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A new method for the characterization of hydrides hydrogen tanks dedicated to automotive applications

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ABSTRACT

In recent years, hydrogen has emerged as one of the best candidates in the field of renewable energy. Hydrogen storage in solid form has created new areas of application. Knowing the thermodynamic parameters of intermetallic compounds featuring stable hydrides is of great importance when using these hydrides in energy sources such as fuel cell generators for embedded or stationary applications. In this work, a new experimental method is described for measuring the hydrogen absorption/desorption characteristics of hydrogen storage material. This method is able to determine the Pressure-Composition-Temperature isotherm of a scale 1 hydride tank used in a fuel cell vehicle. This kind of characterization is useful for optimizing energy management between two vehicle powertrain components: the fuel cell stack and the hydride storage unit.

Introduction

Hydrogen storage has been a subject of intensive research for many years, to help prepare the way for a post-oil economy based on hydrogen as an energy carrier. Currently, hydrogen can be embedded in vehicles using a variety of technologies including compressed hydrogen, liquefied hydrogen, and hydrides [1]. Currently, the usual way of storing hydrogen is in a high-pressure tank. However, this form of storage gives rise to

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challenges in terms of design, development, reliability and security [2], while cryogenic storage is less energy-efficient because of the energy cost involved in liquefying the gas. This energy cost is usually 30% of the energy power of the hydrogen stored. Added to this, the daily evaporation of hydrogen is estimated to be 1% of the hydrogen contained in the tank [3]. An alternative solution, metal hydride storage, offers the possibility of operating at lower pressure (1:10 bar) and ambient temperature. One objective of hydrogen storage is to obtain a high volumetric energy density. Storage in hydrides is a more effective way than other methods of achieving this goal [4]. A compromise needs to be made between the weight of the elements and their specific capacities, which is a major factor in mobile applications. Metal hydride storage may be a good candidate as the main embedded energy tank for automotive powertrains. The phenomenon of hydridation was first highlighted by Thomas Graham [1], who observed that hydrogen pressure inside a waterproof palladium tank decreased when heated at ambient pressure. The information about these properties is generally inferred from PCT (*Pressure-Composition-Temperature*) isotherms. PCT isotherms show how the equilibrium hydrogen pressure depends on the amount of hydrogen absorbed or desorbed from the solid phase at different constant temperatures [5]. Several models of PCT curves are listed in Refs. [6,7]. Some of them are mathematical models [8] and others are physical. Both types of model are based on the occupation of the sites in the crystal lattice [6,7,9]. Generally speaking, there are four possible experimental methods for measuring Pressure-Composition-Temperature (PCTs) during hydrogen absorption and desorption from the hydride: volumetric, gravimetric, chromatographic and dielectric. The chromatographic and dielectric methods are used in the dynamic domain while volumetric and gravimetric methods are applied in the static domain [10–12].

In the case of our study, a good knowledge is required of the thermodynamic parameters of the hydride for a good energy management exchanged between fuel cells and a hydride tank for a vehicle application. The methods mentioned above are generally used to measure the amount of gas absorbed by a hydride sample. These methods are not appropriate in our case for two reasons; on the one hand, the hydride composition and the volume occupied by the hydride are unknown in principle. In our case the tank is considered as a black box where only the supply pressure and the mass flow of hydrogen are controlled, and on the other hand, the hydride will be characterized at system scale. In the context of our project we proposed to implement a new process that would be suitable for the tank system and for every type of hydride.

In this work, a new method to characterize hydrides is presented. The method was developed to evaluate the behavior of unknown hydrides in their storage environment by measuring the PCT isotherms at different constant temperatures. It was applied to a test hydride tank and experimental results were obtained. The method involves characterizing the hydrides and then deriving their thermodynamic parameters (enthalpy and entropy) from van't Hoff plots. The originality of this method is characterizing the hydrides at the scale of the tank. This makes it a useful method for optimizing the energy management between a fuel cell system and a hydride storage unit.

Classical methods of hydride characterization

The thermodynamic parameters, namely the variation of enthalpy and entropy (ΔH, ΔS) respectively of the hydride during hydrogen absorption/desorption can be determined either experimentally or theoretically [13]. The experimental approach includes gas or solid-phase measurement of PCT isotherms at different temperatures. The PCT isotherms are used to describe various hydride phases of alloy compounds. In this section we describe the methods that are usually employed for PCT measurements and discuss their advantages and disadvantages.

The volumetric method

This is the method most commonly used to describe the process of hydrogen absorption and desorption by the hydride [14–16]. The volumetric method is based on the comparison of pressures, volumes and temperatures between two tanks, one containing the sample and the other serving as a reference [1] (Fig. 1).

Knowing the volumes is of primary importance. For gas mixtures, the same method is applied in order to determine the amount of gas absorbed, except that in this case a chromatograph is required to establish the composition of the gas.

In our proposed method, only the pressure and the temperature, and not the volume, are used for computing the amount of hydrogen absorbed by the hydride.

The gravimetric method

This method uses a microbalance to weigh the hydride and consequently to determine the amount of gas absorbed. Results are obtained rapidly and with a high degree of accuracy. Moreover, the method is applicable over a wide range of pressures and temperatures. The main drawback of the gravimetric method is that the gas must be purified. Where there is a mixture of gases, the composition cannot be determined from the mass alone. Gravimetric analysis, as depicted in Fig. 2, consists of comparing the weight of the empty cell and the fully loaded cell. The amount of the absorbed gas is calculated as the difference between the total weight and the gas remaining in the gaseous state. The amount of non-absorbed gas, i.e. the gas which is not absorbed in the hydride, is determined by multiplying the gas density by the free volume of the cell. The density of the gas is obtained from temperature and pressure data. Because the density of hydrogen is low, this method is rarely used for measuring the isotherms of absorption of hydrogen, as explained by P.G. Manon et al. in Ref. [17].

The chromatographic method

As mentioned in the previous section, this method is used for dynamic characterization, where the sample is supplied by constant gas flow rates. This sample contains a specific quantity of absorbent material. The concentrations of outlet and inlet gases continue to be measured until they are equal, which indicates that the hydrogen has been completely