

Short communication

Integrating hydrogen generation and storage in a novel compact electrochemical system based on metal hydrides

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Abstract

The development of efficient and reliable energy storage systems based on hydrogen technology represents a challenge to seasonal storage based on renewable hydrogen. State of the art renewable energy generation systems include separate units such as electrolyzer, hydrogen storage vessel and a fuel cell system for the conversion of H₂ back into electricity, when required. In this work, a novel electrochemical system has been developed which integrates hydrogen production, storage and compression in only one device, at relatively low cost and high efficiency. The developed prototype comprises a six-electrode cell assembly using an AB₅-type metal hydride and Ni plates as counter electrodes, in a 35-wt% KOH solution. Metal hydride electrodes with chemical composition LaNi_{4.3}Co_{0.4}Al_{0.3} were prepared by high frequency vacuum melting followed by high temperature annealing. X-ray phase analysis showed typical hexagonal structure and no traces of other intermetallic compounds belonging to the La–Ni phase diagram. Thermodynamic study has been performed in a Sieverts type of apparatus produced by Labtech Int. During cycling, the charging/discharging process was studied *in situ* using a gas chromatograph from Agilent. It is anticipated that the device will be integrated as a combined hydrogen generator and storage unit in a stand-alone system associated to a 1-kW fuel cell.

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1. Introduction

The development of efficient, compact and reliable energy storage system based on hydrogen technology represents a challenge to seasonal storage based on renewable hydrogen that could be used in stand-alone systems [1]. These systems could replace conventional solutions reducing dependency on fossil fuel and emissions, and moreover promoting an increase in renewable energy penetration. During the past decade the interest in such systems is increased [1–5] offering an alternative that includes off-grid applications.

Introducing hydrogen as long-term energy storage has led to the use of water electrolysis, allowing the match of the primary available energy source to load demand, where previously batteries or diesel generators have been commonly used. The

existing renewable energy generation systems include apart from the electrolyzer – alkaline or PEM technology; a hydrogen storage vessel – either a pressurized vessel with a compressor or a metal hydride with a gas dryer; and a fuel cell system for the conversion of H₂ back into electricity, when required.

Seasonal energy storage exhibits critical barriers, still unsurpassed, such as the high cost of electrolyzer components, low energy “round-trip” efficiency of the hydrogen energy system, lack of easy to use energy efficient control units and not enough life time experience. In this context, it is paramount to look at compact and cost effective solutions that may contribute to promote new applications for the distributed generation of hydrogen from renewable energy sources.

In this work, a prototype developed as a compact unit is proposed as a novel electrochemical system which integrates the functions of hydrogen production, storage and compression in only one device. It has a relatively low cost and higher efficiency than a classical electrolyzer, providing an opportunity for a cost effective integration with renewable energy sources.

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2. The prototype

With an increase in renewable energies penetration and a market potential for the introduction of hydrogen into stand-alone energy systems, aspects related with the immaturity of some of the technologies which integrate the hydrogen sub-system, represent important unresolved technical issues, entailing unavailable components or availability at high costs. As a consequence, there is a growing initiative in the development and implementation of devices that may improve energy efficiency, response time and safety in the storage option looking for an increase in the energy round-trip efficiency of the hydrogen sub-system.

A prototype was developed to be integrated in a hydrogen stand-alone energy system, portraying innovative aspects of the use of metal hydrides in electrochemical systems. The rationale behind this development is based on the need for more sustainable solutions for energy storage in stand-alone energy systems translated into the implementation of compact design and low maintenance cost. Enhanced operational efficiency and reduction in the investment cost regarding the present state of the art technology is also sought.

The developed hydrogen generator prototype integrates the functions of hydrogen production, storage and compression in only one device. It is presented as an electrochemical system consisting of a six-cell assembly. Metal hydride (MH) electrodes and nickel plates as counter electrodes were installed in a stainless steel unit. A 35-wt% KOH solution was used as electrolyte. The MH electrodes has been prepared using a $\text{LaNi}_{4.3}\text{Co}_{0.4}\text{Al}_{0.3}$ alloy, with preparation methods typical for MH-Ni(OH)₂ electrodes in battery production [6].

A general view of the developed prototype apparatus showing the electrochemical reactor and facilities for connection to power supply is shown in Fig. 1.

The functioning principle implies that during the electrochemical charging, hydrogen is absorbed in the metal hydride

and the oxygen, produced by the reaction in the corresponding counter electrode, is conveyed out of the system. Conversely, in the case of discharging, the released hydrogen is delivered to the hydrogen storage up to a pressure of 15 bar. It is to be noticed that the maximum H₂ pressure is set by the mechanical construction of the whole system.

It is anticipated that the developed device will be dimensioned and integrated as a combined hydrogen generator and storage compact unit consistent with 1.2 kW PV solar panels and 1 kW proton exchange membrane (PEM) fuel cell in a stand-alone system, substituting so the electrolyzer and storage vessel in the hydrogen sub-system, with increased operational efficiency and a reduction in the investment cost.

3. Experimental

The alloy selected to integrate the electrode assembly of the electrochemical system proposed in this work, has a chemical composition of $\text{LaNi}_{4.3}\text{Co}_{0.4}\text{Al}_{0.3}$. The alloy has shown properties that convey a good electrochemical absorption of H₂ and corrosion resistance in KOH, as documented in the open literature [7–9].

One kilogram of the alloy has been prepared by high frequency vacuum melting of the metals with 99.5% purity. A high-temperature annealing procedure at 1000 °C was applied after the melting process, during 8 h, in order to destroy the non-equilibrium micro-structures as well as to reduce the stress and strain induced in the fabrication of the produced alloy.

Characterization of the alloy has been firstly carried out by X-ray phase analysis. Data for alloy LaNi_5 is included as reference. The scattering curves were measured with a diffractometer Siemens D 500 (Ni-filtered Cu K α radiation) equipped with LiF monochromator. Rietveld program was used to make profile analyses and determination of the lattice constants of the alloys from the obtained X-ray powder diffraction data.

A thermodynamic study of the alloys has been performed in a Sieverts type of apparatus produced by Labtech Inc. [10], for the investigation of the hydrogen absorption/desorption properties of the alloys. The PCT isotherms were measured at hydrogen pressures of 1–40 bar over the temperature range of 25–100 °C. Prior to PCT measurements, the samples were activated at a hydrogen pressure of 25 bar followed by the performance of three absorption/desorption cycles.

During cycling, the charging was run at 20 A at cell voltages of 1.6 V for 4 h. Hydrogen was released by applying a constant current of 40 A for 2 h until cell voltage rises from 0.5 to 0.8 V, at the end of the processes.

The gases releasing from the developed unit during charging/discharging processes were studied *in situ* using an Agilent micro-gas chromatograph, GC 300. The micro-GC was equipped with a Molecular Sieve 5A column with argon as a carrier gas. Data were instrumental in assessing the hydrogen purity and the efficiency of the process.

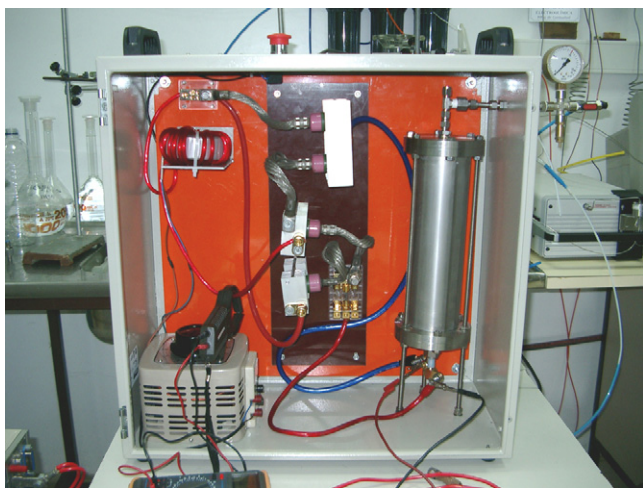


Fig. 1. View of the hydrogen generator prototype integrating hydrogen generation and storage in a novel compact electrochemical system based on metal hydrides.

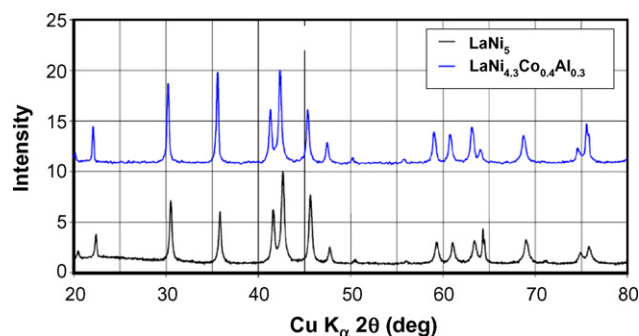


Fig. 2. The XRD pattern of $\text{LaNi}_{4.3}\text{Co}_{0.4}\text{Al}_{0.3}$ and LaNi_5 alloys (Siemens D500, $\text{Cu K}\alpha$).

4. Results and discussion

4.1. Alloy characterization

The XRD study of the synthesized LaNi_5 and $\text{LaNi}_{4.3}\text{Co}_{0.4}\text{Al}_{0.3}$ alloys is presented in Fig. 2. The performed structural and phase analyses revealed typical results for AB_5 -type alloys hexagonal CaCu_5 -structure and no traces of other intermetallic compounds belonging to the La–Ni phase diagram. The only impurity phase was identified as Ni, with an estimated content of less than 0.5%. The calculated lattice parameters for $\text{LaNi}_{4.3}\text{Co}_{0.4}\text{Al}_{0.3}$ ($a = 5.072 \text{ \AA}$, $c = 4.038 \text{ \AA}$, $c/a = 0.796$) are similar to those for LaNi_5 compound [11], showing a slight expansion of the unit cell mainly in the basal plane.

The desorption PCT isotherms were obtained from the gas phase for a $\text{LaNi}_{4.3}\text{Co}_{0.4}\text{Al}_{0.3}$ alloy composition at four different temperatures (25, 40, 70 and 100°C). Results are presented in Fig. 3. As it can be observed, the plateau pressure increases with concurrent temperature increase whilst the amount of absorbed hydrogen decreases. The maximum amount of desorbed hydrogen was found to be $160 \text{ cm}^3 \text{ g}^{-1}$, which corresponds to a capacity of more than 300 mA h g^{-1} . This is close to the theoretical value calculated for a LaNi_5H_6 system [12].

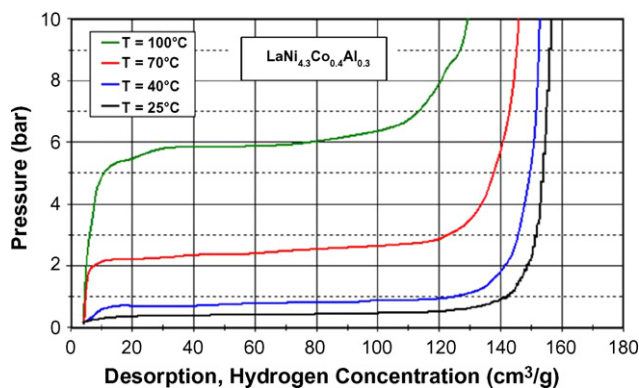


Fig. 3. Desorption PCT isotherms of $\text{LaNi}_{4.3}\text{Co}_{0.4}\text{Al}_{0.3}$ alloy used in the electrode assembly of the hydrogen generator/storage prototype proposed in this work.

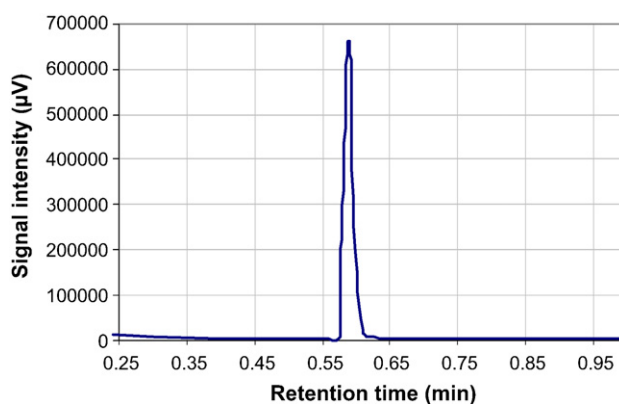


Fig. 4. Typical chromatogram of produced gases in the discharge cycle.

4.2. Performance and efficiency

The theoretical efficiency of the developed system could be quite high: about 3.3 kW per 1000 L H_2 production; this is based on the well known fact, that 1 g of metal hydride needs about 330 mA h [13] to be charged electrochemically and under the assumption that the potential of the system is 1.4 V.

The processes of charging/discharging were studied *in situ* using a gas chromatograph from Agilent equipped with appropriate columns for the detection of H_2 , O_2 and water content.

Results indicated that during a discharging period of 2 h, all hydrogen was desorbed from the metal hydride with no traces of oxygen being observed; Fig. 4 shows typical chromatogram. The delivered hydrogen gas exhibited high purity containing only some water vapour.

However, during the charging, it was observed that a secondary process has taken place which was identified as water electrolysis. As a result, additional amounts of hydrogen and oxygen were released by the system, reducing the hydrogen generator efficiency, as confirmed by gas chromatography. During the studies it was found that the ratio between the above processes has changed during charging time. Fig. 5 displays the hydrogen flow as a function of charging time in two different modes: hydrogen to metal hydride and hydrogen from water

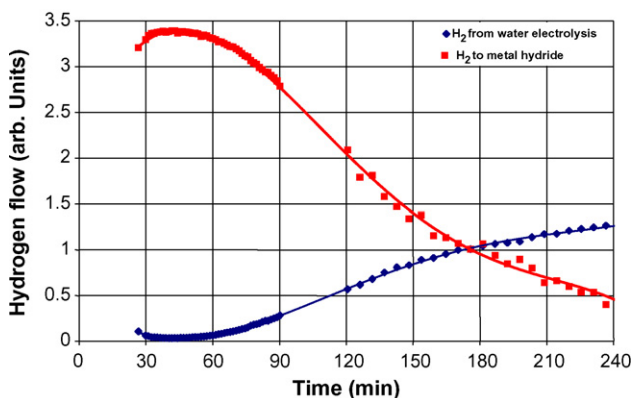


Fig. 5. Hydrogen flow as a function of charging time of the hydrogen generator for two reactions: (■) H_2 to metal hydride; (◆) H_2 from water electrolysis.

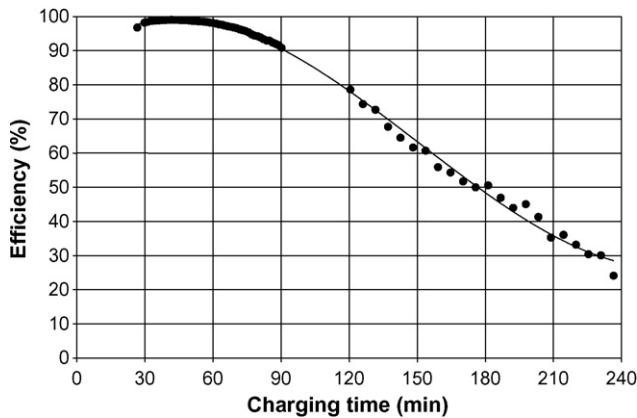


Fig. 6. The efficiency of the charging process of the developed hydrogen generator.

electrolysis according to data obtained using gas chromatography.

Efficiency of the charging process of the developed hydrogen generator is shown in Fig. 6, estimated on the basis of data from gas chromatography. It is clear that because of the mentioned secondary process, the efficiency of the whole system drops with time from 100 to 50–30% in the last 25% of charging time. It should be noticed that the efficiency did not depend on the charging current in the interval from 20 to 40 A, which corresponded to a charging time of 4 or 2 h, respectively.

Even though the charging potential is relatively low for hydrolysis (1.6 V), the secondary process found to take place became more noticeable with increasing of the concentration of the metal hydride phase in MH electrode. Our understanding of this fact is that the metal hydride phase acts as catalyst material, reducing the potential necessary for the splitting of water.

5. Conclusions

- A novel device has been developed and studied. Results show a compact hydrogen generator prototype proposed as a novel electrochemical system which integrates hydrogen produc-

tion, storage and compression in only one device, with higher efficiency than a classical electrolyzer.

- The theoretical efficiency of the system is very high ~ 3.3 kW per 1000 L H_2 produced. Water electrolysis was identified as a secondary process, bringing down efficiency in the last 25% of the charging time. It is thought that the metal hydride phase catalyzed the reaction reducing the necessary potential for water splitting.

Work in progress includes improving the process efficiency by decreasing the resistance between cell electrodes in the assembly.

It is anticipated that the device will be integrated as a combined hydrogen generator and storage unit in a stand-alone system associated to a 1-kW PEM fuel cell.

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