Embedded Sensor for Solid-State Hydrogen Storage Devices

Denis Marcotte and Frédéric Domingue
Institut de recherche sur l'hydrogène
Université du Québec à Trois-Rivières
Trois-Rivières, Canada
E-mail: denis.marcotte@uqtr.ca , frederic.domingue@uqtr.ca

***Abstract*— In this paper, we present two potential sensors used to monitor the state of charge of a solid-state hydrogen storage device. The embedded sensors are based on the variation of the electrical properties of the storage material related to the hydrogen content. Specifically, the proposed sensors are based on variation of the resistivity and the magnetic properties. We present the preliminary results. The measured results confirm the possibility to determine the state of charge of the $LaNi_5$ hydrogen storage devices using the variation of the resistivity while the study of the magnetic properties is under progress.**

Keywords: Embeded sensor; hydrogen monitoring; metal hydride; solid-state hydrogen storage device

I. INTRODUCTION

The continuously growing demand in energy motivated the development of renewable energy sources. An interesting solution is hydrogen, an excellent energy carrier. Its use reduces pollution that traditional fuels emit [1]. There are several products on the market using this energy vector such as cars, buses, power generators, electronic devices and appliances. The hydrogen storage devices are clearly one of the important components in the portable hydrogen energy systems. The hydrogen can be stored in various forms such as pressurized gas, cryogenic liquid, solid fuel as chemical or metal hydride compounds. Metal hydrides provide safety advantages over high pressure, compressed storage or low temperature, cryogenic storage, as the hydrogen is stored in a solid metal matrix at a low pressure with a slow release rate. These metal hydrides are promising mediums for portable hydrogen-powered generators. However, an important challenge with the metal hydride storage devices concerns the hydrogen metering techniques. The current approach consists in estimating the remaining hydrogen in the storage device based on electrical energy consumption. This solution is not precise and needs to be replaced by a specific sensor. The commercial products need low cost and compact sensors embedded into the metal hydride devices for the hydrogen metering.

This paper presents two approaches for the development of sensors embedded in the solid-state hydrogen storage devices to evaluate the state of charge. In this work, the storage material is the lanthanum nickel hydride (LaNi5). As opposed to the gaseous form, the pressure measurement cannot be used to determine the hydrogen content. Indeed, we propose to monitor the hydrogen content through the variation of the electrical properties of the storage material (LaNi5). Specifically, the proposed sensors are based on variation of the resistivity and the magnetic properties. The theoretical approach and the preliminary results are presented.

II. THEORY

The metal hydrides have phases that are named the α phase, where the metal begins to absorb hydrogen, and the β phase, where the metal is returned to its absorption maximum. These phases change depending on the substance used. Fig. 1 illustrates the variation of the pressure during the hydrogen absorption and desorption. Clearly, the pressure remains constant even if the amount of hydrogen changes.

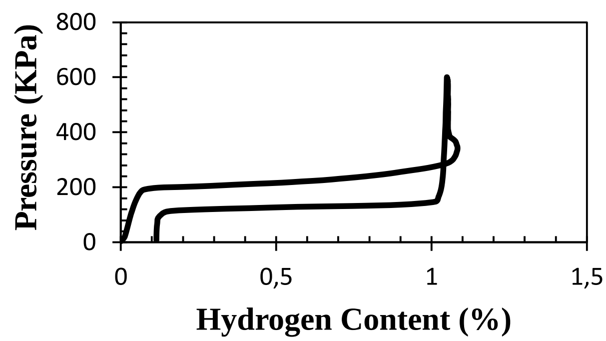

Figure 1. Typical PCT curve for LaNi5.

Several studies have focused on the characterization of intermetallic compounds. The electrical resistivity for various hydride compounds, such as the $MmTm_3$, the $MmNi_{4.5}Al_{0.5}$ and the $LaNi_5$, has been characterized [2-6]. The studies illustrate that the resistivity varies with hydrogen. Especially, the resistivity of the $LaNi_5$ decreases during the absorption of hydrogen. In other hand, the magnetic properties vary also with the hydrogen content. The susceptibility of the $LaNi_5$ is affected by the concentration of hydrogen absorbed by the compound, as discussed in several researches [7-9].

A. *Proposed Sensing Principles*

The recent technologies of micromachining make it possible to manufacture compact and low cost sensors

 ISBN: 978-1-61208-145-8

suitable for embedment in the hydrogen storage device. The mass production of these technologies helps to reduce the estimated cost of the sensors and measuring circuits to less than a few dollars per unit. The variation of the electrical properties of the hydrogen storage material, in this case LaNi5, will affect the output of the sensor.

B. *Resistivity*

The resistance of the LaNi5 changes with the concentration of hydrogen. The measurement device is based on two conductive electrodes in contact with the LaNi5. The state of charge is thus estimated by measuring the resistance between the electrodes.

C. *Susceptibility*

The susceptibility of the LaNi5 changes with the concentration of hydrogen. The state of charge is estimated by measuring an inductance embedded in the $LaNi_5$ storage device. The susceptibility variation modifies the inductance value. Fig 2b presents both sensing approaches.

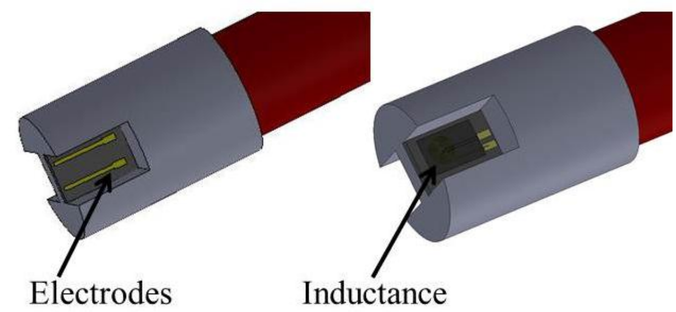

Figure 2. The proposed sensor device :
a) resistive sensor and b) inductive sensor.

III. Simulated Results

The simulations, using a finite element simulator, were performed with the parameters and the data presented in Table I. While the $LaNi_5$ powder is presenting large grains, the parameters for the bulk material have been used. The simulated model includes the variation of the electrical properties of the LaNi5 according to the hydrogen content.

TABLE I
PARAMETERS USED FOR THE SIMULATIONS

H_2 State	Parameter	Unit	Value
Charged	Resistivity [5] Susceptibility [9]	μΩm m^3/Kg	430 $16{,}3 \times 10^{-9}$
Empty	Resistivity [5] Susceptibility [9]	μΩm m^3/Kg	10 $57{,}8 \times 10^{-9}$

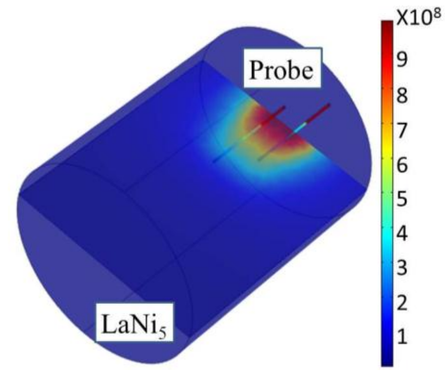

Figure 3. Simulated Current Density (A/m^2) .

TABLE II
SIMULATED RESULTS USING A FINITE ELEMENT SIMULATOR

H_2 State	Parameters	Unit	Value
Charged	Resistance	Ω	0,018530
Empty	Resistance	Ω	0,001307

The resistance variation is 1,72% between the charged and the empty states. However, Fig. 2 shows the current distribution in the material. While the electrodes' spacing is quite small compared to the LaNi5 volume, the current distribution is present only in a local region. Additional characterization are required to determine if longer electrodes are needed.

IV. Experimental Results

A. *Proposed Test Bench*

The PCT (Pressure, Composition and Temperature) test bench enables the absorption and desorption of hydrogen by controlling its pressure and temperature. We have set a Labview platform that captures the data with external equipment. The test devices are: a multimeter, an LCR meter, an oscilloscope and a function generator. This allows monitoring in real time of the sensor and observes its evolution in relation to the change of hydrogen.

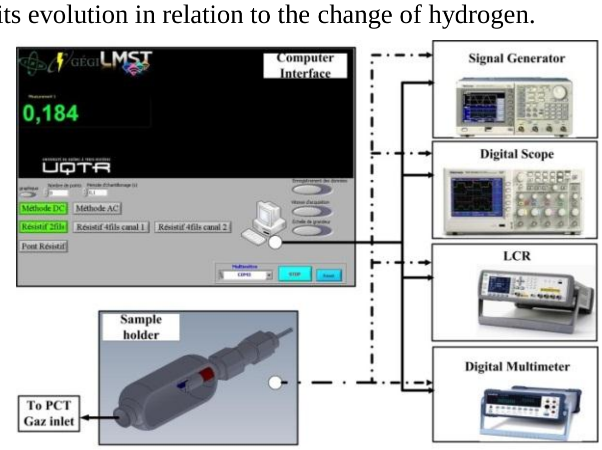

Figure 4. Automated Test Bench for Electrical Characterization during the absorption and desorbtion of hydrogen

 ISBN: 978-1-61208-145-8

B. *Resistivity Measurement*

The experiment was conducted on a sample of 254 grams of $LaNi_5$, with a temperature controlled chamber of 23^oC. The procedure of charging the metal hydride with hydrogen was to: first fill an adjacent tank, then monitor the hydrogen pressure of the reservoir and that of the sample, and when the storage tank was filled to capacity and we had a pressure of 2800kPa, close the valve of hydrogen and open the valve of the sample so that the metal hydride would charge. The changing value of the resistance was collected through an automated test bench. Here are the data stored.

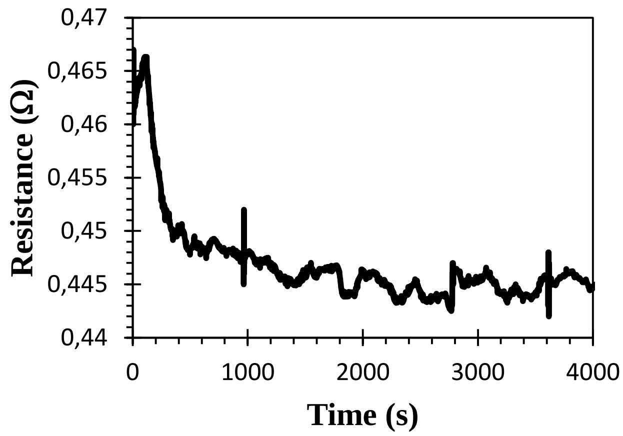

Figure 5. Variation of resistance during hydrogen absorption

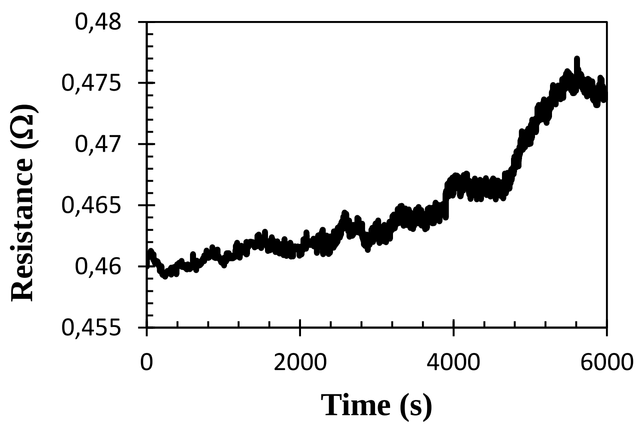

Figure 6. Variation of resistance during hydrogen desorbtion

The simulations illustrate a perfect contact between the block of metal and the electrodes. The resistance of the wire and the contact with the $LaNi_5$ must be taken into account. The measured resistance of the wire used in the test bench is 0.325Ω while the contact resistance is estimated at 0.125Ω. Table II presents the measured results and the simulated results including the correction for the wire and the contact.

TABLE III
COMPARISON BETWEEN EXPERIMENTAL AND SIMULATED RESULTS

H_2 State	Parameters	Unit	Value
Charged	Simulated Resistance with corrections	Ω	0,4513
	Measured Resistance	Ω	0,445
Empty	Simulated Resistance with corrections	Ω	0,4685
	Measured Resistance	Ω	0,464

Further experimentation is necessary to determine if the resistive sensors are suitable for this application. The effects of the temperature have to be investigated.

C. *Developped Sample Holder*

The sample-holder that contains the sensor was assembled by stereolithography. The fabrication was done at the University du Québec à Trois-Rivières. In our case, we used polymer to achieve the coveted results. The circuit was glued with epoxy. An electrical feedthrough allowed the connection of the embedded sensor to the automated test bench.

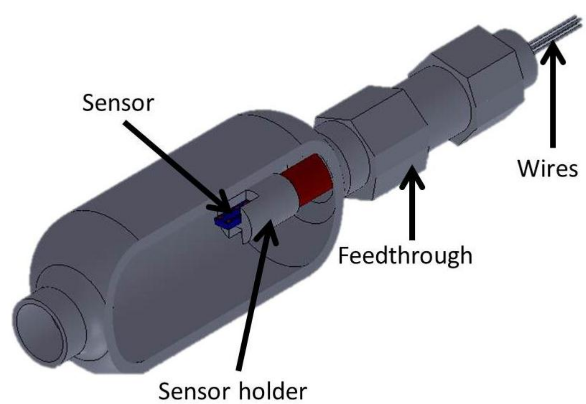

Figure 7. Developped Sample Holder Used in the Projet

V. FUTURE WORK

A. *Theory of Magnetic Properties*

Alternatively, we begin to study another phenomenon, which will reveal the hydrogen content in the sample. The other feature is the variation of the magnetic powder which is influenced by the presence of hydrogen. What will be revealed is the concentration of the entire surface of the cylinder and not just of a specific place. Studies clearly show the variation in susceptibility of $LaNi_5$ by presence or absence of hydrogen [8, 9].

We will discuss this feature by using inductance directly in the sample. The inductance is not required to be in contact with the powder as opposed to resistivity.

 ISBN: 978-1-61208-145-8

We calculate the inductance of the magnetic field in relation to the surface. This relationship has a direct effect on the value of the inductor, because it is the latter, which is multiplied by the number of turns of the coil and everything is divided by the current, see equation 1[10].

$$L = \frac{N \oint B ds}{I} \qquad (1)$$

where L represents the inductance, N is the number of turns of the inductance, B is the magnetic field, ds is the variation of the surface and finally I is the effective current.

B. *Developped Magnetic Sensor*

We propose to fabricate the inductive sensor on an alumina substrate. The proposed inductive sensors will be fabricated using a three-mask process. First, a 40 nm layer of evaporated chromium and a 1 µm layer of gold are defined using a typical bi-layer lift-off technique. Next, a 30 nm TiW adhesion layer and a 0.7 µm PECVD silicon oxide layer is deposited and dry-etched in a reactive ion etching chamber in the second photolithography step. This oxide layer is used as the insulator between the inductance and the LaNi5. Finally, the bridge is formed using a 1.0µm thick electroplated gold on a 100 nm Au seed layer. Fig. 8 shows the proposed inductive sensor.

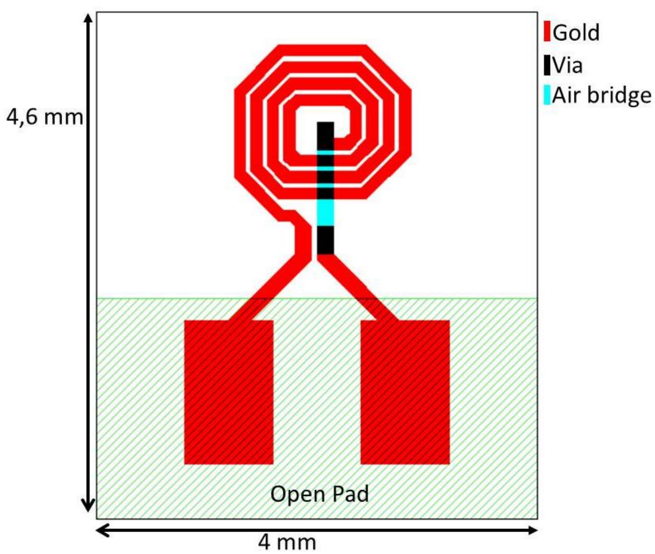

Figure 8. Inductance Sensor

VI. CONCLUSION

In this article, we presented the development of an embedded sensor in a solid-state hydrogen storage device. Two approaches are currently studied based on the variation of the electrical properties of the storage material. The resistive solution has been validated with experimental measurements. While the resistance decreases in the presence of hydrogen. Further experimentation is necessary to determine if the resistive sensors are adaptable to other metal hydride such as magnesium. On the other hand, the variation of the magnetic properties seems a good alternative. An inductive sensor is currently under development.

ACKNOWLEDGMENT

This research was supported by the NSERC Hydrogen Canada (H2CAN) Strategic Research Network. The authors also gratefully acknowledge Palcan Energy Corporation for the financial contribution. The authors are thankful to Dr. Jacques Huot and his team for their support.

REFERENCES

[1] U. D. of Energy, "hydrogen from coal program research, development, and demonstration plan for the period 2009 through 2016," D. o. Energy, Ed., ed, 2009.

[2] A. L. Mohana Reddy, G. Srinivas and S. Ramaprabhu, "Hydriding and electrical resistivity properties of MmTM3-hydrogen (TM=Fe, Co and Ni) system," *International Journal of Hydrogen Energy*, vol. 32, pp. 3356-3362, 2007.

[3] I. P. Jain, Y. K. Vijay and M.I.S. Dakka, "Electrical resistance variations with content of hydrogen in bulk MmNi4.5Al0.5," *International Journal of Hydrogen Energy*, vol. 27, pp. 85-90, 2002.

[4] A. Vashistha, P. Sharma, G. Agarwal and I.P. Jain, "Hydrogen absorption mechanism in obliquely deposited MmNi(4.5)Al(0.5) thin film," *International Journal of Hydrogen Energy*, vol. 33, pp. 404-407, Jan 2008.

[5] F. Ishikawa,H. Tega, I. Yamamoto and M. Yamaguchi, "Relationships between the electrical resistivity and the metal hydride phases," *Journal of Alloys and Compounds*, vol. 231, pp. 182-187, Dec 1995.

[6] G. Adachi,K. Niki and J. Shiokawa, "The effect of hydrogen absorption on the electrical resistivities of LaNi5 and MmNi4.5Mn0.5 films (Mm [triple bond; length as m-dash] misch metal)," *Journal of the Less Common Metals*, vol. 88, pp. 213-216, 1982.

[7] L. T. Tai, B.T. Hang, N.P.Thuy and T.D. Hien, "Magnetic properties of LaNi5-based compounds," *Journal of Magnetism and Magnetic Materials*, vol. 262, pp. 485-489, Jun 2003.

[8] T. P. Blach and E. M. Gray, "Magnetic properties of the LaNi5-H system," *Journal of Alloys and Compounds*, vol. 253, pp. 336-338, May 1997.

[9] L. Schlapbach, "Magnetic-properties of LANI5 and their variation with hydrogen absorption and desorption," *Journal of Physics F-Metal Physics*, vol. 10, pp. 2477-2490, 1980.

[10] M. N. O. Sadiku, Ed., "*Elements of electtromagnetics*," New York: Saunders college 1989, p.357

 ISBN: 978-1-61208-145-8