Expanding Clean Energy Research and Education Program at the University of S. Carolina

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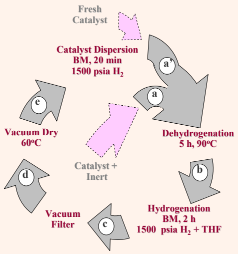
Advanced Complex Hydrides - Ritter

Physiochemical Pathway for $LiAlH_4$ Hydrogenation

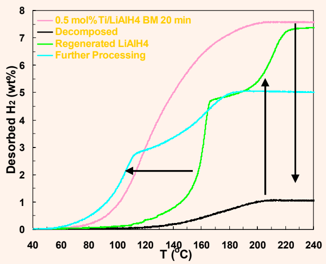
One Dehydrogenation/Hydrogenation Cycle with Ti-Doped $LiAlH_4$



Ti-doped $LiAlH_4$ can be fully regenerated at reasonable conditions through this novel physiochemical pathway.

Since the THF can be readily recovered, only thermal and mechanical energy are required to regenerate the alanate.

TPD: Different Stages Through One Typical Cycle of Ti-Doped $LiAlH_4$



Li alanate can be fully regenerated at reasonable conditions through a proprietary physiochemical route; however, it requires off-board reprocessing.

J. A. Ritter, A. D. Ebner, J. Wang and C. E. Holland, Provisional Patent Application, filed May 18 (2005).

Hydrogen Storage Using Chemical Hydrides Objectives and Approach - Matthews

- Develop hydrogen storage and delivery technology based on steam hydrolysis of chemical hydrides for automotive fuel cel applications

$$NaBH_4 + (2{+}x)H_2O \rightarrow 4H_2(g) + NaBO_2 \cdot x\,H_2O + \Delta H_{rxn}$$

- Quantify/optimize steam + solid chemical hydride reaction kinetics as the basis for production of hydrogen
- Operate reactor at low temperatures (100 –150OC) and pressures (~ atmospheric)
- Conduct basic research to minimize water utilization and maximize H2 delivery rate
- Compare experimental data to FreedomCAR targets
- Develop prototype of steam hydrolysis reactor

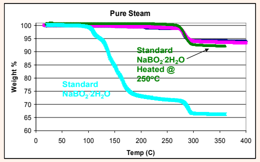
Hydrogen Storage Using Chemical Hydrides Representative Results

Hydrogen Generation Rates in Packed Bed Reactor at 110 °C and Atmospheric Pressure

Condition of Reactant Stream	Initial Rate (mol/kg *min)	Theoretical H_2 Yield %	H_2O Collected (% of amt fed)	Specific Energy*, % (kg H_2/kg reactants) *100%
Pure Steam	0.843	72.5%	53%	**1.34**
Pure Steam	0.892	85.4%	92.5%	**7.31**
Pure Steam	0.906	90.3%	87.5%	**5.01**
1mol% HAc	0.790	92.4%	75%	**3.0**
1mol% HAc	1.044	92.7%	90%	**6.6**
15 mol% MeOH	0.629	72.9%	90%	**4.85**

*Specific energy values assume that condensed water can be recovered and recycled.

Thermogravimetric Analysis (TGA) of Solid Reaction Products after 5 hours of Drying in N_2 Gas.



Reaction with pure steam yields product similar to $NaBO_2 \cdot 2H_2O$ that was preheated to 250°C. These TGA results are consistent with an independent X-Ray Diffraction analysis confirming the presence of $NaBO_2.2H_2O$ in the products of the steam hydrolysis reaction.

Clean Energy Research
Project III: Hydrogen Storage Using Chemical Hydrides
Eyma Marrero, Josh Gray, Carol Stork, Amy Beaird, Casey Campbell, Ashley Rhoderick, Tom Davis, Michael Matthews
University of South Carolina

The PEMFC Cathode Durability-White

Objective

Study the Pt catalyst degradation using the rotating disc electrode (RDE)

Experimental

- Test temperature: 70 °C
- Pt loading on the RDE: 15 $\mu g_{Pt}/cm^2$
- Electrolyte: 0.5 M H_2SO_4
- Reference: Hg/Hg_2SO_4/Sat. K_2SO_4
- The entire test consists of five runs. In each run, the RDE was first cycled at 100 mV/s for 50 times and then at 50 mV/s for 20 times between 0.04 V and 1.13 V in the argon-purged electrolyte to activate the Pt surface. Finally, the RDE was cycled between 1.0 and 0.15 V once at 5 mV/s in the O_2-saturated electrolyte for each of the five rotating speeds, 400, 900, 1600, 2500, and 3600 rpm.

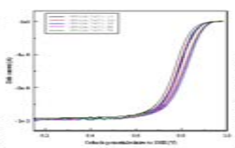


Figure 1 The RDE date measured at the scan rate of 5 mV/s at 1600 rpm for all five runs

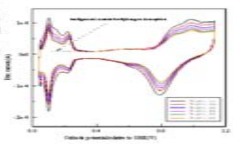


Figure 2 The CV date measured in the argon-purged electrolyte at the scan rate of 50 mV/s for all six test runs

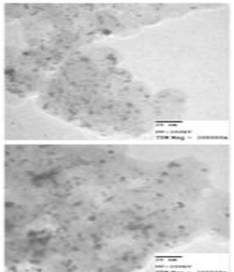


Figure 3 The TEM image of the fresh Pt catalyst sample (top) and the TEM image of the Pt catalyst sample removed from the RDE after five runs of tests and re-dispersed in isopropyl alcohol (bottom)

Conclusion

1. As shown from the hydrogen desorption charge determined from Figure 2, the active Pt surface area decreases with the run number. This indicates that the Pt particle size grows with operation.
2. As shown in Figure 1, the Pt activity was the highest during run #3. This may be explained by the particle size effect on the specific Pt activity (the activity per unit Pt surface area). With an increase in the Pt particle size, the specific Pt activity increases. If the rate of the specific activity increase is faster than the decrease in the active surface area, the measured Pt activity will increase with operation. The highest Pt activity appears when both rates are equal.
3. The decrease in the active Pt surface area with operation can also be confirmed from the Transmission Electron Microscopy (TEM) images presented in Figure 3. As shown in Figure 3, the density of big Pt particles is higher for the Pt catalyst sample removed from the RDE at the end of tests than that for the fresh Pt catalyst sample.

Investigation of the Formation and Stability of Hydrogen Clathrate (co-PI: J. Delhommelle)

- Hydrogen can be stored in structure II clathrates

  Lee et al. Nature, 434, 743 (2005)

Cage A Cage B

Cavities of sII clathrates

- Objectives:
  - to understand the mechanism of formation of hydrogen clathrates
  - to evaluate the role played by additives (e.g. THF) in the stabilization of hydrogen clathrate
- Methods:

  ⇒ molecular dynamics of rare events (umbrella sampling + order parameter)

  R. Radakrishnan et al. J. Chem. Phys. 117, 1786 (2002)

  J. Delhommelle et al. J. Am. Chem. Soc. 126, 12286 (2004)