Electronic Supplementary Material (ESI) for Energy & Environmental Science.

Ammonia Synthesis from N_2 and H_2O using a Lithium Cycling Electrification Strategy at Atmospheric Pressure

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Supplementary Information

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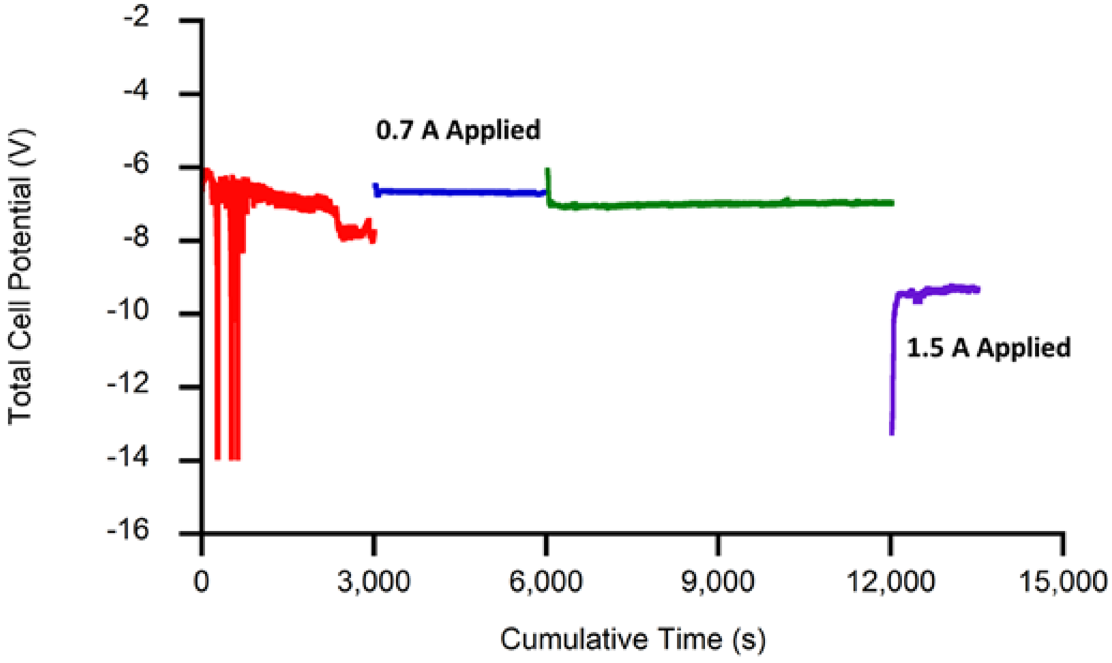

Figure S1. Chronoamperometry. Galvanostatic testing at 0.7 A and 1.5 A (for ~1.5 cm^2 geometric surface area of each working and counter electrodes) demonstrating LiOH electrolysis and initial cell stability. Excess LiOH was added to the anode compartment after 3,000 s, 6,000 s, and 12,000 s to demonstrate cyclability.

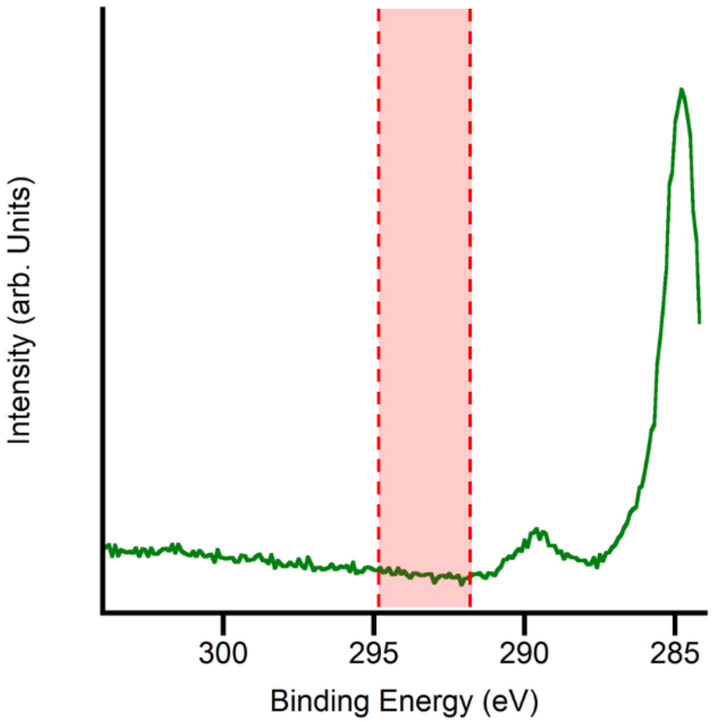

Figure S2. Potassium X-ray Photoelectron Spectrometry. Shows the K2p3 XPS region for a cross-section of Li product from electrolysis at ~9 V total cell potential with peaks from adventitious carbon. The expected region for a potassium signal is highlighted in red, which contains no peaks and thus there was no evidence of potassium species such as potassium metal formation observed in the product.

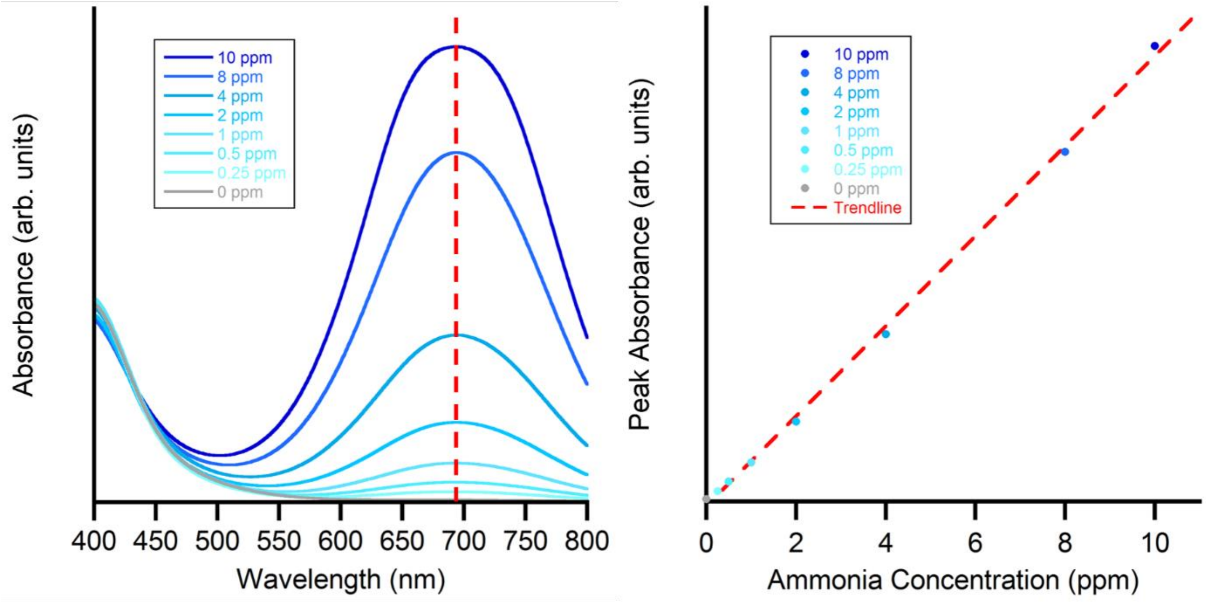

Figure S3. UV-Vis Calibration Curve for Ammonia Quantification. Ammonia standards were produced from a new bottle of ammonium hydroxide and the colorimetric test solutions were applied to evaluate the standards for absorption of UV-Vis light (left). This analysis was performed multiple times and also attempted with ammonium chloride powder with insignificant differences in results. Peak absorbance from these spectra produced a trendline ($R^2 = 0.999$), which was used for subsequent ammonia synthesis quantification.

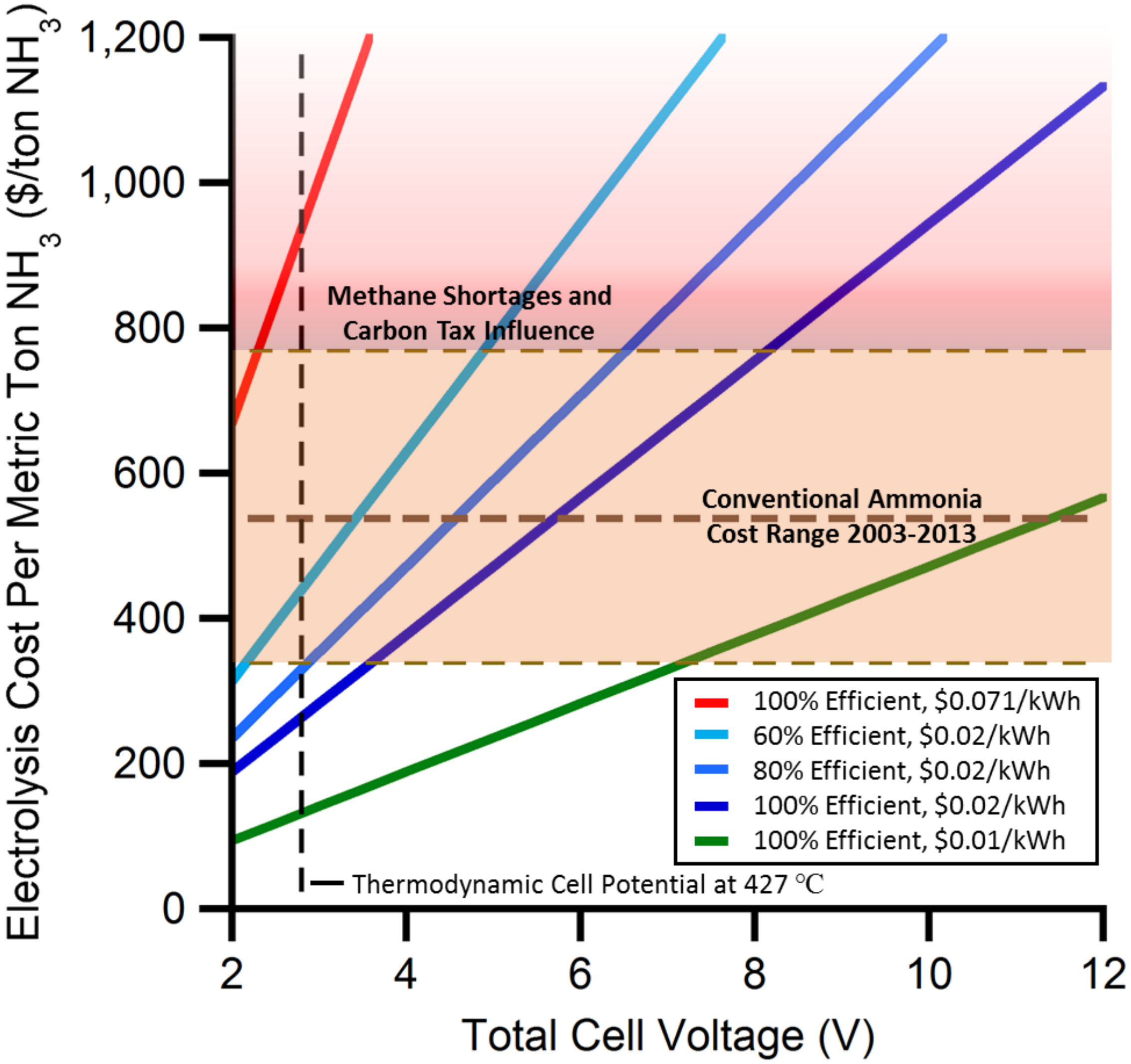

Figure S4. Li$^+$ Reduction Electricity Cost Preliminary Analysis. The electricity cost toward ammonia production accounting only for the LiOH electrolysis cost considering applied voltage, electricity supply cost, and cell efficiency, referenced to the average costs of conventional ammonia production. This analysis indicates that the cost of the high voltage requirement of Li$^+$ reduction itself is significant, though still potentially economically viable for this application.

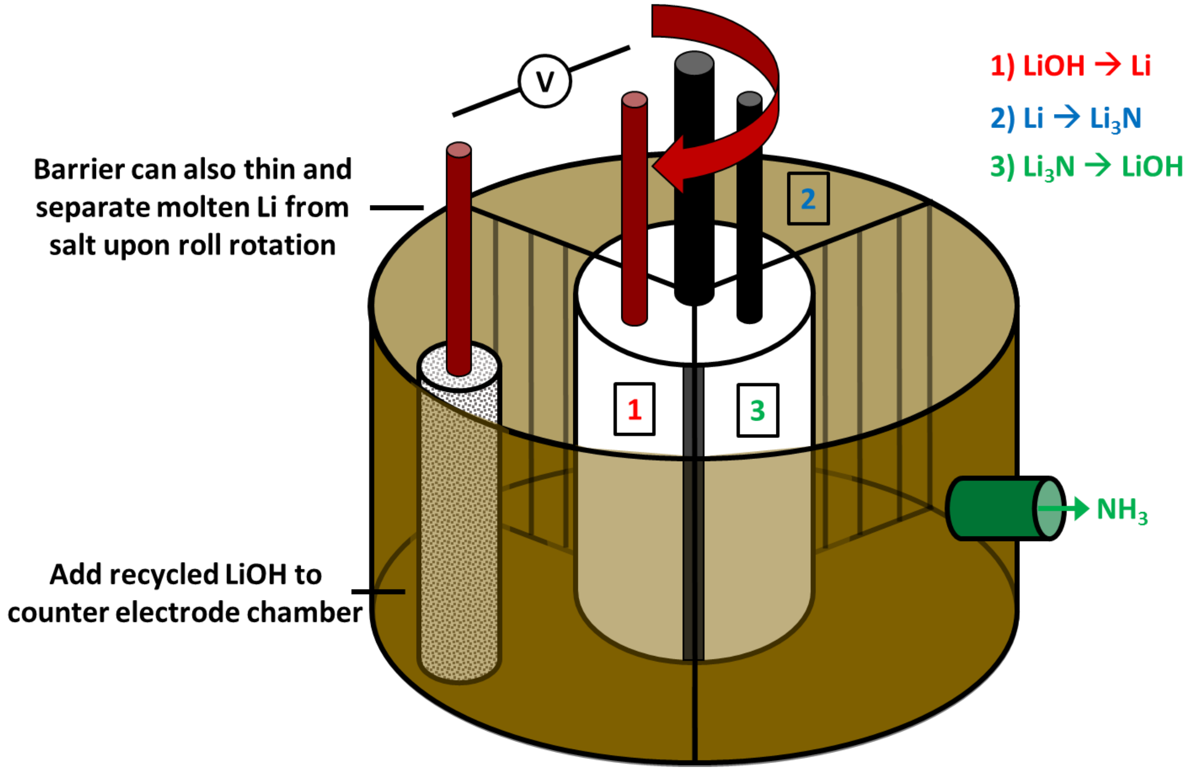

Figure S5. Conceptual Design of a Potential Continuous Cycle Device. In this simplified design, the three steps of the cycle are portrayed in three distinct chambers with barriers between chambers to facilitate continuous operation. The roll in the middle acts as a segmented working electrode to plate molten Li in step one, a thin film platform for nitridation of Li in step 2, and a reaction platform for Li_3N hydrolysis and ammonia production in step 3, which may return to step 1 as a fresh electrode surface to continue the cycle.