Dynamic Measurement of Hydrogen Storage/Release Properties Using Tapered Element Oscillating Microbalance for Mg Doped with Nano-sized Pd Catalyst

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Introduction

Hydrogen storage is one of the key enabling technologies for the advancement of hydrogen power systems, such as fuel cells, in transportation, stationary, and portable applications. For practical application, a reliable measurement of hydrogen absorption/release data is important for the proper design of hydrogen storage devices.

Three different techniques, i.e., volumetric method,[1] gravimetric method[2] and thermal desorption spectroscopy (TDS)[3], have been applied for studying the hydrogen storage/release in solids. The volumetric method measures the pressure drop owing to hydrogen absorption after applying a hydrogen pressure to the specimen contained in a constant volume. Similarly the pressure increase or gas blow off due to desorption can be measured. For volumetric measurement, one has an accumulation of the error. Furthermore, any leakage or temperature instability of the apparatus may give rise to large experimental errors. The gravimetric method measures the weight changes of the specimen due to absorption or desorption of hydrogen. However, data obtained by the gravimetric method are influenced by effects associated with flow patterns, bypassing, and aerodynamic factors such as buoyancy. Gas flow rate smaller than 100 ml/min is required for a reliable measurement.[4] Furthermore, this technique is not sensitive to the nature of gasses absorbed or desorbed since it is only based on weighing. At high temperature or high pressure, the mass resolution of the gravimetric apparatus is significantly reduced. In addition, the response time is 10 to 30 sec, which is not suitable for short duration and kinetics study. Thermal desorption spectroscopy (TDS) measures only the hydrogen desorption in high vacuum utilizing mass spectrometry.

In our laboratory, we are using a technique called tapered element oscillating microbalance (TEOM), where the solid sample is examined as a packed bed, through which the gas passes through. This technique circumvents most of the above problems associated with volumetric method, gravimetric method or TDS.

The main feature of the TEOM technique is an oscillating element that is based on inertial forces, instead of weight, to measure the amount adsorbed. Therefore, errors associated with leakage, flow patterns, bypassing, and aerodynamic factors can be eliminated. Mass resolution of TEOM is also not reduced at higher temperature and high pressure. Consequently, TEOM allows accurate and reproducible measurements. In addition, the fast response time up to 0.1 second makes the short-residence-time measurement and kinetic study possible and reliable. However, there is little literature report on the measurement of hydrogen absorption/release in metal hydride by TEOM.

In this paper, hydrogen storage/release properties of magnesium and palladium-doped magnesium were investigated by using the TEOM technique. The hydrogen storage/release data measured by TEOM were compared with those of measured by the volumetric method.

Experimental

An integrated flow system designed on the basis of a Rupprecht & Patashnick TEOM 1500 pulse mass analyzer (100-mg sample volume) was used for measurement of hydrogen storage and release properties. The active element of the TEOM consists of a tube constructed of a material having a special taper. A feedback system maintains the oscillation of the tapered tube. The natural frequency will change in relation to the mass in the tapered tube. The mass uptake is then determined by the change of the oscillating frequency. The mass uptake is then determined by the change of the oscillating frequency through equation 1.[5]

$$\Delta M = K_0\left(\frac{1}{f_1^2} - \frac{1}{f_0^2}\right) \qquad (1)$$

where ΔM is the weight change, K_0 is spring constant, f_0 is oscillation.

A simplified diagram of the oscillating element is shown in Figure 1. Gases are fed to the unit using Brooks mass flow controllers. The total pressure in the oscillating element is controlled by a backpressure controller. Quartz wool was used at the top and the bottom of the sample bed to keep the hydrogen storage materials firmly packed, which is essential for the stable measurement. Both the feed gas and purge gas was hydrogen and both the feed gas and purge gas flow rate was 100 ml/min. About 30 mg sample was used in the measurements. A detailed description of the TEOM apparatus is available in the literature.[5,6]

Samples used in this paper are magnesium (Aldrich, 99.8%, 325 mesh) and palladium nanoparticle-doped magnesium. The nanoparticle palladium-doped magnesium was prepared by an in-situ catalyst deposition method.[7] The hydrogen absorption was carried out at 573 K and 400 psi. The hydrogen release was measured at 613 K and ambient pressure.

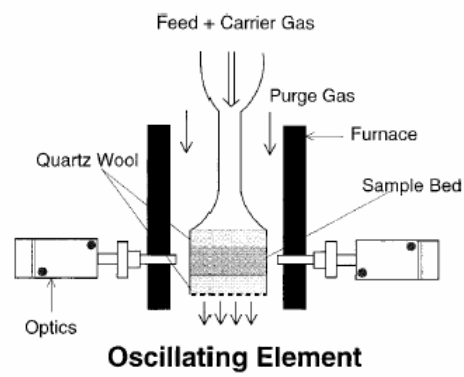

Figure 1. Simplified diagram of the oscillating tapered element with a sample bed.

Results and Discussions

1. Hydrogen absorption measurement

The hydrogen absorption performance of Pd-doped magnesium were measured by TEOM and compared with that measured by volumetric method in our previous study.[7] Figure 2 compares the hydrogen absorption properties of Pd-doped magnesium measured by TEOM and volumetric method at 573 K under 400 Psi. The hydrogen storage capacity measured by TEOM is almost the same as that measured by volumetric method, which indicates the accuracy of the two measurement methods. However, the hydrogen absorption rate measured by TEOM is faster than that measured by the volumetric method. When the hydrogen absorption is measured by volumetric method, the Pd-doped magnesium is sealed in a vessel with high pressure hydrogen gas. Therefore, the hydrogen storage is carried out

in static status and hydrogen concentration gradient exists in the adsorption bed, which results in the slow mass transfer in the absorption bed and slow hydrogen absorption rate. On the other hand, when the hydrogen absorption is measured by TEOM, a high flow rate forces hydrogen gas flow through the adsorption bed, which improves the mass transfer in the adsorption bed and accelerates the hydrogen absorption rate. Another important feature is that the response time for TEOM is very fast, as short as 0.1 second, whereas the response time for the volumetric method is very long. TEOM makes the fast measurement and kinetic study possible and reliable. Chen et al[6] also reported that TEOM provided more accurate data on the catalyst deactivation kinetics than the conventional microbalance.

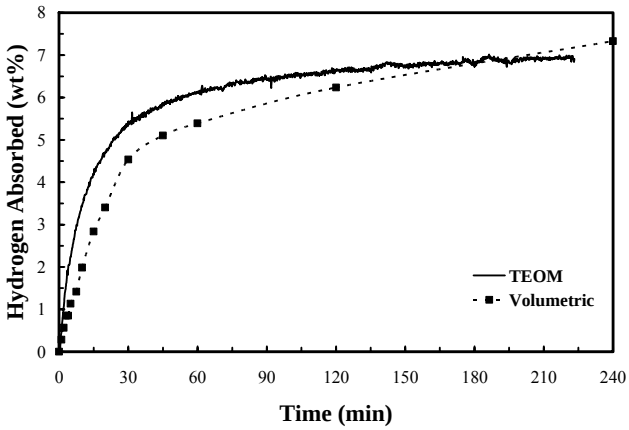

Figure 2. Comparison of hydrogen absorption properties of Pd-doped magnesium measured by TEOM and volumetric method at 573 K and under 400 Psi.

2. Hydrogen release measurement

The hydrogen release properties of Pd-doped magnesium were also measured by TEOM and compared with that measured by volumetric method in the previous study.[7] Figure 3 compares the hydrogen release properties of Pd-doped magnesium measured by TEOM and volumetric method at 613 K and atmosphere pressure. Similarly, the hydrogen release rate measured by TEOM is also faster than that measured by the volumetric method. Due to the elimination of hydrogen concentration gradient in the adsorption bed and the fast response time of TEOM, TEOM provides a more accurate and detailed information on the hydrogen absorption and release kinetic than the volumetric method or other gravimetric methods, which is important for the design of next generation high performance hydrogen storage materials and for the proper design of hydrogen storage devices in practical application.

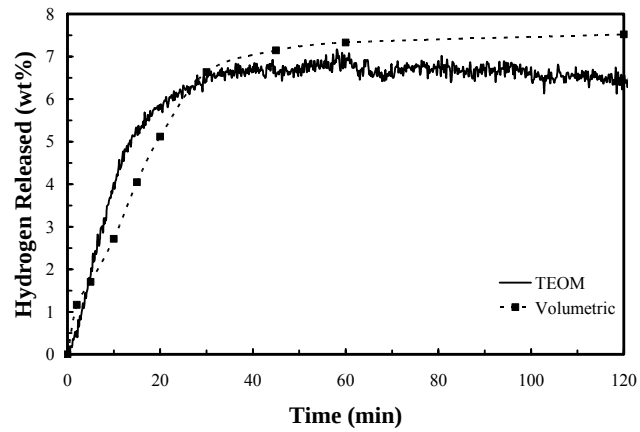

Figure 3. Comparison of hydrogen release properties of Pd-doped magnesium measured by TEOM and volumetric method at 613 K and under ambient pressure.

3. Effect of nano-sized Pd catalysts on hydrogen release

The effect of nanoparticle palladium catalysts on the hydrogen release properties of magnesium hydride was measured by TEOM at 613 K and under ambient pressure and the results are shown in Figure 4. Apparently, the rate of hydrogen release for palladium-doped magnesium hydride is much faster than that for the un-doped magnesium hydride, which is in consistent with that of measured by volumetric method.[7] While the Pd-doped magnesium readily releases hydrogen, the un-doped magnesium needs 5 minutes of incubation time before it releases hydrogen. At 10 minutes, the magnesium hydride and Pd-doped magnesium hydride releases 0.76 wt% and 4.03 wt% hydrogen, respectively. After 40 minutes of hydrogen release, Pd-doped magnesium hydride almost releases all the absorbed hydrogen and the un-doped magnesium hydride only releases about 50% of the absorbed hydrogen.

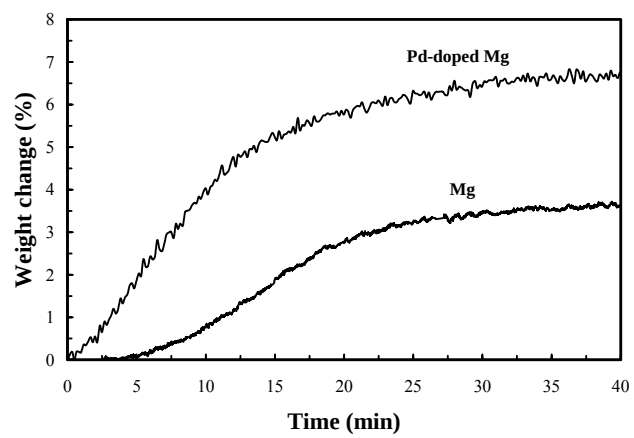

Figure 4. Effect of nanoparticle palladium catalysts on the hydrogen release properties of magnesium measured by TEOM at 613 K and under ambient pressure.

Conclusions

TEOM provides a dynamic, and more accurate information on the hydrogen absorption and release kinetics than the volumetric method or other gravimetric methods, which is important for the design of next-generation high-performance hydrogen storage materials and for the proper design of hydrogen storage devices in practical application.

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