UB Dockets 5874, 5950

High Reversible Hydrogen Storage Capacity with Ultra-Fast Kinetics

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UB Office of Science, Technology Transfer and Economic Outreach

TECHNOLOGY AVAILABLE FOR LICENSING: *This set of inventions describes novel matter (a combination of Lithium Oxide (Li2O)/ Lithium Nitride (Li3N)) and the procedure to employ the same to store (and release) hydrogen. An improved version of the same with LiNH2 pre-added is also presented and described. The objective of these technologies is to capture and use hydrogen as an energy source in fuel cells. The current focus of this technology is on fuel cells for vehicles although there is the intention and potential to adapt and re-engineer this to suit other applications (energy generation, industrial uses, etc).*

OVERVIEW

Most experts and futurologists are in agreement about the emergence of a hydrogen based US and world economy. Several leading energy think tanks such as the US Department of Energy, DERA of UK etc, are confident that the hydrogen energy era is around the corner and will be established in stages starting around 2010 (see Diagram I below showing future energy trends). These predictions are despite claims and research about superior, cost effective alternatives having the potential to force the future.

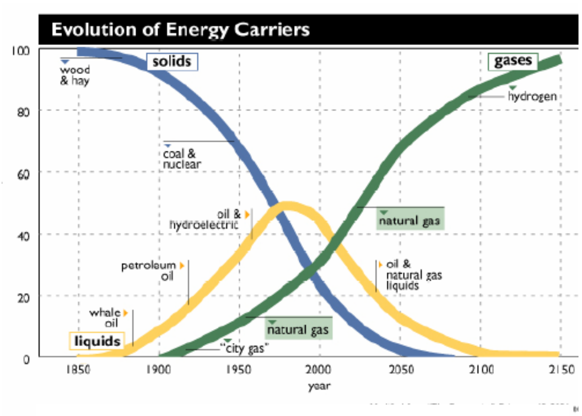

Diagram I:
The future of energy

The hydrogen energy system as it exists today can be sub-divided into the production, delivery and usage sub-systems (see Diagram II below). The last mentioned is a listing of application areas. The area of interest for this invention is the storage of hydrogen.

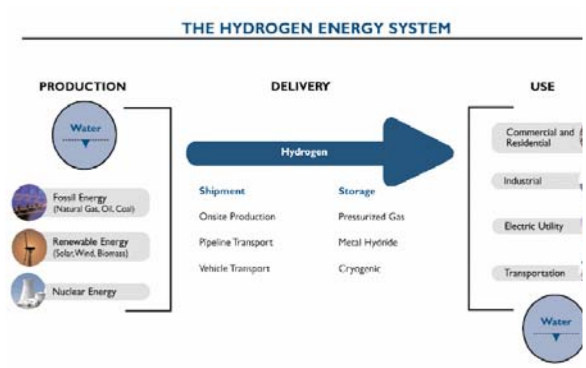

Diagram II:
Hydrogen energy system

Several methods like pressured gas, metal hydride and cryogenic procedures have been suggested for hydrogen storage. Each of these has their attendant advantages and drawbacks, the latter primarily along the dimensions of cost-effectiveness, user-friendliness, market entry barriers, and environmental concerns.

Most often, storage efficiency and safe, controlled release of hydrogen are listed as top priorities in any device designed for hydrogen storage. This invention ably addresses these and while doing so, succeeds in exceeding the standards set by the government and the industry in respect of these dimensions.

INVENTION

The basic invention describes a means of storing Hydrogen in fuel cells through a novel material based on Lithium Nitride (Li_3N). The use of this in hydrogen storage has been known for a long time, owing to its lightness, high hydrogen capacity and fast kinetics. But its extensive use has been prevented by disadvantages such as high heat generation, low stability and a propensity to sinter.

This invention tides over these deficiencies by stabilizing Lithium Nitride with Lithium Oxide (Li_2O) through a process of oxidation and hydrogenation (diagram III below).

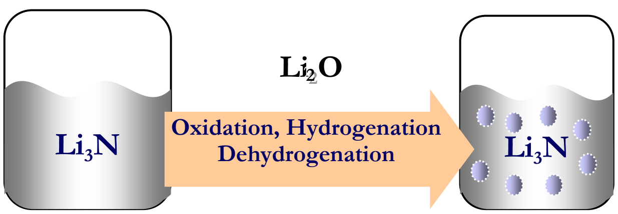

Diagram III
The Invention

The characteristic features of the results obtained are:

a) The new material retains fast kinetics; hydrogen is absorbed and released fast. The material is also seen to lend superior stability to Li_3N.
b) The hydrogen absorption-release kinetics takes place at reduced temperatures (begins at 180 ^oC). Higher temperatures make higher reaction rates possible.
c) The final product is a solid block occupying reduced space and demonstrating superior absorption efficiency in comparison to other *absorbing materials* (5% by weight absorption and release of Hydrogen – against the US DoE targets of 4.5% by 2005, 6% by 2010 and 9% by 2015)
d) The refilling (refueling) time is around 3 minutes which too meets the 2005 DoE target of 12-20 minutes.
e) A fuel tank made of this material will possess a size and weight comparable to regular gas tanks. A regular automobile can travel 300 miles with one fill of such a fuel tank. However, at this time it is likely to be slightly more expensive than a regular gas tank, since the purity of material required is 99%.
f) Scalability and mass production of the material are readily possible.

Improvements

In the newer version of the invention (docket 5950), special attention is paid to improving reaction performance by pre-adding $LiNH_2$ to the Li_3N-Li_2O combination. The basic hydrogenation reaction governing hydrogen absorption kinetics is:

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

The reversible reaction (in the opposite direction) provides the dehydrogenation complement for release of hydrogen. The progression from LiNH2 to Li3N during the dehydrogenation phase is actually the result of two reaction stages as below:

Stage 1: $LiNH_2 + LiH = H_2 + Li_2NH$
Stage 2: $Li_2NH + LiH = H_2 + Li_3N$

Hydrogen is released in both reactions. While the first takes place at temperatures lower than 200 ºC and demonstrates 5.7% transfer efficiency under such conditions, the latter reaction performs at temperatures in excess of 400ºC. There is potential for improvement if the latter reaction step were avoided.

The technique used exploits the fact that LiH is used in both stages and that 2 molecules of LiH exist for every 1 molecule of $LiNH_2$. Therefore, if $LiNH_2$ were to be pre-added to the Li_3N-Li_2O mixture, there would be excess molecules of $LiNH_2$ to react with LiH molecules. This will prevent the second stage of the reaction from occurring since all the LiH molecules would have been used up in

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the first stage itself. All the LiH molecules generated as a result of the Li_3N absorbing Hydrogen are fully consumed through the $LiNH_2$ pre-added or the $LiNH_2$ generated during the hydrogenation phase. A schematic of this is shown below in Diagram IV:

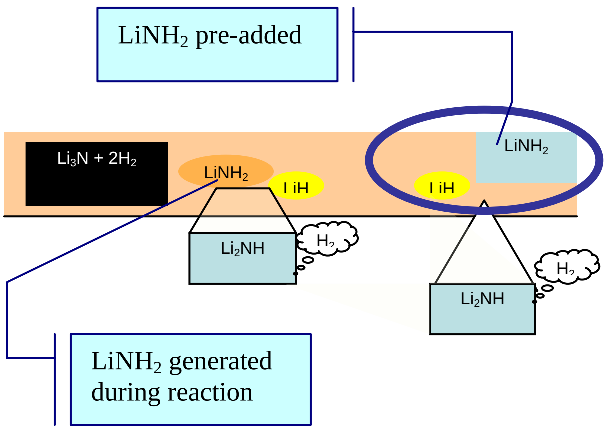

Diagram IV
Reaction environment created by pre-adding $LiNH_2$

Different ratios of $LiNH_2$ were pre-added to the original combination to create different materials of varying hydrogen absorption efficiency. The new value propositions are:

- The new material has reversible H_2 capacity of 6.8wt% (well above the DoE floor of 6wt% by 2010)
- The best results were with $LiNH_2$ molar composition between 28%-50%. Absorption over time was as follows:
  - 6wt% H_2 capacity in 20 minutes
  - 5wt% in 40 minutes
  - 6.8wt% finally
- All advantages of the earlier invention continue, such as
  - Stability (non-sintering), and
  - Good dehydrogenation kinetics

UNIQUE AND PRIMARY BENEFITS

The list below provides all the values and advantages endogenous to this invention.

- Most specialists agree that the best way to store an instantaneously explosive gas like hydrogen is in to have it absorbed within solid-substrate form, a situation this invention squarely covers.
- Hydrogen in an absorbed state within the Li_3N-Li_2O combine as offered by this invention is non-explosive
- The material introduced by this invention has excellent hydrogen absorption kinetics and performs stably at lower temperatures.
- This invention exceeds US DoE standards in more than one dimension (absorption efficiency, refueling time, etc.). Further work is being done on these materials that improves performance even more
- Producing and employing the new material compares favorably with regular gasoline and other fuels along the dimensions of costs, size and weight of the tank, etc.
- There is the commitment on the part of the inventors to make further progress on this technology so that the best combination of materials and parameters that maximizes value can be achieved.
- The application areas and possibilities for this technology are immense. A brief discussion on the same follows.

MARKETS

Statistics regarding US vehicular markets from data available with the government (www.ita.doc.gov), reaffirm that the total market size (revenues) will be $ 303 billions by 2010, after growing at a steady pace of 3% annually. This is also the likely year in which hydrogen powered vehicles will make a significant impact in the market, cornering about 5% share or around $ 15.15 billions. This invention has the potential of capturing an important segment within this market.

Besides, there are the industrial and household use segments to be considered in any valuation of this technology. The technology occupies a broad denominator and can be readily extended and/scaled up to meet different applications.

INVENTORS

Dr. Eli Ruckenstein is Distinguished Professor, Department of Chemical and Biological Engineering at UB. He earned a PhD in Chemical Engineering from the Polytechnic Institute of Bucharest in 1966. His research interests are in the areas of catalysis, surface phenomena, colloids and emulsions and biocompatible surfaces and materials. He is the recipient of numerous felicitations and awards.

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PATENT STATUS as of 02/28/2005

US Provisional Patent applications have been filed in February, 2004 covering all claims.

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