

Low-Pressure electrolytic ammonia production for ammonia-based energy storage

J. Thakare,* J. Masud,* and T. Aulich*

*University of North Dakota Energy & Environmental Research Center, 15 North 23rd Street, Stop 9018, Grand Forks, ND 58202-9018, USA, jthakare@undeerc.org

ABSTRACT

The Energy & Environmental Research Center (EERC) is developing a low-pressure 1-step electrolytic ammonia (1-SEA) process that would enable ammonia-based energy storage technology (NH₃-BEST) in combination with a direct ammonia fuel cell to enable electricity generation unit (EGU) accommodation of load fluctuations while operating within an optimal-performance baseline output range, ensuring EGU operational efficiency and minimum degradation of materials, equipment, and performance due to load cycling-driven stresses.

The 1-SEA process is built around a high-temperature electrolyte to achieve a proton conductivity (PC) at 300°C of $>10^{-2}$ S/cm, similar to that of state-of-the-art Nafion at 70°C. Combined with an appropriate cathode catalyst, the electrolyte is projected to enable production at a total energy input of 7.1 MWh/ton versus 8.5 MWh/ton for state-of-the-art (2018) Haber Bosch-based ammonia production.

Keywords: Ammonia, NH₃-BEST, Energy Storage, Electrolytic Ammonia production

1 INTRODUCTION

Presently, the integration of energy storage technologies with fossil energy assets such as enable electricity generation units (EGUs) is rare. Internationally, most deployed energy storage technologies are pumped hydro energy storage systems (PHES). The effective deployment of PHES systems is dependent upon key factors, including space availability, because of PHES's low energy density, and topography, since a significant elevation change between the upper and lower reservoirs is required. This highly limits the deployment of PHES systems in areas with space limitations and in areas without significant changes in topography. Battery energy storage (BES) technologies have also been deployed; however, these also face issues of system life span, charge degradation, and complications from charge and discharge cycling.

Since energy storage systems both contribute and deduct electrical energy to and from the grid, their modeling and integration poses a unique challenge. Additional research is needed to determine the hosting capacity of the grid and how grid dynamics will change with the integration of energy storage systems. Also, more research and modeling are needed to determine the characteristics of energy storage integration with the subject fossil asset. For example, if the energy storage system requires steam or auxiliary power from the asset, these

parameters will need to be determined and the characteristics of how their integration affects operations of the asset need to be determined. Factors that affect the commercial viability of the storage system include round-trip efficiency, cost, footprint, reaction time, storage duration, output duration, and system life span.

The above challenges will be overcome by capitalizing on NH₃-BEST attributes as a dynamic and high-energy-density system that integrates efficiently with state-of-the-art EGU systems. NH₃-BEST will enable fuel cell-quick reaction to changes in electrical grid demand, economic short- and long-term storage, and small footprint versus HES and other energy storage technologies. In terms of energy density, liquid ammonia contains 15.6 MJ/L, 70% more than liquid hydrogen (9.1 MJ/L at cryogenic temperature) and almost three times more than compressed hydrogen (5.6 MJ/L at 70 MPa).[1] Additionally, the cost of integrating an NH₃-BEST system will be manageable through the utilization of commercially available ammonia compression and storage technologies.

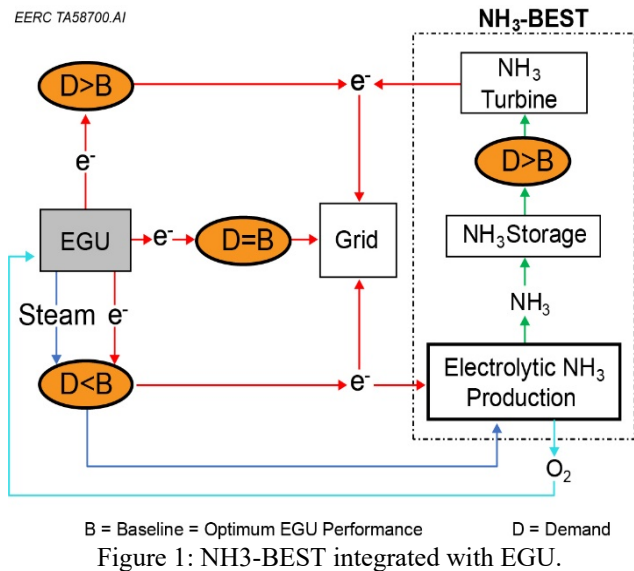
When compared to other energy storage technologies, the NH₃-BEST system will provide a dynamic energy storage system that minimizes footprint, maximizes energy density, utilizes commercial technologies as subsystem components, and has an effective round-trip efficiency, a rapid response time, no stored energy degradation, and a long system life span. In addition, the existence of a highly developed global ammonia industry and high ammonia fungibility in local, regional, and larger markets offers opportunities for selling and buying ammonia for economic and/or operational security benefits.

The integration of energy storage systems with EGU is rare within the United States. The NH₃-BEST system is not limited by geographic location or climate. Therefore, it can be integrated at any fossil generation asset, especially space-limited assets, because of its relatively small footprint. A unique market exists within the plains region of the United States, where both fossil generation assets and renewable generation assets are common and contributing electrical energy to the grid. The integration of renewables and fossil assets into the same electrical grid creates a dynamic, and often difficult, the situation for regional transmission organizations (RTOs), which are tasked with predicting and regulating the electrical grid. By integrating energy storage technologies at fossil generation assets, immediate electrical supply control can be built into the grid.

2 OUR APPROACH

As depicted in Figure 1, NH₃-BEST encompasses the integration of three-unit operations—ammonia production, storage, and conversion (to electricity)—with an EGU. When demand is less than baseline (D>B, power is pulled from NH₃-BEST. The unit operations essentially comprise:

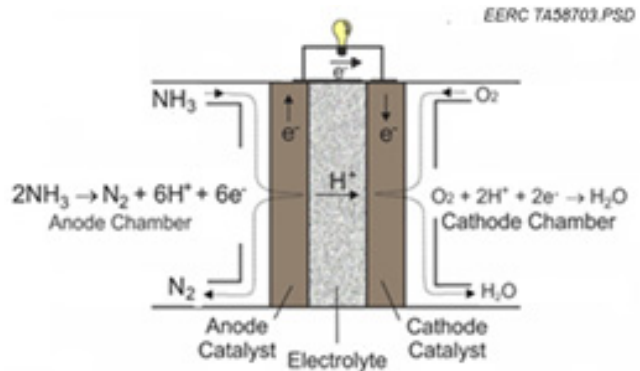
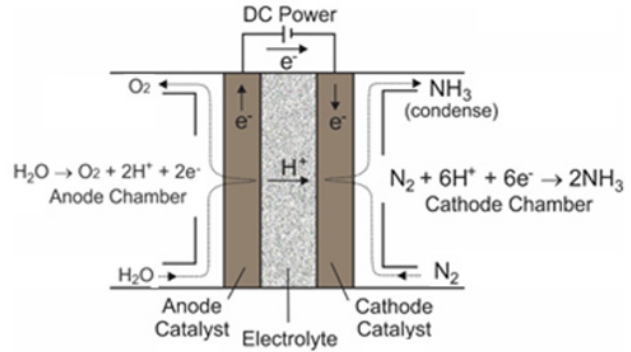
1. Ammonia production via EERC-developed 1-step electrolytic ammonia (1-SEA) process. The process operates at near-ambient pressure and 300°C with inputs of electricity, water, and air, as shown in Figure 2. The 1-SEA process derives from the EERC-developed (TRL4) low-pressure electrolytic ammonia process, which uses externally produced hydrogen rather than water as anode feed.
2. Ammonia storage at ambient temperature and pressure of about 250 psi.
3. Ammonia conversion to electricity in a direct ammonia fuel cell (DAFC), as shown in Figure 3.



2.1 Basic operating principle of NH₃-BEST

When EGU power demand is below the established baseline, power output is routed to the 1-SEA process, which is optimally integrated with available heat/steam resources to enable the lowest cost (in megawatts and dollars) ammonia synthesis. Produced ammonia is stored at 250°C inappropriately sized tank(s). When EGU power demand exceeds the established baseline, stored ammonia is fed to a DAFC for power generation to meet demand. Because energy and power are decoupled, NH₃-BEST offers the operational flexibility to closely follow demand, required to achieve optimum energy storage economics. The existing ammonia industry means that—in response to power and/or ammonia demand/supply economics—ammonia could be sold into the market or purchased for replenishment of supply.

As shown in Figure 2, the 1-SEA anode reaction is water electrolysis, but unlike traditional electrolysis where anode-generated protons travel through electrolyte and recombine at the cathode to form elemental hydrogen, in 1-SEA, protons react at the cathode with elemental nitrogen molecules to form ammonia.



As shown in Figure 4, electrolysis power/electricity consumption can be decreased by replacing electrical energy with thermal energy. NH₃-BEST technical and economic viability is premised on the hypothesis that EGU heat/steam resources can be creatively adapted and deployed to capitalize on this fact—sufficiently to effect major improvements in EGU performance and economics.

2.2 Scientific/engineering basis of NH₃-BEST

As an H₂ carrier, liquid ammonia (~250 psi) contains more H₂ by volume than compressed gaseous or liquid H₂. ammonia energy storage is fundamentally similar to H₂ ammonia energy storage (HES). Both involve the three stages of 1) gas production via electrolysis, 2) gas storage, and 3) gas conversion to electricity. The primary drawback of HES systems is low round-trip efficiency—approximately 30% [2],—due to losses through each stage. Electrolysis via a conventional proton exchange membrane (PEM) electrolyzer operating at 70°C is about 60% efficient [3].

Although hydrogen compression to low storage pressures can be up to 90% efficient, low storage pressure translates to large storage volume and high capital cost. PEM fuel cell conversion of hydrogen to electricity is approximately 50% efficient [4].

While ammonia energy storage systems encompass the same three stages, important differences between ammonia and H₂ offer opportunities for efficiency improvement. By utilizing available EGU steam/heat to operate the electrolysis–ammonia synthesis unit at 350°–450°C as targeted for the 1-SEA process, up to 20% of electrolysis energy can be provided by thermal rather than electrical energy, translating to 20% less electricity, cost, and CO₂ emissions versus standard PEM electrolysis. Ammonia liquid-phase storage at 250 psi means low energy consumption for compression and storage, increasing round-trip efficiency. As a mature technology, affordable and efficient ammonia storage systems are widely commercially available, while H₂ storage systems are often designed to be application-specific, elevating system costs. While ammonia-fired turbines are not a mature technology, they are undergoing study around the world, and represent an achievable first step toward ammonia conversion to electricity, with the ultimate goal of conversion in a direct ammonia fuel cell.

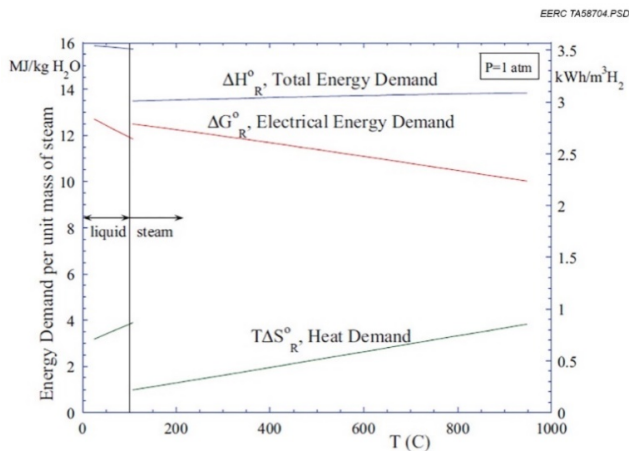


Figure 4: Standard-state ideal energy requirements for electrolysis as a function of temperature. [5]

2.3 Scientific/engineering basis of electrolytic ammonia production via the 1-SEA process –

Because of high molecular nitrogen (N₂) stability, conventional Haber–Bosch processes rely on high temperature and pressure (about 400°C and 3000 psi) to increase the occurrence probability of catalyst-surface hydrogen–nitrogen molecular interactions needed to achieve commercially relevant ammonia synthesis rates. With the use of electricity as a reaction driver and replacement of H₂ with H⁺ ions for ammonia synthesis, the 1-SEA process enables control of catalyst-surface

hydrogen–nitrogen activity, eliminating the need for high pressure.

The low-pressure electrolytic ammonia process (precursor to 1-SEA) operates with hydrogen (rather than water) and is built around a 300°C-capable proton exchange electrolyte comprising a cerium ultraphosphate inorganic proton conductor composited with polybenzimidazole (PBI), a high-temperature polymer. A critically important objective is validating ammonia synthesis via the 1-SEA process (at a commercially relevant rate) using water, rather than hydrogen, as anode input.

2.4 Scientific/engineering basis of NH₃ storage

High-efficiency, affordable, safe, industrial/utility-scale ammonia storage systems are commercially available.

2.5 Scientific/engineering basis of DAFC

DAFC development work has achieved power densities of about 0.6 and 0.7 watts/cm² with high-temperature solid oxide (O²⁻ ion exchange) and proton exchange electrolyte systems, respectively,[6] versus about 1.3 watts/cm² for today’s PEM fuel cells. In addition to higher power density (attributed to higher anode chamber hydrogen concentration), the proton exchange electrolyte eliminates the possibility of NO_x production, a risk associated with the anode-chamber presence of N₂ and highly active O²⁻ ions in a solid oxide electrolyte-based fuel cell.

3 ANTICIPATED BENEFITS

Figure 5 shows the value of ammonia as an easily storable energy carrier versus other energy storage options.[7] Two other benefits include 1) high reliability resulting from the solid-state structure of ammonia synthesis and conversion (to electricity) unit operations and long commercial history of ammonia production,

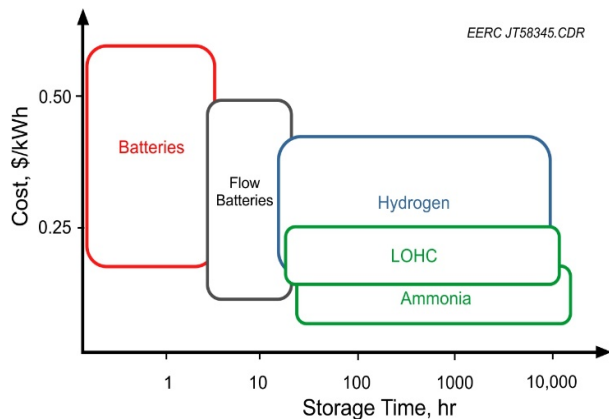


Figure 5: Levelized cost of energy storage options (LOHC = liquid organic hydrogen carrier).

compression, storage, and use as a chemical intermediate in numerous industrial-scale thermocatalytic manufacturing processes and 2) coproduct oxygen for use in combustion means lower-cost CO₂ capture.

[7] Soloveichik, G. Ammonia for Energy Storage and Delivery. Presented at NH₃ Fuel Conference, September 19, 2016; available at ammoniaenergy.org.

4 CONCLUSION

Our approach towards energy storage utilizing the NH₃-BEST system will offer wide applicability because

1. unlike solid-state battery systems (but similar to flow batteries), in NH₃-BEST, energy, and power are decoupled, providing operational flexibility that translates to improved economics,
2. the entire three-stage technology can be driven/operated solely by electricity, and
3. ammonia is an ideal energy storage medium—especially for longer-term needs—because ammonia storage is well-developed technology, widely commercially deployed throughout the world, with an excellent safety history and affordable cost.

5 ACKNOWLEDGEMENT

This work is supported by the U.S. Department of Energy National Energy Technology Laboratory; and Lignite Energy Council of the North Dakota Industrial Commission.

REFERENCES

- [1] Valera-Medina, A.; Xiao, H., et al. Ammonia for Power. *Progress in Energy and Combustion Science* 2018, 69, 63–102.
- [2] O’Neil, S. Unlocking the Potential of Hydrogen Energy Storage. Fuel Cell & Hydrogen Energy Association, www.fchea.org/in-transition/2019/7/22/unlocking-the-potential-of-hydrogenenergy-storage (accessed 2019).
- [3] Zhou, Z.; Zholobko, O.; Wu, X.-F.; Aulich, T.; Thakare, J.; Hurley, J. Polybenzimidazole-Based Polymer Electrolyte Membranes for High-Temperature Fuel Cells: Current Status and Prospects. *Energies* 2021, 14, 135.
- [4] Zholobko O.; Wu X-F.; Zhou Z.; Aulich T.; Thakare J.; Hurley J., A Comparative experimental study of the hygroscopic and mechanical behaviors of electrospun nanofiber membranes and solution-cast films of polybenzimidazole. *J Appl Polym Sci.* 2020;137: e49639.
- [5] Brown, T. Green Ammonia at Oil and Gas Scale: The 15 GW Asian Renewable Energy Hub. Ammonia Energy News, 6 August 2020. Available at ammoniaenergy.org.
- [6] Ishak, F.; Dincer, I.; Zamfirescu, C. Thermodynamic Analysis of Ammonia-Fed Solid Oxide Fuel Cells. *Journal of Power Sources* 2012, 202, 157–165.