Title of Project

Development of High Capacity Energy Storage Materials

Project Start and End Dates

Project Start Date: 03/10/2020
Project End Date: 09/30/2021

Project Highlight

Methods to mitigate ammonia impurities evolved from alkali metal amides were demonstrated for hydrogen storage applications. The use of iridium as an in-situ ammonia decomposition catalysts was demonstrated as well as the use of ammonia resistant fuel cells to enable the usage of these materials for high capacity energy storage applications.

Project Team

Principal Investigator: Patrick A. Ward
Team Members: Hector-Colon Mercado, Zachary Duca
External Collaborators: None

Abstract

Hydrogen fuel cells have the potential to offer energy and power density advantages over lithium ion batteries in automotive and portable power applications when paired with an appropriate hydrogen storage system. Development of the ideal hydrogen storage material has been immensely sought after but plagued by limitations present in each type of material. These limitations typically include non-idealistic operational temperatures, low capacities, excessive costs, lack of reversibility, or evolution of impurities which irreversibly damage fuel cell performance. Many complex metal hydrides possess suitable hydrogen capacities but unfortunately suffer from impurity release. In order to address this problem, our team has explored in-situ catalyst doping of alkali metal amides to demonstrate methodologies to reduce ammonia release. The incorporation of iridium metal in lithium amide significantly reduces the ammonia release and decomposes the ammonia to provide additional hydrogen. Furthermore, we demonstrate, for the first time, high resistance of low temperature fuel cells to ammonia in comparison with typical proton exchange membrane fuel cells. The utilization of these two approaches in tandem provides a novel pathway for the development and implementation of high capacity energy storage materials for fuel cell applications.

Objectives

- Demonstrate methodologies to mitigate ammonia release from alkali metal amides
- Evaluate the effect of Iridium doping in lithium amide-based materials to decompose ammonia
- Develop methodologies to capture and utilize borane-based impurities from borohydride hydrogen storage materials
- Demonstrate minimal performance impact on ammonia resistant fuel cells

REVIEWS AND APPROVALS

1. Authors:

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Name and Signature Date

2. Technical Review:

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Name and Signature Date

3. PI’s Manager Signature:

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Name and Signature Date

4. Intellectual Property Review:

This report has been reviewed by SRNL Legal Counsel for intellectual property considerations and is approved to be publicly published in its current form.

SRNL Legal Signature

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Name and Signature

Introduction

The development of high capacity hydrogen storage materials has been studied for hydrogen fuel cell vehicle applications for decades. Most high capacity hydrides have limitations in reversibility, cost, operational temperature, and the evolution of other gaseous species which poison the fuel cell catalyst or membrane. Recent advances in fuel cells, combined with nontraditional operational configurations, provide promising pathways to significantly enhance the energy density needed for many portable power applications.

Lithium nitride provides a promising pathway toward storing hydrogen due to its high gravimetric hydrogen density upon hydrogenation, reversibility, and relatively low operating temperatures (200 – 270 °C). [1,2,3,4] Li_3N reacts with gaseous hydrogen by direct hydrogenation according to the following overall equation:

$$Li_3N + H_2 \rightarrow Li_2NH + LiH + H_2 \rightarrow LiNH_2 + 2\ LiH$$

Hydrogen release is known to occur in two distinct dehydrogenation steps as

1) $LiNH_2 + LiH \rightarrow Li_2NH + H_2$
2) $Li_2NH + LiH \rightarrow Li_3N + H_2$

Although ammonia is known to react spontaneously with LiH to produce $LiNH_2$,[5] NH_3 evolution is still observed in the Li_3N system during desorption. Ammonia readily reacts with the acidic groups found in Nafion^{TM} proton exchange membranes to significantly reduce fuel cell performance. Previous researchers have demonstrated the addition of N_2 to hydrogen used for rehydrogenation mitigates the nitrogen loss from NH_3 emission resulting in virtually negligible hydrogen capacity losses after 516 cycles. [6] Therefore, decomposition of ammonia to prevent fuel cell damage and rehydrogenation with hydrogen: nitrogen mixtures to regenerate the material provides a promising pathway for the utilization of this material in practice.

Approach

Lithium amide and lithium amide/lithium hydride samples were doped with varying amounts of Iridium black by high energy ball milling. These samples were used to determine the effectiveness of ammonia impurity decomposition during hydrogen release from the samples. Thermogravimetric Analysis (TGA) coupled with residual gas analysis (RGA) was employed to determine the weight capacity loss from the sample at a given temperature and identify the decomposition gases. Dräger tube analysis and titration experiments were employed to quantitatively determine the amount of ammonia decomposition

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[1] Chen, P.; Xiong, Z.; Luo, J.; Lin, J.; Tan, K. L. Interaction of hydrogen with metal nitrides and imides. *Nature*, **2002**, *420*, 302-304.

[2] Hao, T.; Matsuo, M.; Nakamori, Y.; Orimo, S. Impregnation method for the synthesis of Li-N-H systems. *Journal of Alloys and Compounds* **2008**, *458*, L1-L5.

[3] Hu, Y. H.; Yu, N. Y.; Ruckenstein, E.; Hydrogen Storage in Li3N: Deactivation Caused by a High Dehydrogenation Temperature. *Ind. Eng. Chem. Res.* **2005**, *44*, 4304-4309.

[4] Hu, Y. H.; Ruckenstein, E. H_2 Storage in Li_3N. Temperature-Programmed Hydrogenation and Dehydrogenation. *Ind. Eng. Chem. Res.* **2003**, *42*, 5135-5139.

[5] Hu, Y. H.; Ruckenstein, E. Ultrafast Reaction between LiH and NH3 during H2 Storage in Li3N. *J. Phys. Chem. C* **2003**, *107*, (*46*), 9737-9739.

[6] Lamb, J. ; Chandra, D. ; Chien, W. ; Phanon, D. ; Penin, N. ; Cerny, R. ; Yvon, K. Mitigation of Hydrogen Capacity Losses during Pressure Cycling of the Li3N-H System by the Addition of Nitrogen. *J. Phys. Chem. C* **2011**,*115*, 14386-14391.

observed from the Iridium doped samples. Kissinger plots of the decomposition thermograms were derived from TGA thermograms to determine the catalytic effect on hydrogen release from the samples. TGA/RGA analysis shown in Figure 1 demonstrates the effectiveness of Iridium as an in-situ ammonia decomposition catalysts for lithium amide. Methodologies for the mitigation of Lewis acid boron based impurities via scrubber techniques were also developed.

Ammonia impurities in hydrogen gas streams are detrimental to proton exchange membrane (PEM) fuel cells as shown from previous work in Figure 2b. While the Iridium doped amide samples demonstrated significant reduction in ammonia evolution and in turn a high hydrogen capacity, trace ammonia is still detectable in the absence of lithium hydride. To elevate this issue, ammonia resistant fuel cells were constructed and evaluated with a substantial amount of ammonia in the hydrogen gas stream. These measurements demonstrated high resistance to ammonia impurities for the fuel cell utilized with only a slight reduction in power density.

Accomplishments

- Demonstrated significant reduction of ammonia evolution from $LiNH_2$ decomposition in the presence of Iridium. This is the first demonstration of an in-situ ammonia decomposition catalyst for lithium amide. (Figure 1)
- Demonstrated an ammonia resistant fuel cell with only minimal power reduction and a significantly higher current density than most PEM fuel cell experiments. This is in stark contrast to the rapid performance degradation found in most PEM fuel cells with far lower concentrations of ammonia. (Figure 2)

Future Directions

- Continue the development of poison resistant fuel cells and the direct pairing with complex metal hydrides with impurity decomposition catalysts in situ.
- Continue development of integrated systems for portable power applications
- Continue research and development to reduce decomposition temperature of target materials to increase overall system efficiency

FY 2021 Peer-reviewed/Non-peer reviewed Publications

- In preparation

Intellectual Property

- **N/A**

Total Number of Post-Doctoral Researchers

- Dr. Zachary Duca (SRNL)
- Dr. Dustin Olsen (SRNL)
- Dr. Lauren Hanna (SRNL)
- Dr. Willis Jones (SRNL)

Total Number of Student Researchers

- N/A

Include all images, charts and figures with captions, as shown below.

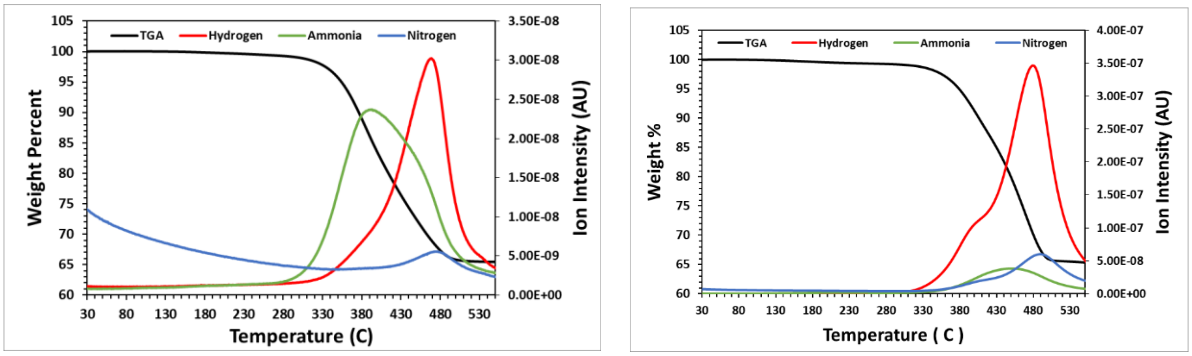

Figure 1: Thermogravimetric analysis/residual gas analysis of pure lithium amide (left) and lithium amide with 5 wt. % Iridium (right)

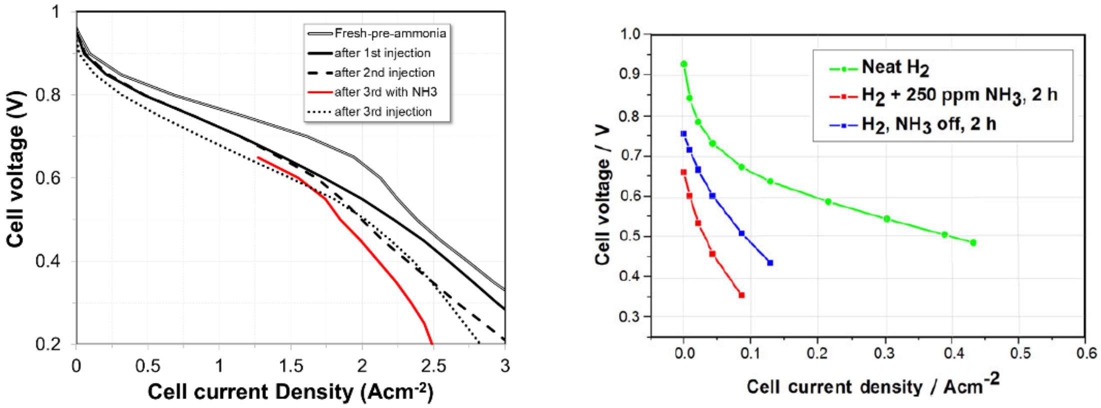

Figure 2: Fuel cell performance of ammonia resistant fuel cell with 7,400 ppm of ammonia in hydrogen gas (left) and proton exchange membrane fuel cell performance with 250 ppm of ammonia in hydrogen gas (right)[7]

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[7] Llerena, F. I.; Jimenez, A. H.; Gonzalez, E. L.; Manzano, F. S.; Marquez, J. M. A. Effects of Ammonia Impurities on the Hydrogen Flow in High and Low Temperature Polymer Electrolyte Fuel Cells. *Fuel Cells*, **2019**, *6*, 651-662.