Hawai'i Natural Energy Institute Research Highlights

Advanced Materials

Reversible Liquid Hydrogen Carriers Containing Magnesium Boranes

OBJECTIVE AND SIGNIFICANCE: The objective of this project is to develop a commercially viable, two-way liquid hydrogen carrier (LOHCs) based on solutions of metal hydrides in heterocyclic LOHCs that have a greater energy efficiency and lower delivery costs than existing hydrogen carriers and conventional compressed H_2 gas transport technology. The successful development of the liquid hydrogen carriers would support acceptance and expansion of hydrogen and fuel cell technologies.

BACKGROUND: A substantial network of tanker trucks and pipelines to transport hydrogen at ambient temperature and pressure already exists. The LOHCs of interest in this work would be able to utilize this infrastructure. Both one-way carriers, which form benign products upon elimination of hydrogen that are released to the environment, and two-way LOHCs which can be cycled between their hydrogenated and dehydrogenated phases have been investigated. A recent comparative cost and energy consumption analysis of LOHCs performed at Argonne National Laboratory showed the one-way carrier, methanol to be the strongest candidate. However, it showed no overall cost advantage over tube trailer delivery of compressed hydrogen and pointed to the need to develop new hydrogen carriers.

Methylcyclohexane, the prototypical two-way LOHC has enthalpy of dehydrogenation of 69 kJ/mol H_2, which is a major drawback to its utilization in practical systems as its dehydrogenation is intrinsically energy extensive. It also has a relatively low volumetric available hydrogen density of 47 g/L which translates to a high cost of hydrogen transport.

Heterocyclic LOHCs have excellent thermodynamic properties but are challenged by low volumetric available hydrogen densities which impose an economic barrier to their application as practical hydrogen carriers. Our approach to overcoming this barrier is the addition of high density hydrogen storage materials, especially $Mg(BH_4)_2$, to the heterocyclic LOHC which can result in up to 19% increase of the available volumetric hydrogen density. The enhanced density, up to 100 g/L, is more than double that of methylcyclohexane.

In collaboration with UH's Department of Chemistry and the DOE-HyMARC Consortium (including Pacific Northwest Laboratory and National Renewable Energy Laboratory) this project targets the generation of two-way LOHCs by charging selected heterocyclic LOHCs with borohydrides. The project aims to identify the best heterocycle/hydride/catalyst combination in terms of rate, cycling capacity, and product selectivity with goal of maximizing energy efficiency of hydrogen storage and delivery.

PROJECT STATUS/RESULTS: The Screening of N-heterocycle-magnesium borohydride (LOHC-$Mg(BH_4)_2$) solutions with and without catalyst for optimal (de)hydrogenation behavior is under investigation. Due to the high volumetric, releasable H_2 capacity that has been found for 1:2 $Mg(BH_4)_2$/pyrrolidine solution, we are screening various concentrations from 1:2 to 1:8 solutions of $Mg(BH_4)_2$ and other N-heterocycles.

The studies allow the identification of the optimal N-hetrocycle based LOHC-$Mg(BH_4)_2$ solutions for development as hydrogen carriers. The N-heterocycles analyzed include (de)hydrogenated methyl imidazole, butyl-imidazole, N-methylindole, morpholine, 1,2 dimethy-imidazole, and quinolone. The screening reactions of the LOHC-$Mg(BH_4)_2$ solutions without catalysts were performed in Parr mini-reactors at 180-200° C for 24 hours. Hydrogen evolution from the solutions was confirmed by the increase in pressure of the reactor vessels. Analyses of the dehydrogenated materials is being performed utilizing ^{1}H and ^{11}B nuclear magnetic resonance spectroscopy (NMR). Products formation upon H_2 release from the LOHC-$Mg(BH_4)_2$ samples was confirmed by ^{11}B peaks at -23 to -31 ppm (cyclic B-N species) and -5 to -18 ppm N-BH_x (borane species).

The best dehydrogenated $Mg(BH_4)_2$-LOHC mixtures based on NMR results and H_2 release pressure, will be subsequently treated to 100-180° C, with and without catalyst, to determine the extent of reversible H_2 uptake of the system, enabling determination of best solutions for development as hydrogen carriers.

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