Pt/C catalyst for ENRR in both PEMELs and HEMELs. As shown in Figure 5, the amounts of ammonia produced in the first 0.5 h are around 50% of those produced within 1 h, which indicates that the ammonia production rate in 1 h are constant in both PEMELs and HEMELs. X-ray photoelectron spectroscopy (XPS) was utilized for the characterization of fresh and spent Pt/C catalysts employed in PEMELs (Figure 6). The binding energies of Pt 4f7/2 and Pt 4f5/2 in the XPS spectra of both fresh and spent Pt/C catalysts were 71.4 and 74.6 eV, respectively, which are similar to the both PEMELs and HEMELs. As shown in Figure 5, the amounts of investigated the durability of commercial Pt/C catalyst for ENRR in both PEMELs and HEMELs. As shown in Figure 5, the amounts of ammonia produced in the first 0.5 h are around 50% of those produced within 1 h, which indicates that the ammonia production rate in 1 h are constant in both PEMELs and HEMELs. X-ray photoelectron spectroscopy (XPS) was utilized for the characterization of fresh and spent Pt/C catalysts employed in PEMELs (Figure 6). The binding energies of Pt 4f7/2 and Pt 4f5/2 in the XPS spectra of both fresh and spent Pt/C catalysts were 71.4 and 74.6 eV, respectively, which are similar to the binding energies of previously reported Pt-based catalysts. 26 The XPS results suggest that only metallic Pt are present in the fresh and spent Pt/C catalysts in PEMELs, and thus the surface state of commercial Pt/C catalyst does not change to any detectable level after ENRR for 1 h.

Conclusions

In conclusion, we have investigated the catalytic performance of five noble metal catalysts (Pt/C, Ir/C, Pd/C, Ru/C, and Au/C) in ENRR at well-defined cathode potentials (−0.2 and −0.4 V vs. RHE) in both acidic and alkaline environments. HER is the dominant reaction on all catalysts in both PEMELs and HEMELs, with ENRR faradaic efficiencies well below 1%, which is consistent with previous computational predictions. Ammonia production rates on noble metal catalysts in PEMELs is roughly one order of magnitude higher than those in HEMELs, while the faradaic efficiency for ENRR is higher in HEMELs than PEMELs. The low ENRR FE show that HER is the preferred reaction on these noble metal catalysts in both acid and base, likely due to the LSR between the hydrogen binding energy and the nitrogen binding energy. Thus, only catalysts with decoupled hydrogen and nitrogen binding energies can be selective toward ENRR. This is consistent with the retarded HER kinetics in alkaline media compared to acidic media. We show that the leaching of quaternary ammonium cations from HEM and ionomer interfere with the ammonia quantification using the Nessler’s method, and a pretreatment step is necessary to avoid any ambiguity in the quantification of ammonia produced in ENRR. Time-dependent results show that Pt/C is stable under operating conditions in both PEMEL and HEMEL within 1 h. These results provide a solid baseline for future ENRR and ammonia production studies using MEA technique.

Acknowledgment

This work is supported by the US Department of Energy under the grant number of DE-SC0016537.

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