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(54) Title: METHOD OF HYDROGEN GENERATION FOR FUEL CELL APPLICATIONS AND A HYDROGEN-GENERATING SYSTEM
METHOD OF HYDROGEN GENERATION FOR FUEL CELL APPLICATIONS AND A HYDROGEN-GENERATING SYSTEM

Field of the invention

The invention discloses a method of generating hydrogen for fuel cell applications, based on a chemical reaction of metal hydrides with alcohols. A hydrogen generator using such reaction is described.

Background of the invention

Fuel cells require a continuous supply of hydrogen and oxygen to produce electricity. At present however, storage and supply of hydrogen is the main limiting step in the use of fuel cell systems. For vehicular applications, large amounts of hydrogen (of the order of several kilograms) are needed on-board between refuelling. However, current methods of hydrogen storage not only cannot provide sufficient hydrogen capacity (or volumetric density) to compete with gasoline cars, but have additional serious limitations. For example, compressed hydrogen tanks operate at very high hydrogen pressure (350 – 700 atm) and so have a serious safety problem. Liquid hydrogen on the other hand needs cryogenic temperatures (about ten to fifteen degrees above absolute zero) and therefore requires costly and demanding cryogenic equipment. In the case of miniature fuel cells for portable applications (for example for laptops or cellular phones) the hydrogen storage is even more critical, because both of these storage methods are totally impractical on the small scale.

Metal hydrides offer a good solution for hydrogen storage: they are safe, stable and provide indefinite storage without hydrogen loss. In general, the use of metal hydrides is based on the reversible cycling of hydrogen absorption and desorption under certain pressure/temperature conditions. A variety of metal hydrides is known, having various hydrogen capacities and different pressure/temperature characteristics.

In general, metal hydrides can be divided into two groups:

- "unstable" hydrides operating at room temperature. These hydrides require hydrogen pressure (typically between 2 and 5 atm) to be maintained in the
tank, otherwise the hydrogen is immediately released from the hydride. These room-temperature hydrides (for example those based on LaNi₅ or FeTi) provide easy and fast hydrogen desorption, but have low hydrogen storage by weight (around 1 wt.%).

- "stable" hydrides operating at elevated temperatures. These metal hydrides can indefinitely store hydrogen at room temperature, even without hydrogen overpressure. However, desorption requires raising the temperature, in some cases significantly. For example, Mg-based hydrides need to be heated to temperatures close to 300°C in order to release hydrogen. Although these hydrides have high hydrogen capacities (reaching 7.6 wt.% in the case of MgH₂), the high temperature of hydrogen desorption is a serious practical disadvantage.

Very few metal hydrides are known where thermodynamic properties allow reversible operation at moderate temperature (below or around 100°C), and also having good hydrogen capacity. One example is NaAlH₄, which can operate reversibly with good kinetics and hydrogen capacity of 5.6 wt.%, but only after advanced catalysis [1,2]. However, currently even catalyzed NaAlH₄ becomes impractically slow at temperatures below 100°C, which is required for the PEM fuel cell applications.

An alternative method for generating hydrogen from these stable hydrides without the need to raise the temperature is through a chemical reaction leading to the decomposition of the hydride. For example, water may be used to release hydrogen via hydrolysis reaction. Water reacts with certain metal hydrides, forming hydroxides and the release of gaseous hydrogen.

Examples of the hydrolysis reaction are as follows:

\[ \text{LiH} + \text{H}_2\text{O} \rightarrow \text{LiOH} + \frac{1}{2} \text{H}_2 \uparrow \]
\[ \text{CaH}_2 + 2 \text{H}_2\text{O} \rightarrow \text{Ca(OH)}_2 + 2 \text{H}_2 \uparrow \]
\[ \text{NaH} + \text{H}_2\text{O} \rightarrow \text{NaOH} + \text{H}_2 \uparrow \]

Generation of hydrogen by a hydrolysis reaction is effective, but has disadvantages. One is that hydrolysis reactions are usually violent and generate large amounts of heat. Once started, they are extremely difficult to control and may proceed in an explosive manner. For example, in the case of LiAlH₄, the heat of hydrolysis causes a very rapid increase of temperature, which results in an instant thermal decomposition of the hydride, so that the reaction cannot be controlled by simply limiting the amount of water, and proceeds rapidly once initiated. One way around is to immerse the hydride in a mineral oil [5], which makes the reaction more controllable. This however reduces the effective hydrogen capacity at least by half, because the oil-based slurry needs to contain about 50 wt.% of the mineral oil. Another method to avoid explosive reaction is disclosed in U.S. Patent No 5,593,640 [6], where a combination of adiabatic hydrolysis and thermal decomposition is claimed to provide a controllable generation of hydrogen. In this generator, LiAlH₄ is allowed to undergo hydrolysis only at temperatures exceeding the temperature of the initiation of thermal decomposition, which is effected by heating the hydride before hydrolysis in a complex generator.

The use of sodium hydride instead of lithium hydrides results in a less violent reaction, but at the expense of hydrogen capacity, which is reduced simply because sodium is much heavier than lithium. A hydrogen generator based on the hydrolysis of sodium hydride is disclosed in U.S. Patents No 5,728,464 and No 5,817,157 [7,8]. This reaction has however another disadvantage. It requires a significant excess of water, because the reaction product, sodium hydroxide, causes solidification of the solution when its content exceeds 50 mol%, thus stalling any further hydrolysis. Among other hydrides, NaBH₄ reacts with water only when specially catalysed, for example by a special Ru-based catalyst [9]. In this case however, the same problems as with NaH occur, namely precipitation of the solid reaction product, NaBO₂, which requires the NaBH₄ solution to be diluted to 20 mol% of NaBH₄ and thus results in
reduced hydrogen capacity. Another technical problem is that controlling the reaction can be done only by either immersing the catalyst in the solution (which promotes the reaction) or by completely removing of the catalyst from the solution (which stops the reaction), so that intermediate reaction rates are not accessible. In another design of the hydrogen generator it was pointed out that for portable applications the heat of hydrolysis of NaBH₄, LiBH₄, LiAlH₄ or NaAlH₃ is so large that the hydrolysis-based generators could be too hot to be practical. In these cases the heat of hydrolysis is used to generate steam for the steam-hydrolysis of the hydrides [10].

All hydrolysis reactions have also one common problem: the use of water limits the temperature range of the hydrogen generator to temperatures above 0°C, because of the water freezing. This is a serious limitation for the outdoor use of the hydrolysis-based generators in a cold climate, which may require a “cold start-up” at temperatures below -20°C, or even -40°C.

Thus at present, none of the above methods of storing and generating hydrogen represents a fully efficient, safe and reliable source of hydrogen for fuel cells. All the above methods suffer from serious limitations and therefore alternative methods of hydrogen generation are needed. It is the aim of the present invention to offer such an alternative method.

Summary of the invention

The present invention relates to a new method of hydrogen generation for fuel cell applications. In this method, hydrogen is produced from metal hydrides in a chemical reaction with alcohols. A following generic reaction is the basis for the hydrogen production:

\[
MH_x + x\text{ROH} \rightarrow M(\text{OR})_x + x\text{H}_2 \uparrow
\]
Where MH$_r$ is a metal hydride, ROH is an alcohol; where R is an alkyl group suitably of 1 to 10, preferably 1 to 6 carbon atoms, especially 1 to 4 carbon atoms, for example, methyl, ethyl, n-propyl, iso-propyl, n-butyl, sec. butyl or tert. butyl.

hydroxyl group (OH) in the alcohol formula. As a result, another compound is formed, alkoxide, and hydrogen is released from both metal hydride and (partially) from the alcohol.

Most metal hydrides examined in our study readily react with alcohols (for example with methanol, ethanol or higher alcohols), and the reaction produces a steady and abundant flow of hydrogen at room temperature and below. Moreover, the amount of the hydrogen released is greater than that obtained from the thermal decomposition of the hydride, because hydrogen comes not only from the hydride, but also from the hydroxyl group of the alcohol. Table I summarizes nominal hydrogen capacities obtained from various metal hydrides in the alcoholysis reaction. The hydrogen capacities are given in wt % with respect to the weight of the hydride, and also in hydrogen volume obtained in the alcoholysis reaction from 1 kilogram of the hydride. Total hydrogen capacities, including both the weight of the hydride and weight of alcohol are also listed. Although in some reactions an excess of alcohol is advantageous for the reaction rate, the alcohol excess was not taken into account in the Table. It should be noted here that in the case of more complex reactions, for example involving bi-metallic hydrides (i.e. with two different metal atoms) the overall hydrogen capacities are dependent on the reaction route and may change depending on the applied temperature, catalysis and excess of the alcohol.

<table>
<thead>
<tr>
<th>Hydride</th>
<th>wt. % of H$_2$ (in respect to the hydride weight)</th>
<th>Litres of H$_2$ obtained per 1 kg of hydride</th>
<th>Total H$_2$ capacity (including the weight of the hydride and the alcohol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>LiH</td>
<td>25.4</td>
<td>2845</td>
<td>5.0</td>
</tr>
<tr>
<td>Li$_3$AlH$_4$</td>
<td>13.2</td>
<td>1478</td>
<td>7.2</td>
</tr>
<tr>
<td>Li$_2$AlH$_6$</td>
<td>16.8</td>
<td>1882</td>
<td>6.1</td>
</tr>
<tr>
<td>LiBH$_4$</td>
<td>23.1</td>
<td>2592</td>
<td>9.4</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>-----</td>
<td>-----</td>
<td>-----</td>
<td>-----</td>
</tr>
<tr>
<td>NaH</td>
<td>8.3</td>
<td>933</td>
<td>3.6</td>
</tr>
<tr>
<td>NaAlH₄</td>
<td>9.3</td>
<td>1045</td>
<td>5.9</td>
</tr>
<tr>
<td>Na₃AlH₆</td>
<td>8.9</td>
<td>996</td>
<td>4.6</td>
</tr>
<tr>
<td>NaBH₄</td>
<td>13.3</td>
<td>1490</td>
<td>7.3</td>
</tr>
<tr>
<td>Li₃Be₂H₇</td>
<td>22.0</td>
<td>2460</td>
<td>7.1</td>
</tr>
<tr>
<td>Li₂BeH₄</td>
<td>22.5</td>
<td>2516</td>
<td>6.7</td>
</tr>
<tr>
<td>MgH₂</td>
<td>15.3</td>
<td>1716</td>
<td>4.5</td>
</tr>
<tr>
<td>CaH₂</td>
<td>9.6</td>
<td>1074</td>
<td>3.8</td>
</tr>
<tr>
<td>FeTiH₂</td>
<td>5.7</td>
<td>641</td>
<td>2.6</td>
</tr>
<tr>
<td>ZrH₂</td>
<td>4.3</td>
<td>484</td>
<td>2.6</td>
</tr>
<tr>
<td>TiH₂</td>
<td>8.1</td>
<td>905</td>
<td>3.5</td>
</tr>
<tr>
<td>MgAl₂H₈</td>
<td>11.7</td>
<td>1307</td>
<td>6.7</td>
</tr>
<tr>
<td>LiAl₂H₇</td>
<td>11.9</td>
<td>1329</td>
<td>8.1</td>
</tr>
<tr>
<td>ZrAl₂H₈</td>
<td>6.6</td>
<td>737</td>
<td>4.6</td>
</tr>
</tbody>
</table>

Examples of the specific reactions of hydrogen generation are as follows:

\[
\begin{align*}
\text{LiH} + \text{CH}_3\text{OH} & \rightarrow \text{LiOCH}_3 + \text{H}_2 \\
\text{NaH} + \text{CH}_3\text{OH} & \rightarrow \text{NaOCH}_3 + \text{H}_2 \\
\text{LiH} + \text{C}_2\text{H}_5\text{OH} & \rightarrow \text{LiOC}_2\text{H}_5 + \text{H}_2 \\
\text{MgH}_2 + 2 \text{C}_2\text{H}_5\text{OH} & \rightarrow \text{Mg(OC}_2\text{H}_5)_2 + 2 \text{H}_2 \\
\text{Li}_3\text{Be}_2\text{H}_7 + 3 \text{CH}_3\text{OH} & \rightarrow 3 \text{LiOCH}_3 + 2 \text{Be} + 5 \text{H}_2
\end{align*}
\]

According to these reactions, metal hydrides produce alkoxides and hydrogen in the reaction with alcohols. Metal alkoxides are derivatives of alcohols (MOR) and constitute an important branch of organometallic chemistry. The research on alkoxides was initiated more than a century ago and now alkoxides find a variety of important applications, for example as drying agents, water-repellents, and paint components. The most common catalytic applications of alkoxides include redox catalysis and olefin
polymerization catalysis. Alkoxides are also used as precursors to metal oxides. High purity oxides can be obtained through hydrolysis, pyrolysis or combustion of alkoxides. Metal alkoxides are usually produced by one of the following methods (as widely described for example in a review book "Metal alkoxides" [11]):

- reaction of metals with alcohols
- reaction of metal halides with alcohols
- reaction of metal hydroxides and oxides with alcohols
- alcohol interchange
- transesterification reactions
- reactions of metal dialkylamides with alcohols.

Although alkoxides can be effectively produced by all these techniques (and most of the above methods are used on an industrial scale) the formation of alkoxides from hydrides has been never considered in practice for a number of reasons. Firstly, the hydrides that are very efficient in the generation of hydrogen in the alcoholysis reactions, were previously either very difficult to fabricate (as for example Mg hydride, or Na₂AlH₆) or not known (for example Li-Be hydrides, or (Li-Na)-Al hydrides). Only recent advances in the metal hydrides synthesis by solid-state reactions enabled easy fabrication of many hydrides [13]. Another reason not to consider formation of alkoxides from hydrides (especially when the use of metals is sufficiently effective) is that the release of hydrogen from the hydride could be a serious complication during the alkoxide production. This potentially negative feature of the alcoholysis reaction is the key of the hydrogen generation in the present invention.

As seen in Table 1, a number of various hydrides can be used for the hydrogen production, and the optimum hydride can be chosen based on the required hydrogen capacity, the hydride cost and the required reaction rate. Methanol (CH₃OH) is the simplest and the lightest of all alcohols, therefore alcoholysis of metal hydrides with methanol gives the highest total hydrogen capacity, as shown in the Table. However, ethanol or higher alcohols provide much better reactivity with certain hydrides (for example complex borohydrides or calcium hydride CaH₂). The type of the
alcohol in the hydrogen generator can be chosen depending on the metal hydride, and also on the required reaction route and kinetics. Since alcohols are easily mixable, a mixture of two or more alcohols can be used in a very wide proportion. For example, a mixture of methanol and ethanol can be used, where methanol provides higher overall hydrogen capacity and ethanol better reactivity. The appropriate proportion of methanol/ethanol mixture can be adjusted during the efficiency testing of the hydrogen generation.

As mentioned above, the crucial advantage of the alcoholysis reaction over the hydrolysis reaction, is the possibility to operate at temperatures below freezing temperature of water. Even more convenient however is to use a mixture of alcohol and water (a common "windshield fluid") to produce hydrogen. In this case, the reaction is a combination of alcoholysis and hydrolysis, with two great enhancements over the hydrolysis alone: a more controllable reaction rate and possible operation at temperatures much below 0°C. The main advantage of the hydrogen generator based on the combined hydrolysis and alcoholysis is its flexibility to the "reactive liquid" used. The "reactive liquid" (i.e. the mixture of alcohol, or alcohols, with water) can be adjusted depending on the climate or season, with higher proportion of alcohol in the liquid when operation at lower temperatures is required, and with more water when more rapid hydrogen desorption is needed.

In certain cases, as for example in the case of alkali metal borohydrides (LiBH₄ and NaBH₄) the alcoholysis reaction needs to be catalyzed in order to increase the reaction rate. The addition of a solid-state catalyst can be very efficient in enhancing the reaction kinetics. Various catalysts can be used for this purpose (depending on the metal hydride and on the alcohol), for example iodine and its compounds, chlorides, or various metals (Ru, Ni, Ti, Fe) and their compounds. The catalyst can be introduced either in the solid state (admixed to the hydride), or in a solution with alcohol, or dissolved in another, neutral solvent.

A single type of hydride can be used in the hydrogen generator, but in some cases a mixture of two or more hydrides can be more advantageous. The main reason for using a mixture of hydrides is modification of the reaction rate or catalysis. Usually there is no
inter-reaction in the mixture of two hydrides in the powdered form at room temperature. However, when the mixture is immersed in alcohol, the reaction route (and the reaction rate) can be completely changed, as compared to the two hydrides alone. This can be effected by either formation of hetero-alkoxides, or by a combined, synergetic reaction, where the more reactive component induces the reaction of the "slower" component. This can be particularly advantageous when the slow hydride is inexpensive and has high hydrogen capacity, and the fast hydride is more expensive or difficult to fabricate. The fast reaction can induce and promote the second reaction in a synergetic way, as shown for example for hydrogen desorption in a mixture of MgH₂ and Mg₂NiH₄ [13].

Usually the most convenient form for the hydride (or hydrides) inside the generator before adding alcohol (or its mixture with water) is in the solid state, typically in a powdered form. However, when a fast refilling of the hydride container is required, the hydride may be contained in a neutral solvent (for example tetrahydrofuran or toluene) and so easily pumped into the tank.

As described above, the alcohololysis reaction of metal hydrides leads to the formation of metal hydroxides. There are two ways of dealing with the reaction products, i.e. recovering the metals. In some cases, simple hydrolysis or pyrolysis of the alkoxides gives a very valuable oxide product of very high purity and dispersion, which is ideal for many catalytic applications. An example is magnesium oxide, zirconium oxide or titanium oxide. Alkali metal in contrast, form hydroxides (for example LiOH or NaOH) as a result of hydrolysis of the respective alkoxides, which can be subsequently thermally decomposed into lithium and sodium hydrides and returned into the hydrogen generator.

In a typical reduction to practice, the metal hydride (or a mixture of two or more hydrides) is allowed to react with alcohol simply by pouring or injecting the alcohol into the hydride container. As a result of the alcohololysis reaction, hydrogen gas is released. Hydrogen is directed toward the fuel cell system. Controlling the supply of alcohol (or a mixture of alcohol and water) can easily control the rate of reaction and the release of hydrogen. Gradual feeding with the "reactive liquid" regulates the amount of the produced hydrogen, and the reaction can be thus stopped or increased depending on
the demand for hydrogen. In a practical way it is effected through an injection system, which reduces the supply of the "reactive liquid" in respond to the increasing pressure of the produced hydrogen.

The invention relates to a hydrogen generator, consisting of the following components:

1. A container with metal hydride (preferably being in a powder form, or in a solution in a neutral liquid). The container can consist of a single reaction chamber, but for large-scale application several separate reaction chambers can be more advantageous in order to have better control of the reaction.

2. A container with the "reactive liquid" (alcohol, a mixture of alcohols or a mixture of alcohol with water)

3. An injection system with a regulator for the controlled supply of the "reactive liquid"

4. A hydrogen outlet towards the fuel cell system, with pressure controller and safety gauge.

The above hydrogen generator can be used either as a main source of hydrogen for fuel cells, or as a start-up device only. In the latter case, the main hydrogen supply can be provided for example by thermal decomposition of metal hydrides.

Although the above reactions of alcohols with metal hydrides are aimed mainly towards the generation of hydrogen, they may actually also open the door to better ways of the formation of various metal alkoxides. In certain cases, complex alkoxides cannot be produced by a simple alcoholyis of metals or other compounds and the reaction with the respective hydride is the only way to produce these new alkoxides. An outstanding example is a newly synthesized Li₂Be₂H₇ hydride. In the dehydrogenated form the material simply consists of a mixture of two immiscible metals: Li and Be. In the hydrogenated state however, hydrogen atoms bond Li and Be together, forming a hydride. Therefore, the alcoholysis reaction with the Li₂Be₂H₇ is different (under certain experimental conditions) than that with Li and Be alone, and therefore more complex compounds can be formed: bi-metallic alkoxides i.e. containing two different metal atoms. This reaction was only possible after an efficient method of the hydride
formation was developed, as described in reference [14]. Other “double” hydrides (for example \( \text{LaNi}_5\text{H}_{6} \), FeTiH\(_2\) or Mg\(_2\)NiH\(_4\)) also offer a possibility to produce unique, double alkoxides, for which this reaction path was never considered before.

References:

13. "Synergy of hydrogen sorption in ball-milled hydrides of Mg and Mg$_2$Ni"

14. "Lithium-beryllium hydrides: the lightest reversible metal hydrides" A. Zaluska,