

How to Measure the Thermal Conductivity of Metal Hydrides

C-Therm's Trident Thermal Conductivity Instrument Provides Optimal Solution for Testing Metal Hydrides for Hydrogen Storage

The use of hydrogen as an energy source has become increasingly important in recent years as the calls to abandon fossil fuels grow. The inherent fluctuations of solar and wind energy have resulted in the search for an energy source with a constant, steady supply. Hydrogen energy has presented itself as a clean, renewable energy with prominent applications in the transportation industry. Hydrogen has a high energy per mass of fuel, but its low ambient temperature density corresponds to a low energy per unit volume. Therefore, developing advanced storage methods that have potential for higher energy density is required. The most popular way to store hydrogen is reversibly in a solid state sorbent material. This solid state sorbent can absorb hydrogen chemically – called chemisorption – or physically – called physisorption. Metal hydrides are a particularly versatile form of chemical hydrogen storage for their low pressure requirements, high gravimetric energy density, and reversibility. Understanding the structures and properties of metal hydride systems is crucial for uncovering their hydrogen storage capacities.

Metal hydrides are formed by the reactions between metal alloys and hydrogen at specific temperatures and pressures. Hydrogen absorption and desorption in metal hydrides are exothermic and endothermic reactions, respectively, and therefore thermal management is an integral part of adequate hydrogen storage. The sorption process is entropically unfavorable, so as temperature increases, the last term of the Gibbs Free Energy equation (below) dominates and can overwhelm the energetics of the system. This slows down hydrogen sorption and results in poor cycling kinetics.

$$\Delta G = \Delta H - T\Delta S$$

Gibbs Free Energy

The thermal conductivity of metal hydrides can be tested when they are in either powder or pressed pellet form; therefore, the optimal method varies. The Transient Plane Source (TPS) double-sided sensor is suited for rough and heterogeneous materials, making it an applicable choice for testing metal hydrides. The Transient Line Source (TLS) is ideal for testing granular materials and powders which makes it another effective method. Likewise, the Modified Transient Plane Source (MTPS) sensor has also proven to be useful when outfitted with the High-Pressure Cell (more details below).



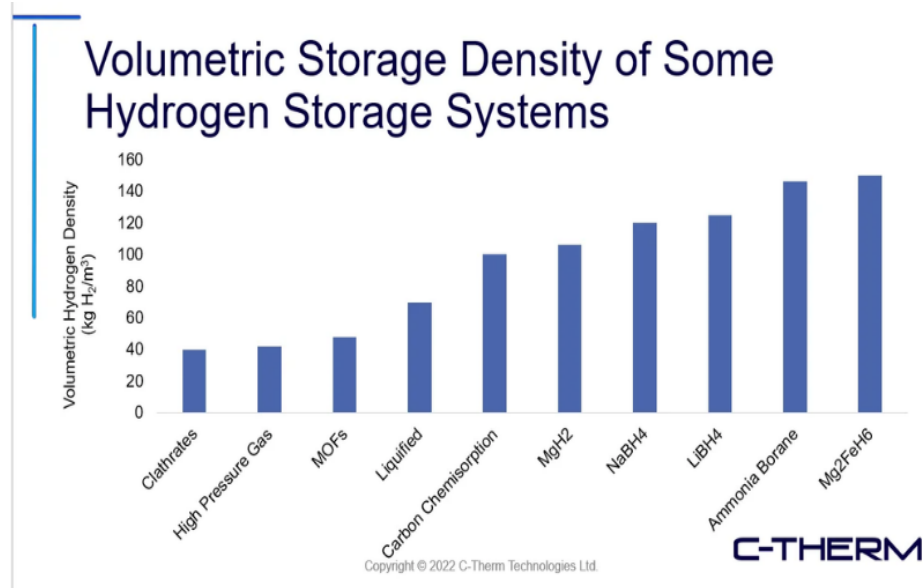
Hydrogen mobility is a growing hydrogen storage application. As the many components of hydrogen vehicles interact, maintaining good thermal management is crucial.



The Transient Plane Source (TPS) sensors are available in sizes of 6 mm, 13 mm, and 30 mm, which provides the user with maximum flexibility when testing samples.



The Transient Line Source (TLS) sensor is C-Therm's most robust sensor and can be outfitted with a pressure cell to test metal hydrides under representative conditions.



A graph showing the volumetric storage density of hydrogen in various storage systems; the solid metal hydrides consistently have high hydrogen densities



C-Therm's High-Pressure Cell for TPS - For measuring the thermal conductivity of metal hydrides as a function of pressure.



C-Therm's High-Pressure Cell for Transient Line Source method



The TLS Needle can also be fitted with a High-Pressure Cell to implement representative environments for metal hydrides.

How is Thermal Conductivity Used and Measured?

Thermal conductivity of metal hydrides is an important performance indicator. Van't Hoff's Law governs the equilibrium of metal hydride systems; it shows that if temperature climbs too high, the kinetics of the cycling will be slow. In contrast, the Arrhenius Equation shows how increasing temperature will increase the reaction rate. Therefore, there are a variety of concerns in terms of thermal management, especially for materials with high activation energy.

$$\ln P_{eq} = \frac{\Delta H}{RT} - \frac{\Delta S}{R}$$

Van't Hoff's Law

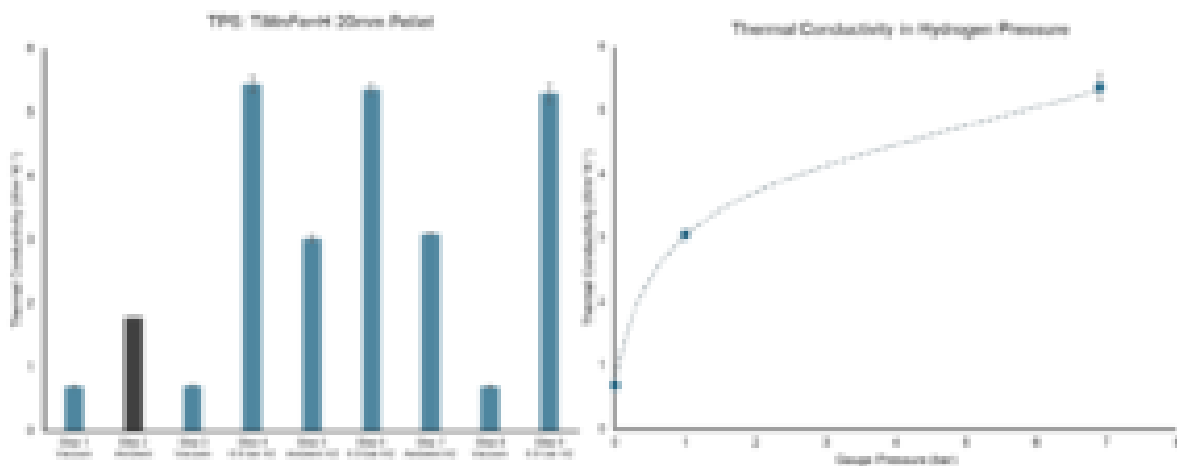
$$K = Ae^{-E_a/RT}$$

The Arrhenius Equation

Metal hydrides also pose unique safety considerations. Due to their reactivity, it's important to test them under inert atmospheres. This can be done by using an inert atmosphere glove box, or by using the High-Pressure Cell (HPC) accessory from C-Therm. The HPC allows for the sample to be isolated from air and therefore safe from combustion. It can safely characterize the thermal conductivity of samples under elevated pressure environments up to 2000 psi. Thermal conductivity also plays a role in determining the rate of hydrogen generation for some storage configurations. Since metal hydrides release hydrogen upon heating, it is important to understand the thermal characteristics of the hydrides and their housings to accurately characterize how much heat the hydride is absorbing.

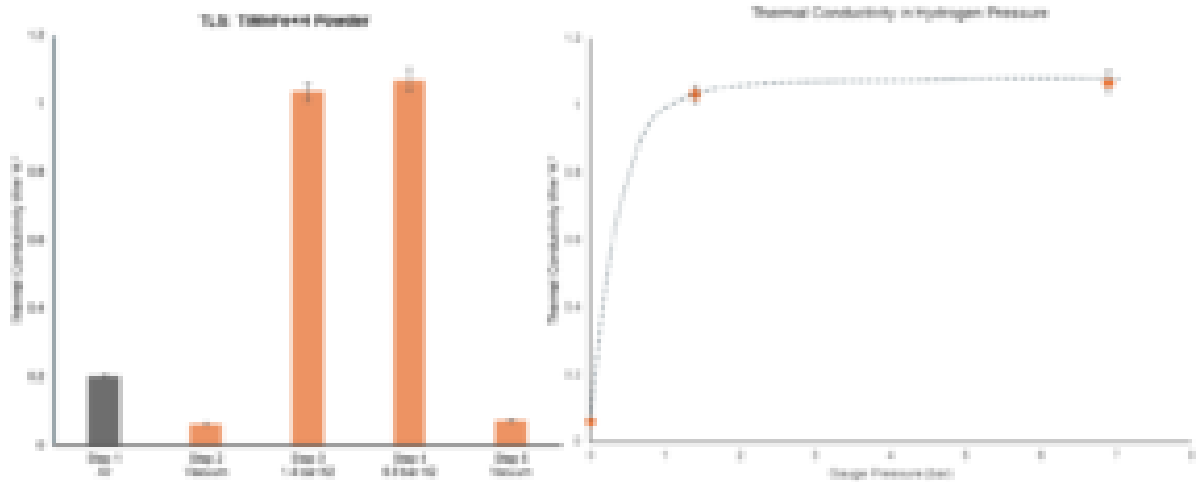
It is crucial to characterize the factors that influence the effective thermal conductivity of a metal hydride bed such that the heat and mass transfer structure of metal hydride hydrogen storage devices can be optimally designed. The FLEX TPS method has been used to measure the thermal conductivity of pelletized TiFeMn

hydride. The entire configuration, consisting of the sensor, a clamping device, and two identical pellet samples was placed inside the pressure vessel. The pellets' thermal conductivity was then measured under various conditions (room temperature, vacuum, air, and hydrogen pressure).



As seen in the figure above, after maintaining the vacuum (Step 1) for about 5 minutes, the TiFeMn pellets' thermal conductivity is measured to be 0.69 W/mK. When the ambient air is restored (Step 2), the thermal conductivity increases to 1.77 W/mK. Inducing the vacuum again (Step 3), the thermal conductivity is measured to be 0.70 W/mK. After applying 6.9 bar of hydrogen gas (Step 4), the thermal conductivity drastically increases to 5.44 W/mK. The hydrogen gas was vented, and the different atmospheric conditions were then repeated, and the measured thermal conductivities measured those previously measured.

Powder forms of the TiFeMn hydride samples were subject to similar experiments using the 50 mm TLS sensor. The powder was packed into a cylindrical container and placed into the pressure cell before the needle probe was inserted into the center of the sample. Thermal conductivity was measured under various atmospheric conditions and the results are shown below. It should be noted that between Steps 3 and 4 when an additional 5.5 bar of hydrogen pressure was applied, the thermal conductivity barely increased, indicating a saturation point in the hydrogenation of the hydride powder.



Trident's FLEX TPS and Needle TLS methods successfully characterized the thermal conductivities of the pelletized and powder TiFeMn hydride under different atmospheric conditions. Measuring the thermal conductivities of the metal hydride within expected high-pressure operating conditions is essential in improving the fundamental understanding of their heat transfer capabilities. C-Therm wishes to thank and acknowledge Dr. Jacques Huot for lending his expertise and use of facilities at the Institut de recherche sur l'hydrogène at the Université du Québec à Trois-Rivières (UQTR) during this project.

Metal hydrides can be characterized by various systems. The AB_5 system of metal hydrides are common for hydrogen storage where the A element often comes from the rare earth elements (like lanthanide) and B is a transition metal (typically Ni). These systems generally have poor gravimetric capacity but very good kinetics and relatively good volumetric capacity. Even in powder form, they tend to have a similar thermal conductivity to that of polymers. With the addition of binders or thermally conductive additives, they can become very conductive and be good for cycling. There are other categories of metal hydrides such as complex metal hydrides in the form of AB_4 , where A is an alkali metal and B is a boron family element. These

alloys tend to have very high volumetric and gravimetric storage capacities but poor kinetics. This is partly due to the high activation energy of hydrogenation and dehydrogenation and also due to their low densities which results in poor packing in powder form and therefore low thermal conductivity. Therefore, the biggest challenge for their application as a hydrogen storage medium is to resolve the issue of low thermal conductivity to enable efficient cycling and good thermal management. It can be seen from this persisting issue that thermal conductivity plays a key role in the research of thermal management for metal hydride systems. C-Therm is committed to catalyzing the research of metal hydride systems through innovative technology, expertise, and collaboration.