**Development of a La$_{0.55}$Y$_{0.45}$Ni$_5$ metal hydride pilot buffer tank for fuel cell car.**

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**ABSTRACT:**

Electrical vehicles powered by a fuel cell will need a buffer tank to supply hydrogen for cold start and/or to overcome possible delay in hydrogen supply system (reformer, dehydrogenation, etc.). To allow hydrogen delivery at low temperature, the hydrogenation properties of the compound La$_{0.55}$Y$_{0.45}$Ni$_5$ have been studied. It has been shown that the thermodynamic behavior of this compound is adapted for the cold start. A cylindrical tank containing 150g of La$_{0.55}$Y$_{0.45}$Ni$_5$ powder has been developed in order to store about 2g of hydrogen gas. The absorption kinetics of this tank have been measured at various temperatures under a 5 MPa quasi-constant pressure. Different time scales are observed depending on the alloy quantity. A strong temperature increase of the alloy is observed during absorption and it has been shown that the kinetic is mainly ruled by the thermal transfer between the metal hydride and the environment.

**KEYWORDS :** Intermetallics, Hydrogen storage materials, gas-solid reaction, buffer tank

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**Introduction**

The use of hydrogen as an energy carrier in automobile is considered as a promising way to limit greenhouse effect gas emissions $^1$. Fuel cell using hydrogen will release only water vapor in atmosphere. Metal hydrides can be used as hydrogen storage materials for supplying fuel cells. However, the kinetic properties of the metal hydride must be optimized to work at a temperature of about 338 K using the heat coming from the fuel cell. This implies a delay time to reach the working temperature especially if the ambient temperature is very low. So, a buffer tank will be needed during the time necessary for start-up. For this application, the buffer tank has to supply 0.2 MPa of hydrogen at 253 K. The storage properties of the pseudo-binary system La$_{1-x}$Y$_x$Ni$_5$ have been investigated previously $^2$. By adjusting the value of x to 0.45, the thermodynamic properties of this alloy were adapted to the desired thermodynamical conditions. In the present work, the kinetic and thermal behavior of a small buffer tank containing 150 g of alloy and able to store 2 g of hydrogen has been investigated at various temperatures.

**Experimental details**

The La$_{0.55}$Y$_{0.45}$Ni$_5$ intermetallic compound was obtained from the Treibacher Company (Austria). It was prepared by induction melting of the pure elements without further annealing treatment. It has been delivered in powder form packed under Argon with a grain size less than 106 μm. Elemental analysis by electron probe micro-analysis (EPMA Cameca SX100) was performed to check the homogeneity and stoichiometry of the alloy. Powder X-ray diffraction experiment (XRD) was obtained at room temperature on a Bruker D8advance Bragg Brentano diffractometer using Cu-K$_{α}$ radiation. Pressure Composition Isotherm
(PCI) curves were measured on a small quantity of powder (0.5 g) with a Sievert’s type apparatus after five hydrogen activation cycles. For the buffer tank, about 150 g of the compound $\text{La}_{0.55}\text{Y}_{0.45}\text{Ni}_5$ have been introduced in a stainless steel container (Volume 75 cm$^3$). This corresponds to a buffer tank able to store about 2 g of hydrogen. A thermocouple was introduced in the container in order to follow the temperature of the powder during hydrogenation reaction (Fig. 1). After four activation cycle at 253 K, kinetic measurements have been performed under adsorption at 253K, 268 K and 298 K using a quasi-static hydrogen pressure of 5 MPa. The tank was immersed in a thermalized bath in order to control and to regulate the external temperature.

![Figure 1: View of the buffer tank with the hydrogen connection (left) and thermocouple inlet (right).](image)

**Results and discussion**

The XRD of the intermetallic compound shows a single phase pattern indexed with the $P6/mmm$ space group (CaCu$_5$ type structure). The cell volume is equal to 84.45 Å$^3$ in good agreement with previous experiments. The composition determined by chemical analysis, $\text{La}_{0.54(3)}\text{Y}_{0.42(3)}\text{Ni}_{5.03(1)}$, is very close to the nominal one.

Thermodynamic properties (PCI) have been measured on the small sample (0.5 g) at 298 K and are shown on Fig 2. Comparison between the industrial material and the lab scale one shows that both compounds exhibit the same thermodynamic behavior with very similar isotherm curves.
Kinetic measurements have been carried out for both the small amount of sample (0.5 g) and the
buffer tank containing 150 g of alloy at 253, 268 and 298 K. The absorption curves as a function of time are
shown in Fig. 3 for the buffer tank. From these curves, the time to reach 90% of conversion ($t_{90}$) has been
determined at each temperature and is reported in table I.

<table>
<thead>
<tr>
<th>Temperature (K)</th>
<th>253</th>
<th>268</th>
<th>298</th>
</tr>
</thead>
<tbody>
<tr>
<td>$t_{90}$ (sec) small sample (0.5g)</td>
<td>234</td>
<td>76</td>
<td>149</td>
</tr>
<tr>
<td>$t_{90}$ (sec) buffer tank (150g)</td>
<td>427</td>
<td>442</td>
<td>750</td>
</tr>
</tbody>
</table>

Table I: Time to reach 90% of conversion ($t_{90}$) at quasi constant pressure (5 MPa) as a function of
temperature for a small sample (0.5 g) and the buffer tank (150 g) for the La$_{0.55}$Y$_{0.45}$Ni$_5$ compound.
The absorption kinetic for the alloys contained in the buffer tank (150 g) is slower than that corresponding to the small sample (0.5 g). The time to absorb 90% of the total capacity reaches 427, 452 and 750 sec respectively at 253 K, 268 K and 298 K. This is due to the fact that the hydrogenation reaction is exothermic ($\Delta H = -31.43 \text{ kJ/molH}_2$) inducing a strong increase of the temperature within the powdered alloy. Such temperature variation can be clearly seen in Figure 4 that shows the evolution of the temperature as a function of time. The temperature reaches 320 to 340 K whatever the external tank temperature is. Consequently, the temperature increase leads to an augmentation of the equilibrium pressure in agreement with the Van't Hoff law $3 \ln P = \frac{\Delta H - \Delta S}{R}$. Accordingly, when the temperature increases up to a value for which the equilibrium pressure is equal to the pressure system, the reaction rate slows down and a thermal equilibrium exists between the heat coming from the hydrogenation reaction and the heat transferred from the buffer tank to the external environment. From the Van't Hoff low, it is possible to calculate the equilibrium pressure of the sample at each temperature and to compare it to the system pressure. Such calculation is shown in Figure 5 where both pressures are compared as a function of time. It clearly shows that the limiting factor is not the intrinsic kinetic of the hydrogenation reaction but the slow heat transfer between the tank and the environment. Since kinetic is ruled by thermal exchanges, optimization of the tank is mandatory in order to obtain high absorption rates.
Figure 4: Evolution of the temperature as a function of time for the buffer tank.

Figure 5: Evolution of the equilibrium pressure (calculated from the Van't Hoff law) and the system pressure (gas pressure) as a function of time for the buffer tank at 298K.

**Conclusion**

La$_{0.55}$Y$_{0.45}$Ni$_5$ compound has an equilibrium pressure of 0.2 MPa of hydrogen at 253 K. It can be used to fill a buffer tank in a fuel cell car and to deliver sufficient hydrogen for the cold start. Kinetic reaction of the
alloy for absorption is high and refilling of the sample can be achieved in short time for small amount of powder. However, for larger quantity, the heat generated by the reaction leads to a temperature increase that slows down the reaction involving longer time for refilling. Optimization of the tank is necessary in order to improve significantly the heat exchange with the external environment and to reach shorter refilling time.

REFERENCES