Electrochemical Synthesis of Aluminium Hydride for Hydrogen Storage

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Received: 23.12.2016   Accepted: 01.01.2017   Published: 30-03-2017
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ABSTRACT

Electrochemical Synthesis of Aluminium hydride material was gaining interest due to usage in storing hydrogen for automobiles. Biofuel reduces pollution and various cardiac diseases all over the world. The most preferred method was Electrochemical Synthesis. The chemical method degrades the particles in three days. So the Electrochemical Synthesis was the best way to prepare Aluminium Hydride. The chemicals used were Sodium Aluminium Hydride as electrolyte, Tetrahydrofuran (THF) as a solvent and it was toxic. It was performed in Argon atmosphere. Aluminium Hydride (Alane) formed in the form of pore which gets evaporated within few seconds.

Keywords: Alane; Argon; Electrochemical; Storage.

1. INTRODUCTION

The DOE is supporting research to demonstrate viable materials for onboard hydrogen storage. Aluminum hydride (alane – AlH_3), having a gravimetric capacity of 10 wt% and volumetric capacity of 149 g H_2/L and a desorption temperature of ~60 °C to 175 °C (depending on particle size and the addition of catalysts) has the potential to meet the DOE Targets.

Presently, hydrogen is the only energy carrier that can be produced in large amounts and in an appropriate time scale. Electric energy, either from renewable energies, for example, solar and wind or future fusion reactors can be used to produce hydrogen from water by electrolysis. The combustion of hydrogen leads again only to water and the cycle is closed. And also hydrogen produces no air pollutants or green house gases when used in fuel cells, it produces only nitrogen oxides (NO_x) when burned in internal combustion engines (ICE's).

2. FUEL CELL

Fuel cell is a device that converts the chemical energy from a fuel into electricity through a chemical reaction of Positively charged hydrogen ions with oxygen or another oxidizing agent. Although development and demonstrations of fuel cells in automobiles usually draw more attention, applications for stationary power generation offer even greater market opportunity. The drivers for both market sectors are similar, higher efficiency and lower emissions. The system design for both applications is similar in principle. The main differences are in the choice of fuel, power conditioning and heat rejection. There are also some differences in requirements for automotive and stationary fuel cell systems. For example, size and weight requirements are very important in automotive applications, while not so significant in stationary applications. The acceptable noise level is lower for stationary applications. Typically noise in the fuel cell systems comes from air and fluid handling devices. Automobile systems are expected to have a very short start-up time while the start-up of a stationary system is not time limited, unless operated as a back-up or emergency power generator. Both automotive and stationary systems are expected to survive and operate in extremely ambient conditions, although some stationary units may be designed for indoor installation. And finally, automotive systems for passenger vehicles are expected to have a lifetime of 3000-5000 operational hours, systems for buses and trucks somewhat longer, but the stationary systems are expected to operate 40,000-80,000 hours.

3. STATIONARY FUEL CELL SYSTEMS

A variety of stationary fuel cell systems are being developed. Design options of stationary fuel cell power systems depends on with respect to application, grid connection, nominal power output, load following, choice of fuel, installation and co-generation capabilities.

A stationary fuel cell power system may be designed to operate at constant/nominal power output all the time. Proton Exchange Membrane (PEM) Fuel cells run on hydrogen.

PEM Fuel cells being energy conversion devices must deal with gas streams and liquid solutions that are either oxidizing or rather reducing and with electrochemical potentials induced by the cell reactions. In principle, any of the materials in the system in contact with an aqueous phase may be subject to corrosion, including supply lines, tanks, pumps, sensors, filters, housings etc., but materials in the stack are particularly the bipolar plate / current collector component are of concern.

For the hydrogen transport through the fuel cell membrane, a PEM requires the presence of water molecules within the membrane. Therefore, PEM fuel cells need a specified humidity to present the membrane from drying. Dehydration may decrease the performance due to increasing resistance and degrade the structure of the membrane. Hence, an additional water supply is needed.

4. HYDROGEN STORAGE

For hydrogen storage units in general, there are different options- Pressurized gaseous, liquefied hydrogen and hydride materials. For portable applications in the low power range, hydride materials are the most commonly used hydrogen system. For hydrides, a pressure container for a pressure of about 10 bar is required. The first development step was the replacement of standard Stainless steel cans by Aluminium cans in order to reduce the weight of the container.

Hydride materials which can be charged and discharged reversibly are metallic alloys. The composition of the alloy determines the temperature and pressure levels for the desorption and adsorption process. The typical storage density of these hydride materials (AB_5 alloy) is 1.3-1.4 wt% of hydrogen.

In addition to the hydride material, there is a container, a filter and a valve to complete the storage system. These components also contribute the weight and size of the system. The hydride materials are considered to be the safety way to store hydrogen. Since the temperature decreases on discharges, hydrogen release is decelerated. The alloys can be charged and discharged several thousand times, depending on the purity of hydrogen used for charging. These hydrides can only be used once and their synthesis procedure is complicated chemical process.

5. METAL HYDRIDES

Metal hydrides are promising candidates for many stationary and mobile hydrogen storage applications. The main advantages of storing hydrogen in a metal hydride are the high hydrogen volumetric densities(sometimes higher than in liquid hydrogen) and the possibility to absorb and desorb hydrogen with a small change in hydrogen pressure.

Metal hydrides can be defined as a concentrated single – phase compound between a host metal and hydrogen. The first metal hydride was discovered by Graham who observed that palladium absorbed a large amount of hydrogen. Only a few simple hydrides were known before the twentieth century and hydride chemistry did not become active until the time of world war II. Simple binary metal hydrides can be grouped into four basic types according to the nature of the metal-hydrogen bond.

a) Ionic or Saline Hydrides

This group include the binary hydrides of all alkali metals and of alkaline earth metals from calcium to barium. Examples of ionic hydrides are calcium hydride, sodium borohydride, Lithium aluminium hydride etc. Due to the complicated synthesis process, it is not used for hydrogen storage.

b) Covalent Hydrides

Covalent metal hydrides are compounds of hydrogen and non-metals. Examples of covalent hydrides are water, hydrogen sulfide, silane etc. Because of the difficulty in synthesis, covalent hydrides are not good candidates for hydrogen storage applications.

c) Metallic Hydrides

Most of the hydrides that could be used for hydrogen storage are metallic in nature. Metallic hydrides are formed by transition metals including the rare earth and actinide series. Examples of metal hydrides are Titanium hydride, Thorium hydride etc.

d) Borohydride

Nowadays some of the complex borohydrides($NaBH_4$, KBH_4) are widely used in organic synthesis for the reduction of aldehydes or ketones to alcohols. One important property is the high gravimetric H_2 density of complex borohydrides. The low atomic weight of boron and the high amount of bound hydrogen makes the complex system interesting for hydrogen storage.

Most of the metal borohydrides have higher amount of hydrogen content. But, we cannot use for hydrogen storage, because it show high thermal stability, making the liberation of hydrogen difficult. They cannot be decomposed with the waste heat of a PEM fuel cell, which makes their use impractical. Another important disadvantage is that it shows unfavourable thermodynamics for use as reversible hydrogen storage material.

6. ALUMINIUM HYDRIDE

Aluminium hydride(Alane) has been discussed for storing hydrogen because of their attractive properties. Aluminium hydride is a covalently bonded hydride that exists in a metastable state as a solid at room temperature. It is a trihydride material (AlH_3) with three hydrogen atoms to every aluminium atom.

Aluminum hydride (alane – AlH_3), having a gravimetric capacity of 10 wt% and volumetric capacity of 149 g H_2/L and a desorption temperature of ~60 °C to 175 °C (depending on particle size and the addition of catalysts). Discovering efficient and economic means for storing hydrogen is critical to realizing the hydrogen economy. Extensive research work has been conducted, worldwide, to develop new materials or revisit known materials in an effort to achieve the material properties needed for hydrogen storage. Unfortunately, the majority of these compounds fail to fulfill the dynamic and kinetic requirements for an onboard storage system. However, aluminium hydride not only has the required gravimetric and volumetric density but also has thermodynamic and kinetic conditions of operation compatible with the use of waste heat from PEM fuel cells or hydrogen burning internal combustion engines.
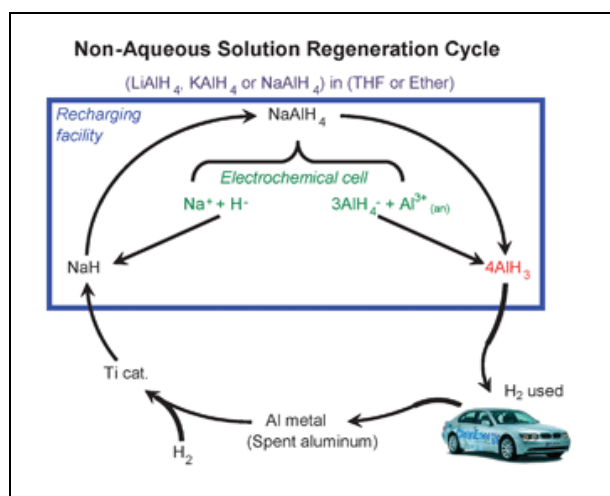
7. SYNTHESIS

An electrochemical cell was taken and cleaned thoroughly. An aluminium sheet was taken as an anode and it is scratched to remove aluminium particles and other compounds and finally it was rinsed with IPA (Isopropyl alcohol). This sheet was folded and pressed and to square shape. The dimension of the sheet was about 5.5 cm X 3 cm and it weighs 0.94 g. Then, Platinum sheet of 3.55g was taken as a cathode with dimensions 3.8 cm X 3 cm. These electrodes were placed in an electrochemical cell and it was closed with Teflon stopper. The setup was kept inside a glove bag.

Sodium Aluminium hydride of 0.5M was dissolved in150 ml of Tetrahydrafuran (THF).

$$NaAlH_4 + THF \text{ (Solution)} \longrightarrow Na^+ + AlH_4^- + THF$$
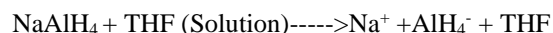
A potential is applied to the electrodes through the potentiostat. It is held at constant potential of 1.5V and current is measured. When this appropriate voltage is applied, alane is produced at the anode. Two separate reaction mechanisms can produce alane at an aluminium electrode.

The desired half reaction at the anode for alane production is

$$AlH_4^- \rightarrow AlH_3 + 1/2\ H_2 + e^-$$

This reaction mechanism has the lower reduction potential and thus requires less energy input to drive the oxidation in an electrolytic cell.

The second mechanism for alane production is by the equation:

$$3AlH_4^- + Al \rightarrow 4AlH_3 \text{ (in THF)} + 3e^-$$

The respective equilibrium potentials of anode and cathode are -1.57V and -2.71V.

At the cathode sodium ions can be reduced to elemental sodium as,

$$Na^+ + e^- \longrightarrow Na$$
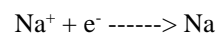
The plating of sodium at the cathode is slightly more energy intensive than formation of sodium hydride, but can directly be used to regenerate the starting material. At the proper voltage sodium can be collected from the cathode. Once in elemental form, sodium is easily converted to its hydride by direct hydrogenation at 100 °C.

Sodium hydride can also be directly formed to precipitate in the cell when hydrogen is bubbled at the cathode, resulting in atomic hydrogen, to form NaH.

$$Na + \tfrac{1}{2}\ H_2 + e^- \longrightarrow NaH$$
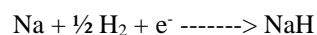
$NaAlH_4$ can be regenerated by reacting sodium and aluminium or sodium hydride and aluminium at 150 °C under moderate hydrogen pressure (100 bars) in the presence of Ti catalysts as shown in equation.

$$NaH + Al + 3/2\ H_2 \overset{Ti}{\longleftrightarrow} NaAlH_4$$
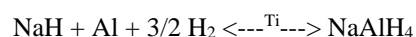
The experiments should be done in an argon atmosphere at standard pressure and temperature. Voltage was applied for approximately 24 hrs.

The figure shown below represents how regeneration process occurs when hydrogen is used as a fuel.

During, electrochemical synthesis we have to consider Gibb's free energy.

GIBB'S FREE ENERGY

Gibb's free energy is the amount of energy in a reaction can be used for work.

$$\Delta G = - nFE$$

n - the number of moles of electrons
F - Faraday constant (Charge of mole of electron)
$\qquad$ (1.6*10^{-19} C * 6.023*10^{23} / mol)
F = 96,500 C/mol
E = Difference in electrode potential

In thermodynamics, the Gibb's free energy also known as free enthalpy to distinguish it from (Helmholtz free energy) is a thermodynamic potential that can be used to calculate the maximum or reversible work that may be performed by a thermodynamic system at a constant temperature and pressure.

The decrease in Gibb's free energy is the maximum amount of non-expansion work that can be extracted from a thermodynamically closed system, this maximum can be attained completely reversible process. When a system transforms reversibly from an initial state to a final state, the decrease in Gibb's free energy equals the workdone by the system to the surroundings minus the work of the pressure forces.

The Gibb's energy is also the thermodyanamic potential that is minimized when a system reaches chemical equilibrium at constant pressure and temperature. Its derivatives with respect to the reaction co-ordinate of the system vanishes at the equilibrium point. The Gibb's energy must be smaller than non-PV work which is often equal to zero.

Gibb's free energy is also defined as

$$G(P,T) = U+PV-TS$$

The Gibb's free energy is one of the most important thermodynamic functions for the characterization of a system. It is a factor in determining outcomes such as the voltage of an electrochemical cells and the equilibrium constant for a reversible reaction.

$\Delta G < 0$ = favoured reaction (Spontaneous)
$\Delta G = 0$ = neither the forward nor the reverse reaction
$\qquad$ prevails (equilibrium)
$\Delta G > 0$ = disfavoured reaction (non spontaneous)

The Gibb's free energy value should be negative for spontaneous reaction.

8. RESULTS & DISCUSSION

There is an alane formation in the form of a pore which gets evaporated within few seconds. It may be due to the undissolved electrolyte. Because, Sodium Aluminium hydride is not dissolving properly in THF. At the time of dissolving, some particles were settled down. This precipitate may be a aluminium. Optimization is required for proper dissolving of the electrolyte.

Alane was again synthesized by electrochemical methods. Here, Sodium aluminium hydride was dissolved using magnetic stirrer at room temperature for 24 hours. This electrolyte was sucked using peristaltic pump and the process was done in argon atmosphere. It was notices that the no electrolyte found in electrochemical cell. The electrolyte may be vapourised when it reacts with air. So, Sodium aluminium hydride of cannot be taken as anelectrolyte with this conditions.

Aluminium hydride cannot be synthesized easily by ordinary chemical methods. If it is synthesized by complicated electrochemical methods, it can be recycled easily and corrosion is aso prevented. After Synthesizing these materials, it can be put in a Hydrogen tank. These materials can produce and regenerate hydrogen of gravimetric capacity of 10% wt whereas other materials like sodium aluminium hydride cannot produce rehydrogenation effectively.

9. CONCLUSION

No alane containing hydrogen cylinder is available up to date. As the research is continuously going on in this field, in future there may be a reduction in cost of alane products due to new techniques and materials.

FUNDING

CONFLICTS OF INTEREST

The authors declare that there is no conflict of interest.

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