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Supplementary Information:

Electrolysis of Liquid Ammonia for Hydrogen Generation

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Calculation of E

The thermodynamic potential for electrolysis, E_{cell} , is related to the free energy change of the reaction, ΔG_{rxn} , by (S1) where *n* is the number of electrons involved in the electrochemical reaction, and *F* is Faraday's constant.

$$E_{cell} = \frac{-\Delta G_{rxn}}{nF}$$
(S1)

The reaction of interest is the decomposition of ammonia (NH₃), shown by (S2).

$$\mathrm{NH}_{3}(l) \longrightarrow \frac{1}{2} \mathrm{N}_{2}(g) + \frac{3}{2} \mathrm{H}_{2}(g) \tag{S2}$$

The free energy change of formation is related to the changes in entropy and enthalpy by (S3):

$$\Delta G_f^o = \Delta H_f^o - T \Delta S_f^o \tag{S3}$$

NH₃ is not liquid under standard conditions (T = 298 K and 1 atm pressure), however, where values for ΔH_f^o and ΔS_f^o are available. Thus, E_{cell} at the temperature of this study, 203 K, was estimated by using ΔH_f^o and ΔS_f^o at 298 K, (which are easily obtained from tabulated values)¹ and a temperature of 203 K in equation (S3). ΔS_f^o is determined from S^o for the reactant and both products as shown in (S4).¹

$$\Delta S_{rxn}^{o} = \left[\frac{1}{2}S^{o}(N_{2}(g)) + \frac{3}{2}S^{o}(H_{2}(g))\right] - S^{0}(NH_{3}(l))$$

$$\Delta S_{rxn}^{o} = \left[\frac{1}{2}\left(191.6 \text{ J mol}^{-1} \text{ K}^{-1}\right) + \frac{3}{2}\left(130.7 \text{ J mol}^{-1} \text{ K}^{-1}\right)\right] - \left(103.3 \text{ J mol}^{-1} \text{ K}^{-1}\right)$$

$$\Delta S_{rxn}^{o} = 188.6 \text{ J mol}^{-1} \text{ K}^{-1}$$
(S4)

Plugging into (S3):

$$\Delta G_{rxn}^{203K} \approx (67200 \text{ J mol}^{-1}) - (203 \text{ K})(188.6 \text{ J mol}^{-1} \text{ K}^{-1}) = 28900 \text{ J mol}^{-1}$$
(S5)

Plugging the result from (S5) into (S1):

$$E_{cell} = \frac{-\Delta G_{rxn}^{203K}}{nF} = \frac{-(28900 \text{ J mol}^{-1})}{(3)(96485 \text{ C mol}^{-1})} = -0.100 \text{ V} = -100 \text{ mV}$$
(S6)

Onset Potential Definition

Throughout this study, the "onset potential" is defined as the point where a line drawn through the linear portion of a redox wave of the CV curve would intersect with the baseline. A sample of this method is depicted in Figure S1. This definition is particularly suited to this study, which features redox waves that are essentially linear. With this definition, it is possible for two CVs curves to have similar onset potentials, but significantly different current densities at their onsets.



Figure S1: Illustration of how the onset potential would be calculated from a sample curve.

Tafel Analysis of NH4⁺ Reduction Wave

Figure S2 depicts a Tafel plot from the data shown in the black curve of Figure 4c. There are 89 mV of overpotential per decade current. Since the reaction is irreversible, there is only Tafel behavior seen at negative overpotentials. The slope of the fit line (taken as the average of fits to both the forward and back scans) suggests a 1 electron transfer process with $\alpha = 0.6$.



Figure S2: Tafel plot of the data shown in the black curve of Figure 4c.

Gas Chromatography (GC)

Figure S3 shows GC results from analyzing the headspace of the liquid NH_3 reaction vessel after 0, 30, and 60 minutes of electrolysis at 2 V. Because of the Ar carrier gas and thermal conductivity detector, the sensitivity for H_2 is significantly higher than that for N_2 and O_2 . Accounting for this difference in sensitivity, the ratio of $H_2:N_2$ produced is 3.8. This value is larger than the expected value of 3.0 due to anodic inefficiency. This is likely related to the anodic poisoning discussed in the manuscript.



Figure S3: GC results after applying 2 V between two Pt disk electrodes in liquid NH₃ for 0, 30, and 60 minutes.

XRD Characterization of KNH₂



Figure S4: Powder XRD spectrum of KNH_2 synthesized from KH and liquid NH_3 . A reference spectrum for KNH_2 is shown in the red, dotted line. The large amorphous feature at 20° is due to the sample holder, which included a dome to maintain a nitrogen atmosphere for the powder.

AES Characterization of Poisoned Pt Electrode

Auger Electron Spectroscopy (AES) was used to characterize the poisoned nitride state that forms on a platinum anode during ammonia electrolysis. To accomplish this, a 10 nm film of Pt was sputtered onto a wafer of Si. Two pieces of the resulting Pt/Si wafer of roughly the same size were submerged in 0.1 M H₂SO₄ and cleaned by the same procedure used for the Pt disk electrode. Then, one Pt/Si wafer electrode was submerged in a 1.0 M NH₄PF₆ solution in liquid ammonia, and the potential was cycled 20 times between 0 and 2 V versus the custom Ag/AgNO₃ reference to allow for the surface to be poisoned. This electrode was then rinsed with liquid ammonia.

Both of these electrodes were measured using AES to determine the amount of surface nitrogen. Then, each electrode was sputtered with Ar^+ at the site of measurement, and a new AES spectrum was taken. For the poisoned electrode, this sputtering treatment was repeated a total of three times. The resulting AES spectra are shown in Figure S5. The peak for Auger electrons from nitrogen atoms is expected at 380 eV. The peaks in Figure S5 are shifted to slightly higher energies due to surface charging from the electron microscope. All spectra are normalized to an intensity of 0 at 350 eV.

It is clear from Figure S5b that the poisoned surface of the platinum is due to the formation of platinum nitride. Also, since it required several minutes of sputtering to completely remove the nitrogen, it is clear that the nitrogen is diffusing into the platinum instead of simply remaining a surface state.

Derivative spectra corresponding to the AES spectra of Figure S5 are shown in Figures S6 and S7. The W impurity is the result of tungsten residue inside the sputtering chamber when the Pt films were deposited. In Figure S7, a small amount of the NH_4PF_6 salt residue is also visible due to the presence of F and P peaks. The nitrogen peak, however, is too large to be only the result of salt residue. The conclusion, therefore, is that platinum nitride forms on the surface of the electrode and intercalates into the sub-surface of the electrode.



Figure S5: AES spectra of a Pt electrode cleaned electrochemically in sulfuric acid (a), and of a similar electrode cleaned electrochemically and then anodically poisoned in 1.0 M NH_4PF_6 in liquid ammonia (b).



Figure S6: Derivative spectra corresponding to the AES spectra of Figure S5a. The native platinum oxide is clearly visible in the pre-sputtered spectrum (top), while it has been eliminated in the post-sputtered spectrum (bottom).



Figure S7: Derivative spectra corresponding to the AES spectra of Figure S5b. The nitrogen signal is much stronger in the pre-sputtered spectrum (top) than in the spectrum after two rounds of Ar^+ sputtering (bottom).

Cathodic STVs in Liquid NH₃:

Sampled-Time Voltammograms (STVs) were measured in liquid ammonia in the cathodic direction, and are depicted in Figure S8. All processes are analogous to Figure 4c, and the color schemes match respectively. The CVs in Figure S8 are exactly the same as those in Figure 3b. The STVs in both electrolytes show the reduction of adsorbed H^+ at 1 ms – to a much greater extent with 1.0 M NH₄⁺ than with 1.0 M K⁺. We attribute this to the very basic nature of the liquid ammonia with dissolved KPF₆. After 100 ms, the STV with 1.0 M NH₄⁺ more closely resembles the CV with NH₄⁺, and the STV with 1.0 M K⁺ more closely resembles the CV with NH₄⁺.



Figure S8: Cathodic CVs in liquid ammonia of 1.0 M KPF₆ (green) and 1.0 M NH₄PF₆ (black). Also included are STVs measured at 1 and 100 ms in 1.0 M NH₄PF₆ (dark red and light red triangles respectively), and at the same times in 1.0 M KPF₆ (dark blue and light blue circles respectively).

References

(1) Jolly, W. L. Chem. Rev. 1952, 50, 351–361.