Best Practices for the Characterization of Hydrogen Storage Materials

Preface

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1 Preface

1.1 Mission

The ultimate goal of the United States Department of Energy's Hydrogen Storage Program is the development of hydrogen storage materials that meet or exceed the DOE's targets for onboard hydrogen storage in a hydrogen-powered vehicle. The recent rapid expansion of research efforts in this field has brought the talents of a wide range of researchers to bear in solving the grand challenge of hydrogen storage. There is a need for common metrics and best practices for measuring the practical hydrogen storage properties of new materials that are being developed within the US DOE Hydrogen Storage Program as well as at an international level. A clear and comprehensive resource that will provide guidelines to common metrics and best practices in the measurements of hydrogen storage properties is critical to the success of the Hydrogen Storage Program.

1.1.1 Objective

The objective of this Best Practices for the Characterization of Hydrogen Storage Materials Project is to create a reference guide of common methodologies and protocols for measuring critical performance properties of advanced hydrogen storage materials. This document is designed to serve as a resource to the hydrogen storage materials development community to aid in clearly communicating the relevant performance properties of new materials as they are discovered and tested.

1.1.2 Benefit to the DOE

The benefit of this series of Best Practices reference guides to the DOE is to facilitate the transfer of knowledge and experience in making these critical measurements from some of the world's experts in this field to the entire DOE and world-wide hydrogen storage community. The short-term benefit will be to provide a clear knowledge base in the form of a published resource to aid those just entering this rapidly expanding field. The long-term benefit will be to create strong ties between government, university, and small and large business entities that will lead to more open communications and ideally the establishment of uniform measurement practices and reporting.

1.2 Definitions

1.2.1 Mechanisms

For all sorption mechanisms, the suffix -ate (sorbate) refers to the substance taken up while -ent (sorbent) refers to the sorbing substance. The suffix -tive (sorptive) refers to the sorbate substance in its natural state, i.e. the bulk gas state. The coupled terms are generally considered counterparts.[1]

1.2.1.1 Sorption and Desorption

Sorption is the non-specific term that describes both adsorption and absorption. It is most often used when it is difficult or impossible to differentiate between adsorption and absorption or when both processes occur simultaneously. Desorption is the inverse process of sorption. It is important to note that the sorption and desorption of the sorbate by the sorbent is a dynamic process.

1.2.1.2 Adsorption and Absorption

Adsorption is the enrichment or depletion of one or more components in an interfacial layer. Absorption occurs when the adsorbates are incorporated into the phase of the adsorbent. In absorption, the structure and/or the chemical nature of the absorbate and absorbent may be modified. It is important to keep in mind that adsorption and absorption refer to the location of the sorbed species with respect to the sorbent, i.e. surface or bulk respectively.

1.2.1.3 Chemisorption and Physisorption

Chemisorption, or chemical sorption, includes adsorption and absorption and occurs when the forces involved are valence forces of the same kind as those operating in the formation of chemical compounds. Physisorption, or physical sorption, is restricted to adsorption and occurs when the forces involved are weak intermolecular forces of the same kind as those responsible for the imperfection of real gases and the condensation of vapors. Weak intermolecular forces are also known as van der Waals forces. Physisorption does not involve a significant change in the electronic orbital patterns of the species involved; however no absolutely sharp distinction can be made between chemisorption and physisorption. It is useful to make a distinction between molecular physisorption, in which the H-H bond in the gas phase is preserved in the sorbed state, and chemical sorption, in which the H-H bond is broken during the sorption process. For more details on features useful in distinguishing between chemisorption and physisorption, the reader is encouraged to review Everett.[1]

1.2.1.4Spillover

Spillover involves the dissociation of hydrogen on a metal and subsequent transference, or spillover, to the metal's support via a chemical bridge. Spillover is highly dependent on the metal dissociator and the bridges linking the metal and the support. Typically graphitic or nano-structured carbon is used as support because of its high specific surface area.[2]

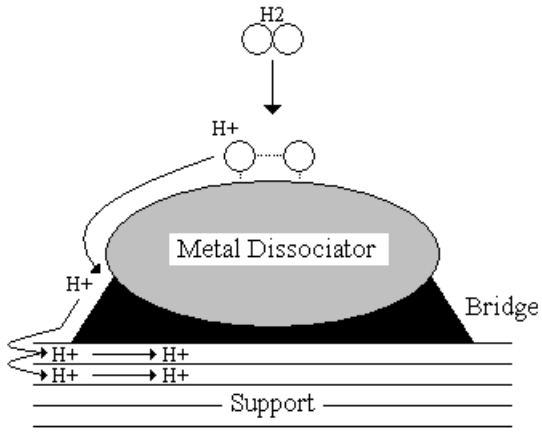

Figure 1. Diagram of spillover material structure.

1.2.2Materials

Materials for hydrogen storage can be divided into two families: traditional bulk or chemisorbed materials[3], which include hydriding alloys, complexes, ammonia-based compounds, and hydrocarbons and surface or physisorbed nano-structured materials[4] such as carbon fullerenes, nano-tubes and highly porous media like metal-organic frameworks and aerogel. The family tree in Figure 2 illustrates the relationships between different types of hydriding alloys and complexes.

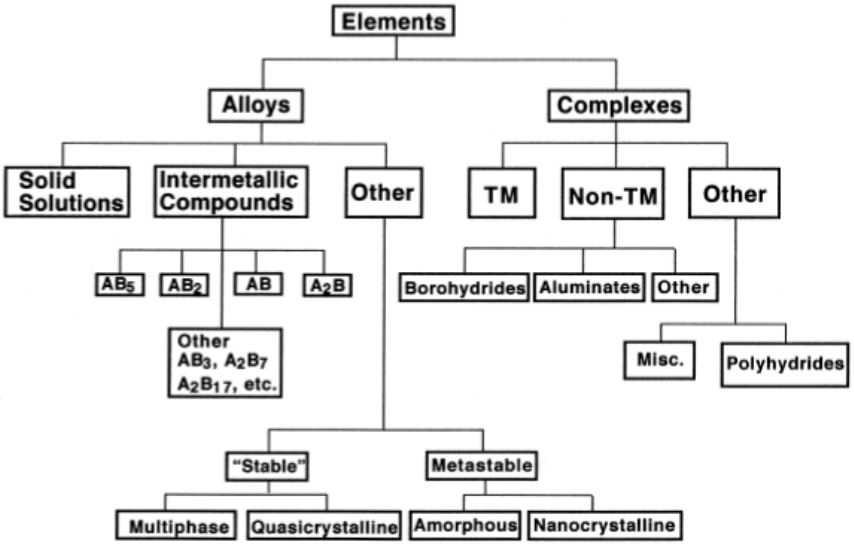

Figure 2. Family tree of hydriding alloys and complexes. [3]

1.2.2.1 Metal Hydrides

1.2.2.1.1 Solid Solutions

The host hydrogen storage materials may consist of a solid solution alloy. Th are characterized by varying composition and disordered substitution of one element for another on crystal lattice sites; they are formed by dissolving one or more minor elements into a primary element. Solid solutions based on Pd, Ti, Zr, Nb and V form hydrogen storage materials with some attractive features such as moderate reversible storage capacities near ambient conditions but cost and the heat released on hydrogen absorption deter the use of these materials for transportation applications. For example, $(V_{0.9}Ti_{0.1})_{0.95}Fe_{0.05}$ has a reversible storage capacity of $(\Delta wt.\%)_r = 1.8$ at T = 36°C and atmospheric pressure but costs but are relatively expensive for hydrogen storage.[3] Vanadium-based solid solutions (V-SS) are compared to other metal hydrides in Table 1.

1.2.2.1.2 Intermetallic Compounds

Intermetallic compounds (ICs) are characterized by homogenous composition and crystal structure. ICs for hydrogen storage combine a strong hydriding element A with a weak hydriding element B to create a compound with the desired intermediate thermodynamic affinities for hydrogen. Hydrogen absorbs atomically into the host metal lattice as a solid solution at low concentrations and via hydride-forming metal/hydrogen bonds at higher concentrations. The host intermetallic compound elements A and B are typically present in an integer or near-integer stoichiometric relationship. Element type A and/or B may be an ordered or disordered mixture of several metal elements. The total compositional variation has a strong impact on hydriding properties. This ability to form A_xB_y ICs containing up to 10 or more elements has been extensively studied and exploited in the commercialization of metal hydrides for hydrogen storage and Nickel-Metal Hydride battery applications. Common classifications of ICs for hydrogen storage are AB_5, AB_2, AB and A_2B; $LaNi_5$, $TiCr_2$, TiFe and Mg_2Ni being representative examples. Table 1 provides an overview of the relative attributes of these different classes of hydride forming Intermetallic compounds. This includes; versatility (meaning the ability to tune the alloy to operate over a wide range of pressures and temperatures) and PCT meaning the ability to reversibly provide hydrogen gas over a narrow range of pressures (relatively flat plateau pressure) at room temperature conditions.

Attribute	AB_5	AB_2	AB	A_2B	V–SS
Versatility	+	+	+	−/0	0
H-Capacity	0	0/+	0/+	+	+
PCT	+	+	+	−	+
Activation	+	0	−/0	0	0
Impurity effects	+	0	−	0	−/?
Cyclic stability	−/0/+	−/0/?	−/0	0/?	?
Ease of manufacture	+	0	+	0	?
Pyrophoricity	0	−	+	+	+/0
Cost	0	+	+	+	−/0

[a] Attribute key: − = problem; 0 = neutral; + = good; ? = uncertain.

Table 1. Qualitative overview of metal hydride types as to attributes.[3]

1.2.2.2 Hydride Complexes

Hydride complexes occur when combinations of ligands, metal ions and hydrogen form molecules. Hydride complexes are differentiated by whether they contain transition metals; those that do are called TM hydride complexes, those that do not are called non-TM hydride complexes. The difference between hydride complexes and ICs is that complexes release hydrogen through a series of decomposition and recombination reactions. Some combinations of elements, for example Mg and Fe, form hydride complexes but cannot form ICs; hydrogen is required for these two elements to form a stable compound (Mg_2FeH_6).

1.2.2.3 Nano-Structured Materials

Nano-structured materials have much higher surface area to volume ratios than bulk materials, enabling adsorption to play an important role. Nano-structuring of materials also improves reaction kinetics by increasing the diffusivity, reducing the reaction distance and increasing the reaction surface area. Metal hydrides and hydride complexes can be nano-structured by a variety of different processes including sputtering, pulsed laser deposition, and mechanical milling.

Nano-structured carbons, such as nanotubes, fullerenes and graphitic sheets are examples of nano-structured materials that have been extensively studied for hydrogen storage.

1.2.2.4 Porous Materials

Porous materials are being studied for use as hydrogen storage media due to their high surface area to volume ratio and the ability of hydrogen to adsorb to these internal and external surfaces. Although adsorption via physisorption is significant for porous media, absorption may also contribute to the overall hydrogen storage capacity of advanced materials. Examples of porous materials

being investigated for hydrogen storage are various forms of aerogels, clathrates and metal-organic frameworks (MOFs).

1.3 Summary

The intent of the preface has been to introduce terminology commonly used in hydrogen storage materials research and to provide an overview of the fundamental processes and measurement considerations. We hope that this information proves useful and ultimately contributes to progress in the research and development of new and better hydrogen storage materials.

1.4 Acknowledgements

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1.5 Disclaimer

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Summary of Document Structure

The Best Practices for the Characterization of Hydrogen Storage Materials series of documents is designed as an introduction to and overview of hydrogen storage materials, properties and measurements. Due to the breadth of the subjects covered, material will be presented in its most concise and accessible form. The authors will use examples from literature to add clarity to key topics and to provide the reader with avenues for further detailed inquiry into a specific subject. The Best Practices document is divided into an introductory section and will be followed by four or more chapters that cover the topic areas of: concentration and capacity, kinetics, thermodynamics and cycle life measurements of hydrogen storage materials as well as other important hydrogen storage materials properties.

This introductory section is intended to provide the reader with the basic information necessary for productive and accurate hydrogen storage measurements. Introductory topics include: 1) evaluating the experimental setup and procedures with respect to the ultimate purpose for making a set of measurements, 2) the relationships between direct and indirect (measureable vs. derived) quantities (which we will refer to as variables) used to describe hydrogen storage materials properties, and 3) an overview of common methods used to measure these hydrogen storage properties.

This introduction document will be followed by separate documents (chapters) covering the best practices associated with the measurement of concentration and capacity, kinetics, thermodynamics and cycle-life properties among others. These chapters will each include: a review of theory, an evaluation of the purpose of measurements for the selection of appropriate methods, and detailed experimental considerations that are of particular importance to each property being measured.

2 Introduction

2.1 Purpose of Measurements

For simplicity, hydrogen storage properties measurements can be broken down into three basic categories: storage system level performance measurements, materials development measurements, and fundamental science measurements. It is important to understand the purpose of a particular experimental investigation before making measurements because the experimental setup and procedures can vary greatly depending on the purpose of the measurements and results and conclusions can be misleading if they are not presented in the proper context. Of course, these categories overlap and support each other. Testing the design and performance of a storage system, comparing storage properties across new or improved materials, and gaining insight into the underlying phenomena of hydrogen storage require experimental apparatuses and procedures that may be significantly different. Care should be taken to match the experiment well to the purpose of the study to avoid misleading results.

2.1.1 Purpose: System Performance

System level measurements are concerned with the performance of materials at an operational scale. The primary difference between experimentation at the system level versus other levels is the importance of application-specific considerations. Depending on the utilization of the hydrogen storage system, any combination of properties may be most important for performance optimization. Properties such as energy density, reversibility and safety at standard operating conditions are some of the primary 'real world' considerations. For example, one consideration central to portable hydrogen storage systems like those envisioned for transportation is energy density because the system must be transported. Stationary applications, in contrast, may be more concerned with total energy than energy density.

To gain useful system performance information, enough material should be tested to provide results representative of the material's behavior in a full-sized operating storage system. In general, this means between 10 grams and 1 kilogram of storage material. The authors believe 100 grams is a good tradeoff between the practical issues of synthesis and handling of the materials and a characteristic, uninterrupted volume of material that would be found in a large-scale system.

An example of an experimental setup that may be appropriate at a system performance level but not for other purposes, is the use of flow meters to study rates of hydrogen uptake or release. This requires that the material performance has already been well characterized at a smaller scale. This is because, conventional thermal mass flow meters generally have fairly narrow dynamic measurement ranges (often less than one decade). Thus, some prior knowledge of the material's performance is needed to select flow meters with the appropriate flow range. This can be a severe limitation when a material's hydrogen sorption/desorption rates may vary over several orders of

magnitude depending on state of charge, temperature and pressure. An alternative is Coriolis flow meters, which have a robust dynamic measurement range, maintaining accuracy over several decades.

2.1.2Purpose: Materials Development

The purpose of experimentation at the analytical level (typically tens of milligrams to a few grams) is to pursue the development of advanced materials with desirable hydrogen storage properties. It is important to realize that hydrogen storage properties of a material can be strongly influenced by any number of individual sample characteristics including total chemical composition and distribution, microscopic and macroscopic structure, etc. In the realm of materials development, parametric and comparative studies are generally the best approach to producing reliable and productive studies. There is an extremely wide range of material characteristics (including such things as doping and nano-structuring) that can be modified and manipulated to produce a profound changes in hydrogen storage properties. For example, the effect of elemental substitution in the $LaNi_5$ family of Intermetallic compounds ($LaNi_{5-x}A_x$) is demonstrated in Figure 1.[1] In this case Ni has been substituted with tin or aluminum to form materials with decidedly different hydrogen storage properties, including changing the thermodynamic stability of the hydride that is formed.

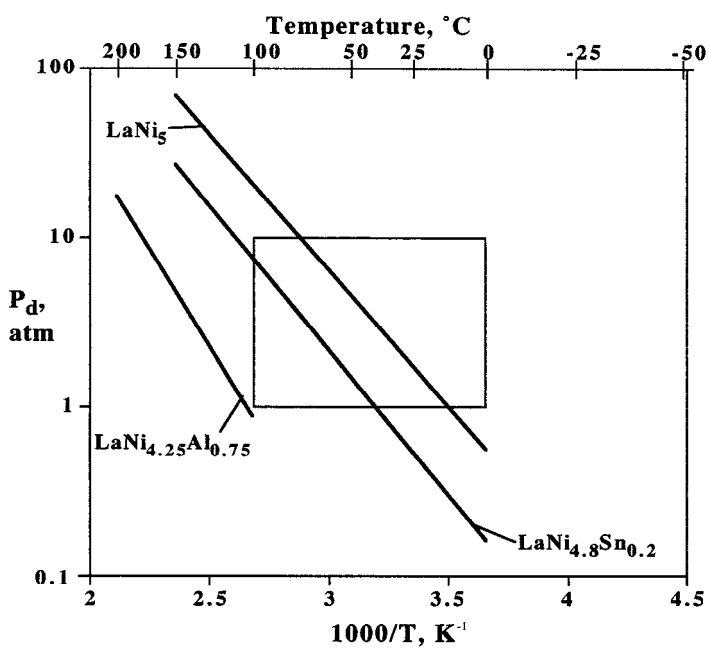

Figure 1. Van't Hoff diagram representing the hydriding thermodynamic properties of several different $LaNi_5$-based materials.[1]

In order to conduct instructive parametric studies, it is especially important that measurements are conducted under identical conditions (pressure, temperature, sample size etc.) using identical measuring equipment. This minimizes the number of free variables associated with the experiment and allows for the accurate determination of the effect of a specific material property. The effect of some material properties on

hydrogen storage can be quite small and easily masked by variation in testing conditions and measuring equipment if the proper precautions are not taken.

2.1.3 Purpose: Fundamental Science

As the title suggests, fundamental science research is concerned with identifying and understanding the physics and chemistry that governs a material's hydrogen storage properties. This fundamental knowledge can be used in research at the materials development and system performance levels. It may help to validate models that describe hydrogen-material interactions or aid in making enlightened decisions on new directions in improving materials. Without some level of fundamental understanding, system and materials development measurements would be conducted solely through intuition or pain-staking systematic studies. By using knowledge gained from fundamental science, researchers can eliminate much of the trial and error and more efficiently conduct measurements for material development.

2.2 Hydrogen Storage Properties

Measurements at all three of the levels investigation described above, probe similar hydrogen storage properties of both systems and materials. The relative importance of each property may depend on the application or the purpose of investigation. The following is a very brief summary of the principal measured properties of hydrogen storage materials and systems. Each property is investigated in more detail in the individual chapters of the Best Practices Documents.

2.2.1 Property: Capacity

Capacity is the maximum steady-state hydrogen content of a storage material. Capacity can have several different definitions that reflect the application or material considerations including reversible capacity, usable capacity and excess material capacity. These definitions in turn may depend on the material's stability, composition, temperature, pressure and number of cycles. Each of these variables has the potential to change the capacity of a material. Additionally, there is a very important distinction between concentration and capacity: capacity is a material property that does not vary at a set state (after an extended period of time). In this text, a material's capacity will be referred to as its maximum steady-state hydrogen content and concentration as its temporal hydrogen content. For a more detailed discussion of capacity definitions and theory, please see the chapter on concentration and capacity.

2.2.2 Property: Kinetics

Kinetics is the relationship between concentration and time in a storage material. Kinetics is a measure of the rate of hydrogen sorption or desorption of a material and may not be exclusively dependent on intrinsic material properties. Sample size, heat transfer effects and other parameters that are highly dependent on the experimental method can affect kinetic measurements and conclusions. Minimizing the effects of external influences on kinetics is very difficult and requires a great deal of knowledge and preparation. Thus, extreme caution should be used in ascribing measured kinetics

to fundamental sorption mechanisms or an intrinsic property of a given material. For a more detailed discussion of experimental considerations for kinetics, please see the chapter on kinetics.

2.2.3Property: Thermodynamics

The intrinsic thermodynamic properties of hydrogen storage materials influence a number of other parameters, most notably the capacity based on temperature and pressure. Unfortunately, the relationship between measured temperature and pressure conditions and intrinsic thermodynamic properties may be complicated by kinetics considerations. In many of today's materials, the temperature and pressure conditions required for hydrogen uptake and release are dictated by kinetic considerations, not necessarily the intrinsic thermodynamics of hydrogen bonding. The ability to distinguish between the two material properties is especially important because the techniques used to improve one property are often ineffective or not available for the other. For a more detailed discussion on the thermodynamics of hydrogen storage, please see the chapter on thermodynamics.

2.2.4Property: Cycle-Life

Cycle-life testing is restricted to reversible hydrogen storage materials such as metal and complex hydrides, amides and physisorbing materials. Materials that store hydrogen irreversibly (ie. not reversible under practical conditions), like chemical slurries of elemental hydrides (e.g. LiH, $NaBH_4$), cannot be cycled. Cycle-life measurements are typically performed to characterize the effect of cycling on capacity that stems from activation effects, grain growth, structural degradation or chemical degradation due to gas impurities. However, kinetics may also be impacted by cycling and some of the observed change in capacity may in fact be due to changing kinetics during cycling. For example, if measurement time intervals during a cycle-life experiment do not reflect the changing kinetic properties of the material, the measured capacity will not be representative of capacity at quasi-equilibrium. For a more detailed discussion of cycle-life considerations, please see the chapter on cycle-life.

2.3 Types of Measurement

With respect to characterizing a material's hydrogen storage performance there are two principal types of measurements, kinetics measurements and pressure-composition-temperature (PCT) measurements. Kinetics measurements can be considered the fundamental measurement of hydrogen storage because other types of measurement, including PCTs, are collections of several individual kinetics measurements. The relationship between kinetics and PCT measurements will be discussed further at the end of this chapter. Beyond these two main characterization measurements, there is a host of other measurement such as scanning temperature measurements that have value in rough screening for potential new hydrogen storage materials.

2.3.1 Measurement Type: Kinetics

Kinetics measurements track the rate of change of hydrogen concentration in a sample after the sample has been perturbed from quasi-equilibrium. Because hydrogen storage measurements can only approximate thermodynamic equilibrium due to their experimental nature, equilibrium will be used synonymously with quasi-equilibrium throughout the rest of this manuscript. Perturbation from equilibrium is accomplished by changing the thermodynamic state of the sample's environment, which causes the sample to sorb/desorb hydrogen in the attempt to restore equilibrium. For the gravimetric and volumetric methods, kinetics measurements are almost always conducted under isothermal conditions, with changes in pressure used to perturb equilibrium. This is done partly for compatibility with PCTs and partly because of the profound effect of temperature on the kinetic character of almost all materials. The profiles and interpretations of kinetics curves and the considerations for kinetics measurements are the subject of the kinetics chapter of the Best Practices Document.

It is instructive to introduce a few fundamental features common to almost all kinetics measurements. The degree of perturbation from equilibrium is the driving force behind sorption/desorption in hydrogen storage materials: large perturbations cause relatively large rates of change in concentration while smaller perturbations cause relatively small rates of change. The rate of change of hydrogen concentration in a sample is largest at the beginning of a kinetics measurement, when the sample is furthest from equilibrium with its environment. The distance from equilibrium diminishes as hydrogen is sorbed by the sample, slowing the sorption rate. This process continues until the sample reaches equilibrium with its environment and the hydrogen concentration remains constant indefinitely. These effects are illustrated in the sorption kinetics measurement in Figure 2. At the beginning of the experiment, the concentration changes quickly because the sample is furthest from equilibrium. As hydrogen is sorbed and time increases, the rate of change of concentration decreases until it becomes effectively zero, representing equilibrium.

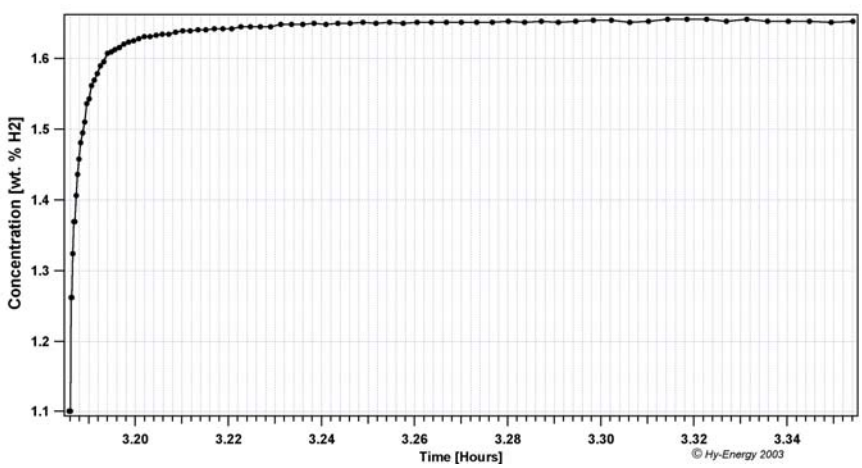

Figure 2. Representative kinetics measurement of a porous material.

2.3.2Measurement Type: Pressure-Composition Isotherm

Pressure-composition-temperature measurements (PCTs) are the most reported hydrogen storage measurement type in academic literature (composition in this context is synonymous with the concentration of hydrogen in a sample.). A PCT measurement is a collection of data points that represents the pressure, concentration and temperature of a sample in equilibrium and relates the influence of the thermodynamic variables on concentration. PCTs are also commonly referred to as PCI (Pressure-Composition Isotherms) because they are taken at isothermal conditions. This minimizes the number of free variables and allows the relationship between concentration and pressure to be presented via two-dimensional graphics. The effect of temperature on hydrogen storage properties can be determined by comparing PCT isotherms at various temperatures. Because PCTs represent a sample in equilibrium, they can also be used to determine the thermodynamic properties of a hydrogen storage material. Unfortunately, the absolute interpretation of PCT data must be kept in perspective because it is difficult to make true equilibrium measurements. For more information on thermodynamics as they relate to hydrogen storage properties, please review the thermodynamics chapter in the Best Practices Document.

It is instructive to conceptualize the relationship between PCT measurements and kinetics measurements as follows: a sample is perturbed from equilibrium by a change in the pressure of the system and is allowed to reach equilibrium through the dynamic process represented by a kinetics measurement. The last data point of each kinetics measurement, which most closely represents equilibrium, provides a single point of hydrogen concentration, pressure and temperature equilibrium. This process is performed repeatedly at one temperature until there are enough equilibrium data points are collected to construct a full PCT diagram. In this sense the PCT measurement can be thought of as a cumulative series of mini-kinetics measurements. In Figure 3, the volumetric method is used to conduct a series of small dose kinetics measurements to construct a PCT diagram of a porous material. In each kinetics measurement (separated by recharging the dosing volume which appears as discontinuities), the final pressure at the last data point represents the equilibrium pressure at a given concentration. In the volumetric method, the concentration is determined from the change in pressure with each dose (refer to the volumetric section for details). Therefore the equilibrium pressure of the sample corresponding to each equilibrium concentration point is also known and a full PCT can be constructed from the series of kinetics measurements.

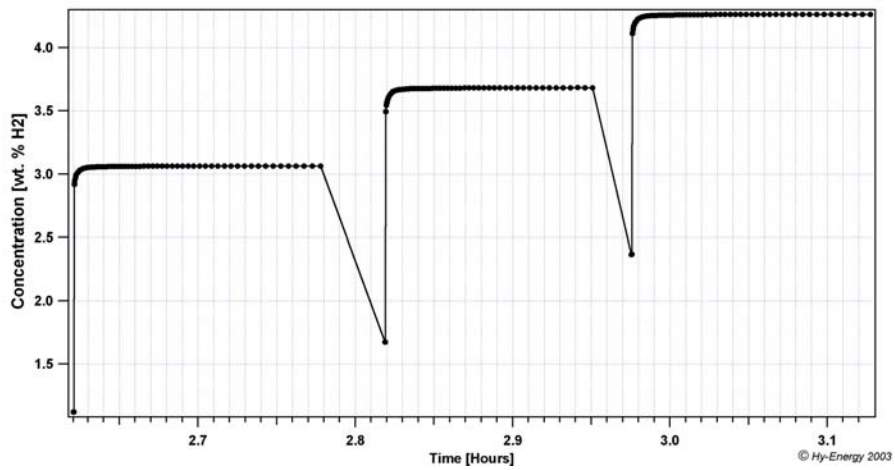

Figure 3. Representative measurement of a porous material. The last point in each 'row' of points is taken as representative of the equilibrium concentration of hydrogen in the sample at the pressure and temperature of experimentation.

This is shown in

Figure 4 where the Pressure / Time data is translated to Pressure / Concentration data to form a PCT diagram. The relationship between pressure drop due to absorption (rise on desorption) and concentration is depicted in Figure 5.

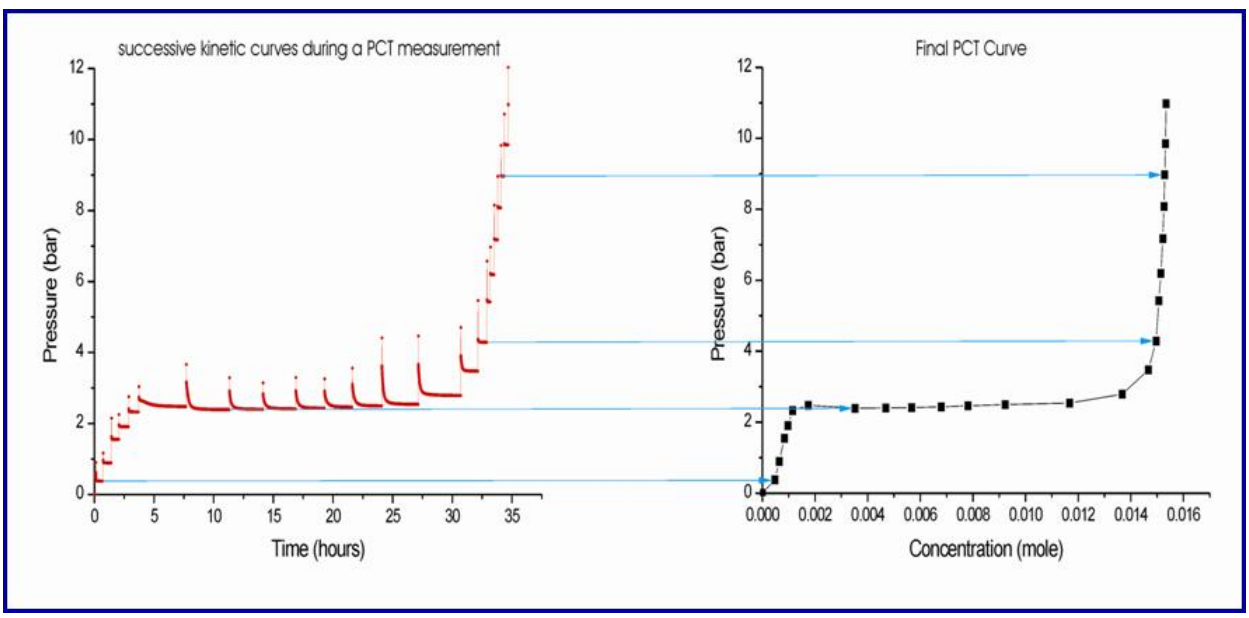

Figure 4. Representative pressure / time measurement and the resulting PCT plot of hydrogen absorption to form a metal hydride. The last point of each gas sorption dose provides the concentration of hydrogen in the sample at the equilibrium pressure and temperature of each dose.

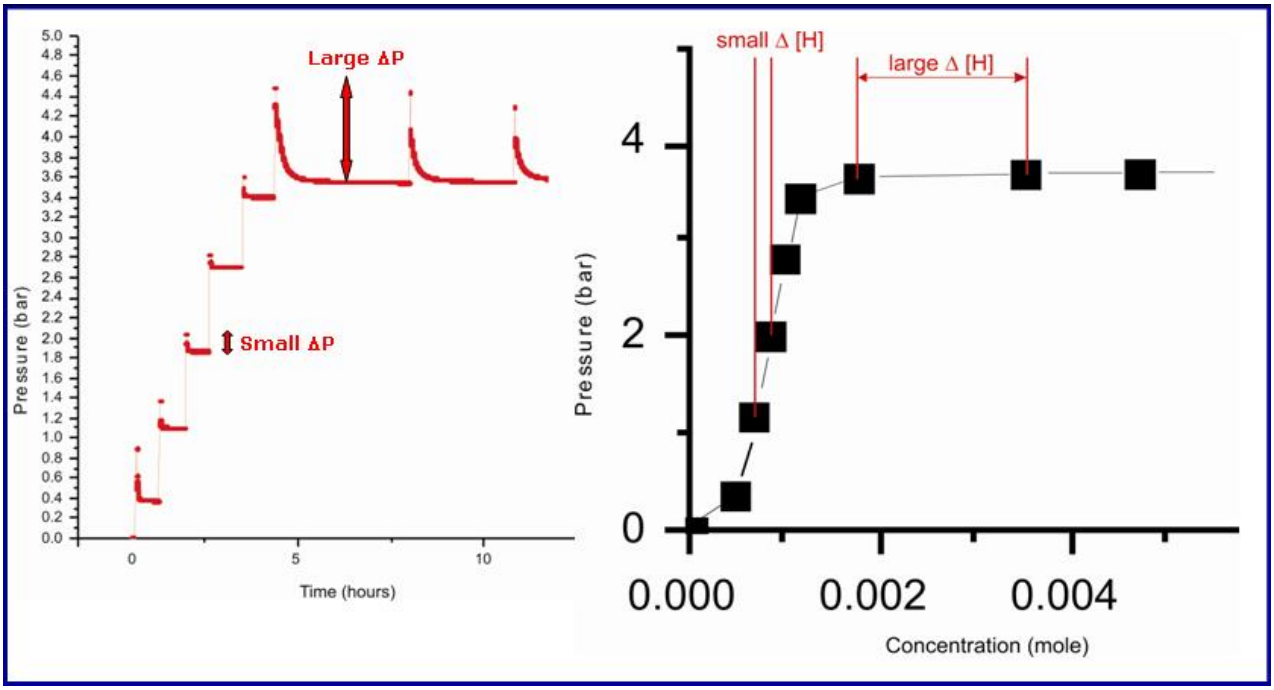

Figure 5. The relationship between pressure drop on absorption and the concentration associated with this pressure drop that is used to create each point on the equilibrium PCT diagram.

2.4 Hydrogen Storage Variables

Because the concentration of hydrogen in a sample is not measured directly; this important parameter necessarily relies on indirect determination from directly measured variables. Accurate measurement of direct variables is important for all hydrogen storage properties and perhaps more so for the determination of concentration than any other.

All storage properties are determined by the relationships between the variables: concentration, sample weight, temperature, pressure, cycle and time. The important distinction between direct (weight, temperature, pressure, time, cycle) and indirect (concentration) variables is made to differentiate between variables that can be measured directly from those that cannot. The last five (mass, temperature, pressure, cycle and time) are termed direct variables because they can be directly measured with traditional measuring devices such as balances, thermocouples and transducers. Concentration is considered an indirect variable because it cannot be directly measured and must be determined by correlating a direct (measurable) variable with concentration through the use of an empirical relation. Because of its dependence on measurable variables and its explicit ties to capacity, concentration will be addressed in detail in the Concentration and Capacity chapter.

The direct variables present problems in accurately collecting and interpreting data. Weight, temperature and pressure are difficult to accurately measure in all testing methods because errors can be introduced by testing equipment, sample holder design and secondary effects such as buoyancy. Errors associated with measuring the direct variables affect all property investigations and therefore the sources of these errors will be reviewed in the introductory chapter. Measurement errors specific to a particular testing method will be addressed in the appropriate methods section. In addition to this section on the direct variables, the effects of testing and variable collecting methods unique to a particular storage property (e.g. capacity, kinetics) will be addressed in the appropriate property chapters.

At this point, the reader is encouraged to briefly review the section on testing methods to become familiar with the nomenclature and general principles of each testing method. Material in the sections on variables and also static and dynamic measurements will refer to basic concepts associated with the measurement methods. Familiarity with the material in these sections will aid in gaining an overall understanding of the subject.

2.4.1Accuracy and Precision of Measurements

In measuring direct variables, it is important to understand the distinction between the accuracy and precision of testing equipment and convey pertinent accuracy and precision information to the reader. Accuracy is the degree of conformity of the measured variable to the actual value while precision is the degree of reproducibility of the measurement. A measurement can be accurate and precise, one or the other, or neither. An excellent and frequently used parallel to explain the relationship between accuracy and precision is the target analogy. The distance from the marks to the center of the target is the measure of accuracy and the size of the mark cluster is the precision. Figure 6 illustrates the possible combinations of accuracy and precision in the target analogy. As a thought exercise, consider the limiting cases of perfect accuracy and perfect precision. In the case of perfect accuracy, precision must also be perfect. The reverse however, is not necessarily true: perfect precision does not ensure perfect accuracy. These cases can be easily shown in the target analogy. The limiting case of perfect accuracy necessitates that all of the marks lay one on top of another at the center of the target; obviously this ensures perfect precision because the spacing between the marks is zero. Perfectly precise marks lay one on top of another but can be located anywhere on the target, hence perfect precision does not ensure perfect accuracy.

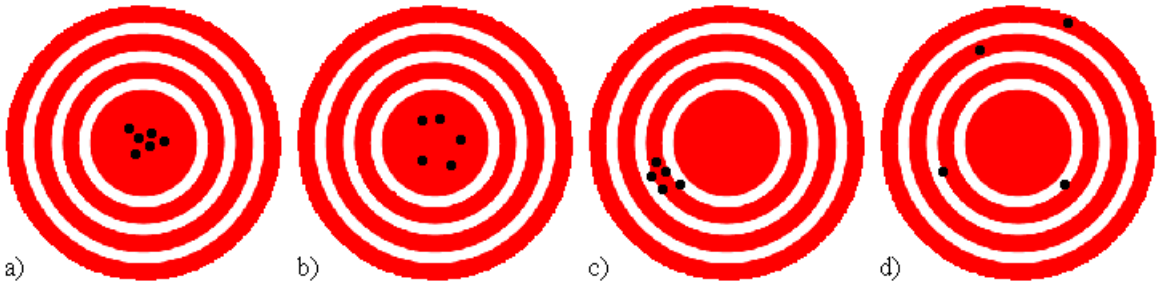

Figure 6. The target analogy for accuracy and precision. The proximity of the marks to the center of the target is the accuracy and the size of the mark luster is the precision. a) Accurate and precise, b) accurate but not precise, c) precise but not accurate, d) not accurate and not precise.

2.4.1.1Analog to Digital Conversion Error

The accuracy and precision of all direct variable measurements are influenced by analog to digital conversion effects. Traditional analog measuring devices such as thermocouples and pressure transducers output continuous signals that must be converted into discreet digital values. The analog to digital conversion process (ADC) has three principal sources or error: quantization, non-linearity and aperture error. Quantization error is caused by the finite resolution of converting a continuous analog signal to discreet digital values, non-linearity error is caused by physical imperfections in the conversion device itself (but can be mitigated by proper calibration) and aperture error arises from uncertainty in the ADC sampling rate. In addition to errors caused by ADC, measuring devices for some direct variables have unique considerations for accuracy and precision. These considerations will be reviewed in detail in the following variable sections.

2.4.1.2Error Bars in Data Representation

Error bars are used in experimental science to serve a number of important functions in relating the precision of an experimental measurement to the reader. An error bar indicates the range of one standard deviation of the measured variable and can be used to visually compare the precision of two measurements, determine whether differences are statistically significant and determine the statistical fit of experimental data to a given function. It is important to include error bars in graphics in literature when reporting hydrogen storage properties to both reflect the experimental nature of hydrogen storage testing and aid in comparing the performance of materials and the precision of testing methods.

Experimental data is often a collection of dependent variable measurements at a given independent variable value. The collection of measurements is presented as their mean value and standard error, which is based on the standard deviation of the collection. Standard error of a collection of measurements is determined by dividing the standard deviation of the collection by the square root of the number of measurements in the collection. Standard error is represented in mathematical form by Equation 1 (M is a vector of measurements with m entries):

$$SE = \frac{std(M)}{\sqrt{m}}$$ **Equation 1**

For example, a (24.30, 24.68, 25.73, 26.08) collection of molar specific volume (L/mol) measurements at standard temperature and pressure would be summarized as v = 25.2 +/- .38 L/mol and presented graphically as in Figure 7.

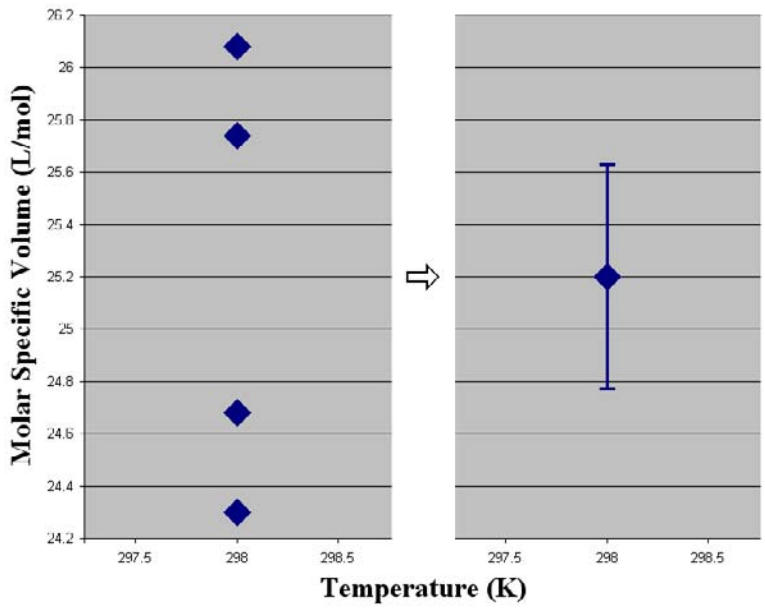

Figure 7. Graphical representation of collection of data points in mean/error bar format.

2.4.2Variable: Weight

The weight variable measured in the gravimetric method is often considered a direct measurement of concentration; unfortunately, this is not the case. The balance in the gravimetric method (used to measure sample weight) actually measures the resultant force of a number of discrete forces: the weight of the sample, the buoyancy force caused by the displaced gas and the forces associated with mechanical disturbances and fluid convection. The resultant force is often referred to as the *apparent* weight of the sample in order to differentiate between the measured weight and the actual weight of the sample. In order to determine the actual weight of the sample (from which concentration can be determined), it is necessary to account for and minimize the extraneous forces acting on the balance. The buoyancy force can be determined by an understanding of the skeletal density of the material while proper vibration damping can minimize mechanical forces. Forced and free convective forces are caused by pressure changes during charging/discharing and thermal gradients, respectively, and are transient in nature; patience is essential to minimize convective forces. Gravimetric measurements often use constant gas flow past the sample. In these cases, the flow drag forces must also be known and taken into account. Generally the flow drag force changes with the gas density, and therefore is a function of both temperature and pressure. Proper calibration of gas flow forces is necessary if the flow forces are significant in the particular apparatus or experimental arrangement.

In addition to the significant measurement considerations discussed above, the accuracy and precision of measuring weight depends on the type of balance used. A common weight-measuring system is an electronic strain gauge attached to a cantilever or balance (see gravimetric method section). The accuracy and precision of the strain gauge and cantilever/balance system are based on the properties of the strain gauge and the cantilever/balance material. The deflection varies with the modulus of elasticity of the material and the weight of the sample; a low modulus of elasticity leads to greater deflection and a more sensitive instrument but the instrument is more susceptible to noise due to external forces. The modulus of elasticity will vary with temperature and this must be taken into account when making measurements at different temperatures or when ramping temperatures. The sensitivity of the balance must be considered along with other trade-offs when choosing gravimetric instruments.

2.4.3Variable: Pressure

The pressure variable is intimately associated with hydrogen storage research and influences several important properties including concentration correlations, capacity and the kinetics of charging and discharging. Pressure is a commonly used measurable variable in concentration correlations and is therefore of practical interest to the measurement of all hydrogen storage properties. For example, the volumetric method measures changes in equilibrium pressure, along with volume and temperature information, to determine concentration. Changes in pressure are often used to control sorption/desorption reactions during both testing and practical operation. Isothermal measurements such as PCTs, one of the most common representations of capacity, use pressure variation to drive charging and discharging during storage property characterization. Pressure variation can also be used to control sorption and desorption in functioning storage systems, depending on the application. In fuel cell (FC) applications, hydrogen supplied at initially isothermal conditions (ambient) and elevated pressure is used to charge the storage system at the pump. The elevated pressure causes the reversible storage material to charge with hydrogen for future consumption by the fuel cell.

In addition to its obvious effect on reaction kinetics, pressure profoundly affects capacity measurements and practical capacities. Among the many capacity definitions are two based on thermodynamic considerations, reversible and usable capacity. Reversible capacity is of concern at the materials development level and is the measure of capacity available under feasible conditions. Reversible capacity is of particular importance to chemisorbing materials. Usable capacity is the capacity defined by the thermodynamic restrictions placed on the storage system by the environment and the end application. Once again, fuel cells present an excellent example of the importance of the thermodynamic variables on practical storage. The range of temperatures and pressures accessible to charge and discharge a storage system are restricted by availability; in classic PEMFC applications, this translates to operating temperatures from ambient to (~353K) and roughly ambient to a few bar pressures (assuming no external pressurizing or regulating equipment is used). It is highly probable that

maximum capacity of a given storage system does not occur within these limited ranges; therefore it is important to quantify usable capacity.

Electronic pressure transducers are the most common means of measuring pressure in hydrogen storage testing equipment. The accuracy limitations of transducers are generally described by two different types of error bands, those based on a percent of the actual reading (Capacitance Manometers) and those based on a percent of the full scale (Strain Gauge Transducers) (see Figure 8). For this reason, percent reading error bands are more accurate at low pressures while percent full-scale error bands may be more accurate at high pressures depending on the total error rating of the transducer. For hydrogen storage testing, particularly volumetric methods, the low-pressure range (0-15 bar) is often the most critical range for investigating storage properties. This makes the percent reading error bands the preferred error band for hydrogen storage.

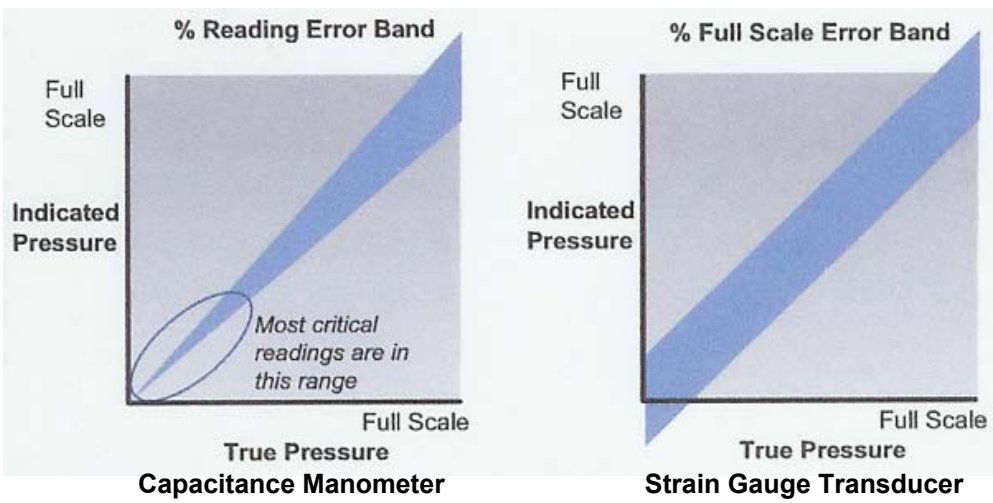

Figure 8. Depiction of the two types of error bands in pressure transducers.[2]

A simple calculation demonstrates the percent reading advantage at low pressures. Take two pressure transducers rated to 300 bar, one has a 1 % reading error band while the other has a 0.1 % full-scale error band; the 'break even' pressure for these two transducers is 30 bar. The percent reading transducer is more accurate for pressures below 30 bar, the range of pressures most often encountered in hydrogen storage experiments. For optimum accuracy, several percent reading transducers rated to different pressures should be used.

The sensitivity of pressure transducers requires that the pressure signal change from all other sources, DP_0, is minimized. It is conceivable to potentially account for these other pressure signal changes and correct the data for their influence, but in practice it is more fruitful to minimize erroneous DP_0 signals. Background pressure signal change can be caused by a number of factors including transducer sensitivity, zero drift, mis-calibration and hysteresis effects.

With a near instantaneous change in pressure, there may be some error introduced into the immediate response of the pressure transducer, especially with respect to pressure measurements made by measuring the strain or deflection of a gauge's diaphragm. There are a couple of 'tricks' that can help determine the true measurement signal from a pressure transducer. After the transient from gas introduction has decayed, the measurement signal becomes pseudo-differential in the sense that the current signal can be compared to the measurements that came before and will come after. The signal curve is expected to show a smooth behavior and therefore noise superimposed on the curve can be "reduced" through standard procedures such as smoothing. If the sample shows marginal sorption/desorption during the transient, the pressure vs. time curve contains both the calibration data and the sorption/desorption data. In other words, since very little absorption occurred during the transient, the transient can be ignored and the pressure reading at t = 0 is the pressure with "no absorption". Thus the ideal sample, ideal in the sense that it is easy to measure, would have no sorption/desorption signal until after the transient but would come to equilibrium before other longer-term error signals such as temperature fluctuations have a chance to impact the data.

2.4.4Variable: Temperature

Temperature is the second thermodynamic variable with important implications to hydrogen storage properties. It has many of the same hydrogen storage effects as pressure; it can be used to determine the binding energy of hydrogen in a sample (as in Differential Scanning Calorimetry), drive the sorption/desorption reactions in several testing methods and applications, and temperature influences a number of different definitions of capacity. To continue with the fuel cell example, temperature variation is the primary mechanism used to release hydrogen after initial charging because of the relatively limited pressures available due to FC structural considerations. Temperature affects practical capacity in much the same way as pressure. The two capacity definitions derived from thermodynamic considerations are based on temperature considerations as well as pressure considerations. Although, in hydrogen storage research, pressure and temperature are intimately linked, their measurements have their own, unique considerations.

Temperature-related measurement error is one of the most common errors associated with hydrogen storage measurements, particularly kinetics measurements. The accuracy of temperature measurements is typically limited to the accuracy of the thermocouples used and the heat transfer characteristics of the sample material and sample cell. Like pressure transducers, the accuracy of a thermocouple measurement depends on what type of thermocouple is used and the temperature regime of the measurement. Some thermocouple types have a wide temperature range but are less accurate compared to those with limited temperature ranges. Because most hydrogen storage experiments are conducted under isothermal conditions, the authors advise the use of limited-range durable thermocouples that offer greater accuracy in measurement.

An important consideration is that thermocouples of all types generally present nearly the same voltage at room temperature. It is only at elevated temperatures that the

deviation in the type (J, K, N for example) will become apparent. As most modern temperature measuring devices offer many thermocouple options, it is important not only to validate the devices thermocouple type settings but also to validate by using separate secondary temperature measuring devices and to run calibrations on measurement devices on a regular basis.

Heat transfer between the sample material, sample cell and thermocouple is one of the primary sources of error in hydrogen storage measurements.[3] Sorption and desorption reactions can be highly exothermic and endothermic and the energy loads must be transported efficiently to maintain isothermal conditions during testing. Insufficient heat transfer can lead to pockets of sample at higher temperature than the temperature read by the thermocouple, effectively invalidating the isothermal assumption and conclusions based on that assumption. Thermocouples that are not in intimate contact with the sample, or perhaps not even in contact with the sample holder, can produce very large in-accuracies with respect to the actual sample temperature. On a system level where kilograms of storage material may be used, excellent heat transfer characteristics are required to supply and dissipate the significant amounts of energy necessary to charge and discharge a sample. The importance of heat transfer considerations will be discussed on several occasions throughout the course of the Best Practices Document.

2.4.5Variable: Cycle

The desire for reusable hydrogen storage systems necessitates the ability to charge and discharge (cycle) repeatedly without loss of performance. Nearly all storage properties, particularly capacity and kinetics, vary with cycling and the variation can have a profound impact on system efficacy. Cycling phenomena include capacity activation effects and poisoning (capacity) and retardation (kinetics) due to the gettering of impurities during cycling.

Some important considerations for the cycle variable are primarily aimed at minimizing activation and gas stream impurity effects on measurements and are not testing method-specific. For activation effects for both capacity and kinetics, the authors advise cycling the sample at least ten times in order to measure the intrinsic properties of the material. It is also critical to evaluate the effects of poisoning and retardation on performance, especially in metal hydrides; for practical application, storage systems will commonly be charged with hydrogen gas that contains impurities like CO_2, H_2O and NH_3. The impurities adsorb to the material, occluding catalytic sites and diffusion pathways, and can be difficult to desorb because of their high thermodynamic affinity. As cycling increases with impure hydrogen gas, the impurities build to levels that poison capacity and retard kinetics.[4] Therefore, it is important to develop materials that can withstand the effects of gas stream impurities in order to avoid performance deterioration.

Several other phenomena occur when cycling a hydrogen storage material. In intermetallic compounds, decrepitation, self-pulverization due to shear stresses caused by lattice expansion upon hydriding, and disproportionation[5], dissociation of a compound into its fundamental components during repeated cycling (e.g.

$LaNi_5 + \quad {}_2Mg_{17} \rightarrow 3 \quad + 5 \quad {}_2 \quad + 7 \quad$), cause variation in storage properties and system performance. Decrepitation and disproportionation are generally considered activation phenomena and initial cycling mitigates their effects.

2.4.6Variable: Time

The effect of time on hydrogen storage measurements is manifested by the rate at which measurements are taken. However, some confusion surrounds how measurement rates affect data representation. Measurement data is collected in two distinct steps: the data acquisition hardware converts the continuous analog output from the measuring device (e.g. thermocouple, pressure transducer) to a digital value at a certain rate R_1 and the computer software samples the digital value from the data acquisition hardware at another rate R_2.

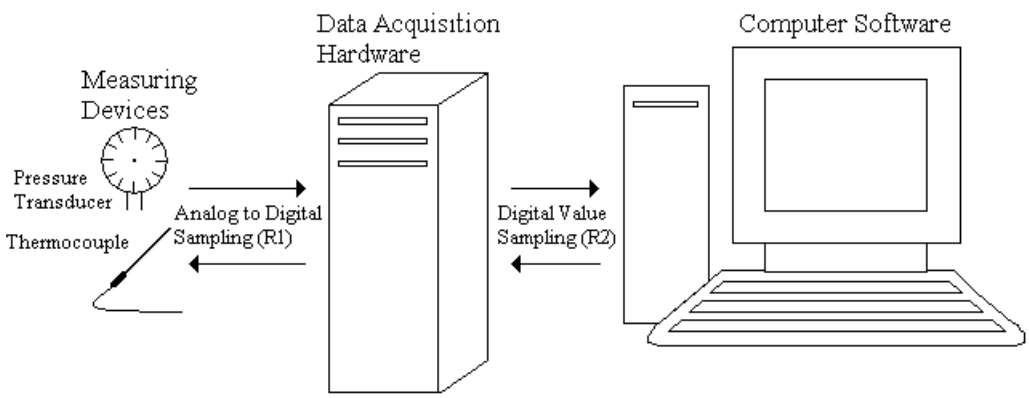

Figure 9. Schematic of a typical hardware/software set-up and the flow of information in a hydrogen storage testing system.

As Figure 9 illustrates, information is exchanged between two interfaces but not necessarily at the same rate. The sampling rate of the data acquisition hardware can be faster or slower than the sampling rate of the computer software. The difference between the rates may lead to the collection of multiple data points at the same value of the measured parameter and/or a step-wise rather than continuous change in the measured parameter. Both of these effects are most pronounced at small time steps that approach the limits of the sampling rates and are an artifact of data collection. The average results of the measured parameters are still representative of the homogeneous change in the properties being measured.

Figure 10 illustrates a number of data collection artifacts. At the beginning of the experiment, the R_2 sampling rate of the computer software is faster than the analog to digital conversion rate R_1 of the data acquisition hardware. Therefore, the computer software samples the data acquisition hardware several times before the hardware updates. This leads to several consecutive data points collected at the same pressure, an artifact that disappears as the R_2 sampling rate decreases (by design) below the data conversion rate R_1 as the experiment progress. The step-wise rather than continuous change in the data at the beginning of the experiment is caused by the

difference between the sampling rates and the initial gradient in the measured parameter. Figure 10 shows the measured pressure directly after the sample is dosed with hydrogen; the pressure gradient is initially large but slowly levels off as the sample approaches equilibrium. This is reflected in the data as the pressure step size becomes less and less and the data eventually appears continuous. These kinds of data artifacts do not affect the overall accuracy of the measurement and the conclusions that can be drawn, but may be missinterpreted when first observed.

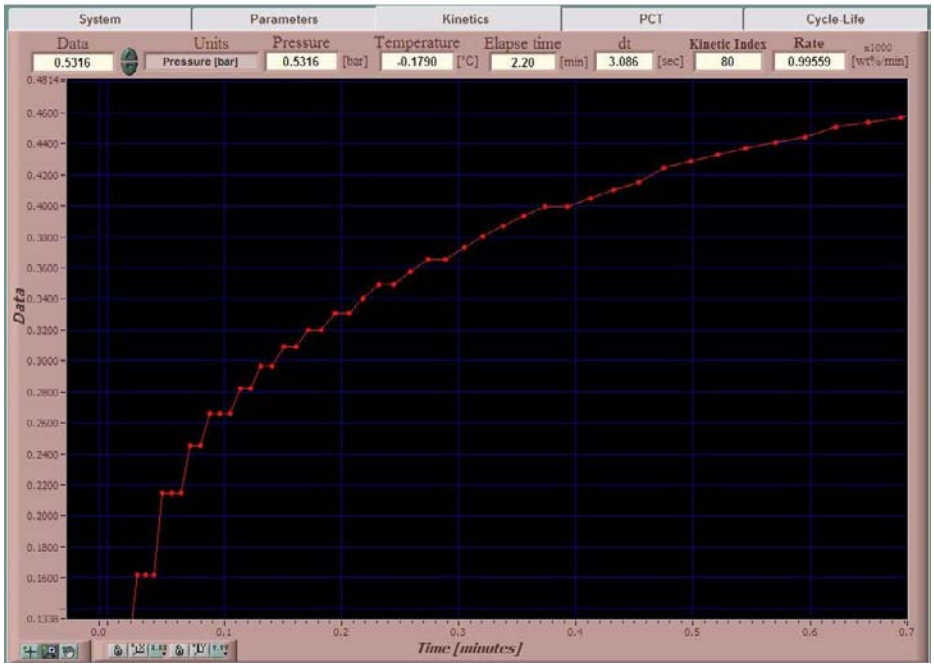

Figure 10. Example of constant and step data collection artifacts. The ordinate is measured pressure.[6]

2.5 Static and Dynamic Measurements

Hydrogen storage testing can be divided into static and dynamic testing based on whether or not the sorption/desorption reaction is allowed to reach equilibrium at any point during the experiment. In volumetric and gravimetric methods for example, hydrogen gas can be introduced or removed either by aliquots (static) or through a variable flow or pressure regulator (dynamic). In thermally driven methods such as TPD and TGA, the temperature of the sample can be raised in steps (static) or continuously (dynamic).

In static testing, a sample in equilibrium at a certain temperature, pressure and composition is perturbed by a sudden change in pressure (volumetric and gravimetric methods) or temperature (TPD and TGA). The sample is allowed to reach equilibrium at some new temperature, pressure and composition before it is perturbed again. This process continues until the sample is fully sorbed or desorbed. This step-by-step, or

equilibrium state-by-equilibrium state process allows static testing to be used to determine the thermodynamic properties of a material by van't Hoff diagram analysis. Static testing is the most frequently reported testing method in literature when using volumetric and gravimetric methods.

Dynamic measurements are characterized by continuous changes in pressure and temperature and do not allow for equilibrium. Although they are not ideal for investigating purely thermodynamic properties, they can provide information on the kinetic activity of a material. When hydrogen flows at a constant rate into an evacuated hydrogen storage system, the pressure in the system increases linearly until the material begins to sorb. After this point, the pressure in the system is a function of the material's ability to sorb hydrogen; if the system is to remain at constant pressure across the pressure plateau in Figure 11, the rate of hydrogen flowing into the system must be equal to the rate of hydrogen sorbed by the material.

Dynamic measurements are more useful for evaluating a material's hydrogen storage performance during application than static measurements. For example, fuel cells require hydrogen at a specified constant pressure to operate efficiently and safely. In order to supply hydrogen at constant pressure, a regulator is connected between the FC and the hydrogen storage system through which the flow rate varies. Dynamic measurements allow testing of storage materials at flow rates representative of the flow through the pressure regulator in the fuel cell/storage system and the dynamic pressure limits associated with such flow rates. These results are highly dependent on the impact of heat transfer on sorption/desorption kinetics.

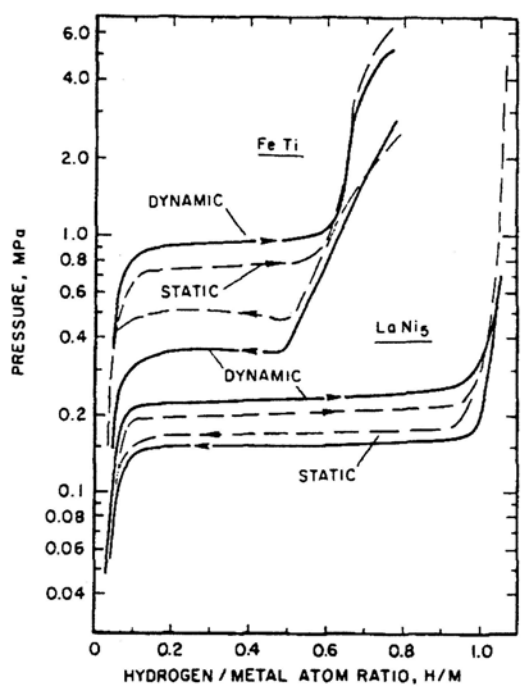

Figure 11. Comparison of static and dynamic pressure-composition isotherms for $LaNi_5$ and FeTi at 298K. Results are after about 200 test cycles.[7]

2.5.1dC and dP Dosing Methods

In isothermal testing, the sample is charged and discharged by changes in hydrogen pressure in the sample holder. Hydrogen can be added step-by-step in aliquots or continuously through flow or pressure regulators. These techniques are used to provide static and dynamic methods of storage testing. Static and dynamic dosing can also be referred to as dC (differential concentration) and dP (differential pressure) dosing, respectively. In dC dosing, a specific amount of hydrogen calculated from the temperature, pressure and volume of the aliquot is dosed to the sample. In dP dosing, a flow or pressure regulator is used to increase the pressure in the sample holder a specific amount per dose. The terms dC and dP originate from the relationship between the different types of dosing and PCTs; dC dosing steps along the PCT concentration axis and dP dosing steps along the PCT pressure axis.

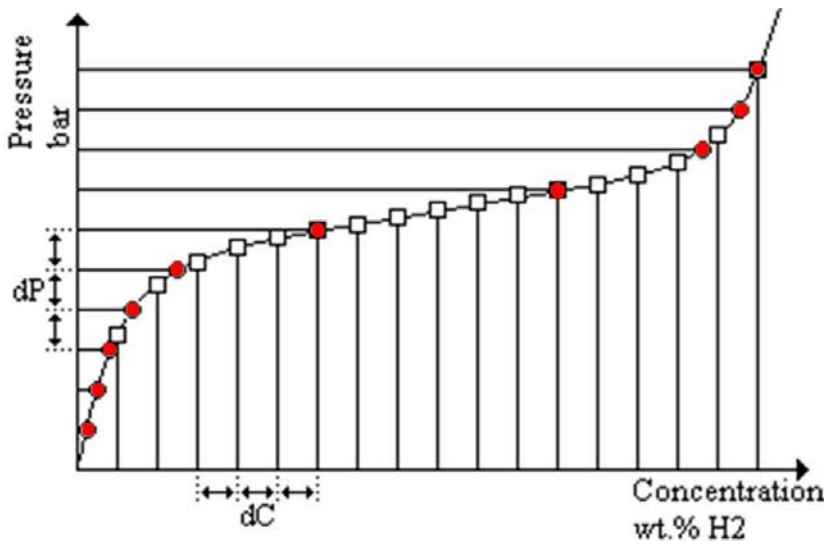

Figure 12. PCT of classic metal hydride material with plateau. dC (squares) and dP (red circles) dosing provide different information in solid solution (vertical) versus hydride formation (horizontal) portions of the PCT phase diagram.

Figure 12 shows the relationship between dC and dP dosing and PCTs for a metal hydride. dC dosing (squares) enables limited investigation of the solid solution phases, represented by the regimes with greater slope at low and high concentrations, compared to dP dosing (circles). However, the reverse is true for the investigation of transitional regimes at intermediate concentrations. dC dosing can provide much greater information across plateaus in metal hydrides and the saturation regimes of physisorbing materials. A common complaint in hydrogen storage testing is incomplete or uninformative investigation of metal hydride plateau regimes due to dP testing. In some cases where the plateau slope is very small, the plateau may be missed altogether.

An advantage of the dC stepping of the volumetric method is that samples can be prepared to specific hydrogen concentrations. This may be very useful for ex-situ examination of the materials using other analytical techniques.

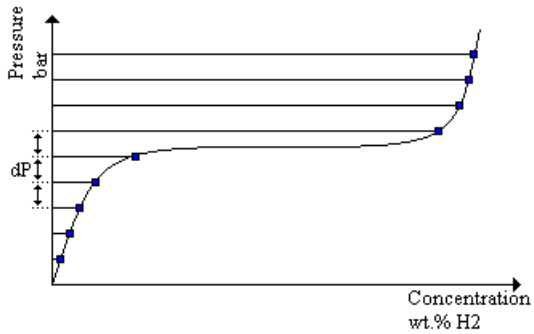

Figure 13. Example of PCT with missing plateau information due to inherent limitation in dP dosing.

2.6 Methods of Measurement

There are a number of measurement methods that can be used to investigate hydrogen storage materials and systems. Gravimetric and volumetric methods are the two primary methods and the most robust in terms of depth of analysis; temperature-programmed desorption, differential scanning calorimetry, and thermal gravimetric analysis are also used. All measurement methods quantify a change in a measurable property to indirectly calculate the hydrogen storage capacity of a material. It is important to keep in mind that all methods indirectly calculate hydrogen concentration and each have complications associated with indirect methods. For example, characterizing the hydrogen storage capacity of highly porous media has proven difficult using gravimetric and volumetric methods because both require an understanding of the amount of gas displaced, calculated from the skeletal density of the material, and the corresponding buoyancy (gravimetric) and volume calibration (volumetric) effects on measurements.

This section will summarize each method and give techniques for measuring hydrogen storage variables. Errors and considerations associated with measuring variables with the different summarized methods will be addressed as well.

2.6.1.1Consideration: Gas Composition

All testing methods (with the possible exception of TPD spectroscopy) rely on the assumption that the change in the direct variable used for correlation during desorption is due to hydrogen gas alone. Unfortunately, this assumption is not always valid. During desorption, it is possible to evolve gases other than hydrogen by chemical reaction of the sample material itself. These evolved gases can affect pressure and weight measurements and can contaminate experimental data.

Unless the gas evolution properties of the material are well established, for many materials it may be highly incorrect to assume that the change in the [directly measured] correlation variable, such as weight or equilibrium pressure, is due entirely to hydrogen. In particular, this can produce seriously misleading results in making hydrogen storage measurements during desorption. In addition, impurities (water, oxygen…) in the hydrogen gas stream used to charge a sample may be gettered out of the hydrogen, causing a significant weight change that may be misinterpreted as hydrogen absorption. In terms of hydrogen absorption capacity measurement this contaminated gas problem is much more significant for gravimetric measurements than volumetric measurements because of the ratio of the quantity of gas to sample size and the fact that sample weight change is being equated to hydrogen content. In volumetric measurements the pressure change due to sorption of ppm level impurities would be minimal, if even measureable. Whenever possible we recommend using a secondary technique, such as mass spectrometry, to validate weight loss or gain measurements in gravimetric systems. Volumetric measurements should likewise be tested for evolution of gases other than H2 which can lead to capacity loss or possibly decreased kinetics with cycling (e.g. Nitrogen loss in amides) or detrimentally affect fuel cell catalysts (evolution of ammonia from amides).

One way to account for non-hydrogen gases is to use a mass spectrometer to determine the composition of the desorbed gas. The mass spectrometer is connected to the outlet line of the sample holder and tests a representative sample of the evolved gas, outputting the relative composition of the individual species via their partial pressures. One caveat when using mass spectrometers is the production of a virtual H_2O signal. Water and air are often present in the background spectrum, especially in the absence of a complete bake-out of the experimental equipment. However, depending on the state of the mass spectrometer being used, the filament itself can be partially oxidized and when testing H_2 for impurities, the H_2 can reduce the filament to create water. Although the mass spectrometer registers the water, it may not necessarily be coming from the material.

In some alanate-amide mixtures, the gas evolved from a sample during desorption is not entirely hydrogen. Trace amounts of ammonia can be found as well, as shown in Figure 14.

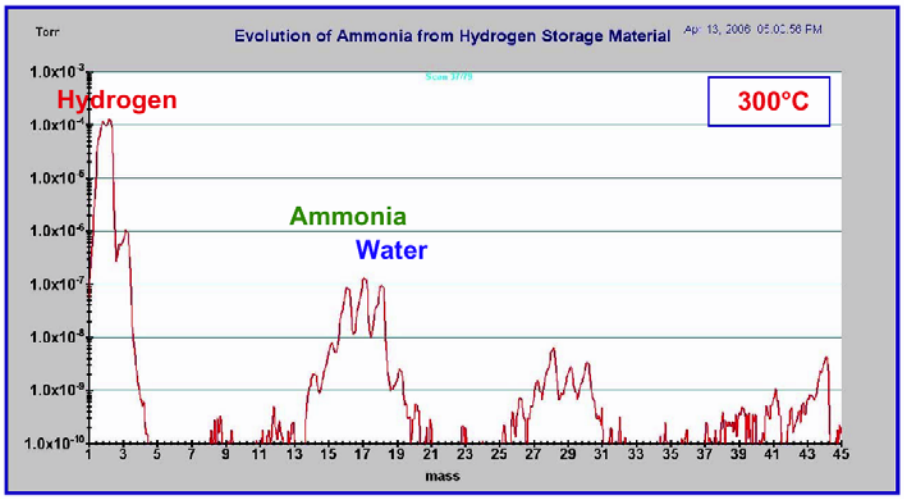

Figure 14. Residual gas analysis of alanate-amide sample discussed in the Kinetics section.[2]

Water is a common background contaminant, but is also found as a contaminant of hydrogen storage materials, generally due to adsorption from air due to improper sample handling prior to testing. The presence of ammonia is much more interesting in this case. Under elevated temperature, the alanate-amide mixture reacted to measureable amounts of ammonia as well as hydrogen, although the exact mechanism for the reaction is unclear. This type of unexpected gas evolution points to the critical need to apply other analysis to validate the gas composition assumption inherent in the testing methods. Simultaneous measurement of gas composition and (inferred) concentration is highly preferred until it can be assured that co-evolution of other species does not occur from the particular material.

2.6.2Volumetric Method[8] [9]

The volumetric method of hydrogen storage measurement, also known as the manometric method, or as Sieverts method in honor of the German chemist of the same name, uses temperature-pressure-volume correlations to determine hydrogen concentration and the storage properties of a material. A generalized volumetric systems with commonly employed components is shown in Figure 15.

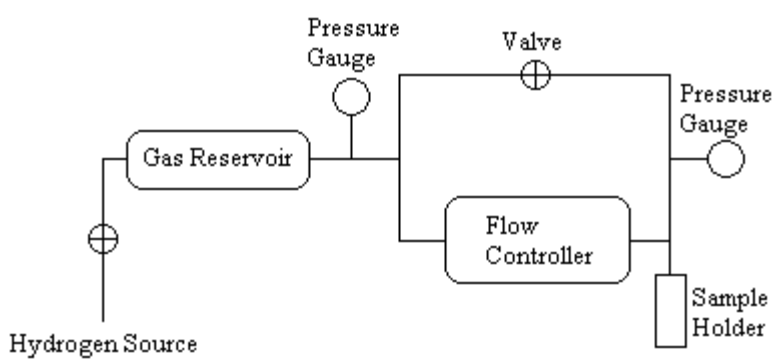

Figure 15. Multipurpose Gas Sorption/Desorption Apparatus. The pressure gauge on the right is only required when using the flow controller.

The apparatus consists of a gas reservoir connected to a specimen reactor. Because the volumetric method measures concentration indirectly through temperature-pressure-volume correlations, the volumes and temperatures of the reservoirs and sample holder (system) must be known in advance. The system volumes are carefully pre-calibrated, and the reservoir and sample holder are maintained at constant (but not necessarily equal) temperatures using an external temperature controller. By fixing volume and temperature, reservoir and sample holder pressures can be measured using pressure transducers to provide isothermal pressure-concentration data.

The volume of the sample holder must be calibrated while filled with sample in order to get an accurate measurement of the free gas volume in the system. Although a generally straightforward procedure for chemisorbing media, calibration can be tricky for highly porous and nano-structured media at low temperatures due to inaccurate or incomplete skeletal density information and the possible physisorption of helium used to perform the calibration.

Volumetric testing requires accurate measurement and control of the instrument and sample holder temperatures and the associated temperature gradients. The temperature of the instrument should be controlled in order to minimize temperature fluctuations due to external sources such as room heating, ventilation and air-conditioning. The temperature of the sample can be precisely controlled below room temperature by cryogenic cooling accompanied by PID heating or above room temperature by PID heating and appropriate insulation.

To test a sample using the static method, the gas reservoir is filled with H_2 to a pressure P and then allowed to react with the specimen reactor by opening the top valve. An equilibrium pressure P' is reached between the gas reservoir and the specimen reactor that, once paired with temperature, initial pressure and volume information, can be used to precisely determine the amount of hydrogen sorbed by the material. Dynamic testing allows the slow and continuous introduction of hydrogen to the specimen reactor. Hydrogen gas from the gas reservoir flows into the specimen reactor via the electronic flow controller while continuous pressure readings are taken by the pressure gauges attached to the reservoir and reactor. The pressure, temperature and volume data are analyzed to generate dynamic (non-equilibrium) pressure-composition isotherms.

One intrinsic advantage of the volumetric method is that, unlike gravimetric methods, the quantity of gas dosed to or from the sample can be small compared to the total capacity of the sample. Thus, the method allows the direct preparation of sample of known hydrogen contents. This may be useful for doing in-situ or ex-situ secondary measurements such as X-ray or neutron diffraction, NRM, IR, Raman, etc.

2.6.2.1Volumetric: Differential Pressure Method[10]

The differential pressure method is a modification of the standard volumetric testing method and is designed to increase the accuracy of Sieverts measurements. An example of a differential pressure method apparatus is shown in Figure 16.

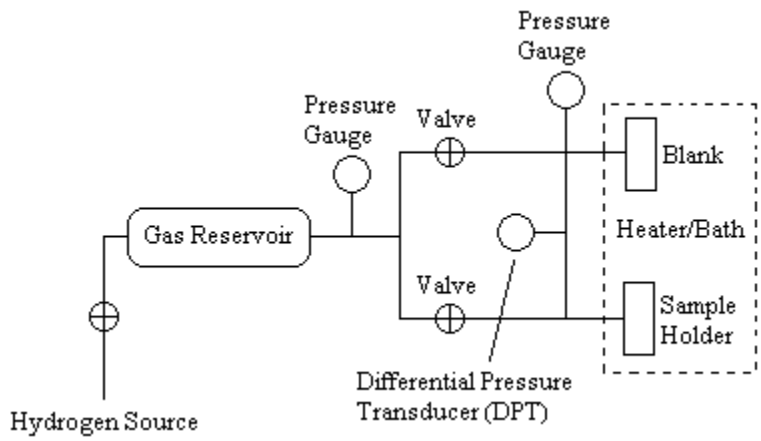

Figure 16. Schematic of the Differential Pressure Adsorption Unit.

The sample holder and a blank are maintained at the same temperature and are initially under the same pressure with the two valves in Figure 16 open. Immediately after dosing, the valves are closed, isolating the two volumes (sample holder, blank and associated tubing) from each other except for the differential pressure transducer connecting them. The differential pressure transducer measures the pressure change between the two volumes caused by the sorption/desorption of hydrogen by the sample. While adding significant complications, by measuring pressure with a differential pressure transducer instead of an absolute pressure transducer (gauge), the differential pressure method can take some advantage of the higher accuracy afforded to percent reading pressure transducers at low pressures (see Pressure variable section).

The most important consideration when testing with the differential pressure method is thermal equilibrium; the sample holder and the blank must be maintained at exactly the same temperature for the duration of the experiment for accurate isothermal data. This is often accomplished by placing the two volumes together in a heater or bath. Unfortunately, even small temperature variations like those caused by endothermic or exothermic reactions can lead to pressure fluctuations that can impair the accuracy of the differential pressure method. Excellent heat transfer and thermal management capabilities are essential to accurate testing using the differential pressure method.

2.6.2.2Volumetric: Data Corrections

Volumetric systems determine the concentration of hydrogen in a material from changes in the concentration of hydrogen gas in the reservoir/sample holder system. The concentration of hydrogen gas in the system is determined by knowledge of the pressure, temperature and volume of the reservoir and sample holder. Pressure changes are measured on a pressure transducer inside the volumetric equipment that is

at the same temperature as the instrument. Ideally, the system volumes are calibrated and the temperature is known and constant throughout so that the measured pressure is directly related to the concentration of hydrogen gas in the system. Unfortunately, temperature can vary both spatially and temporally and can be difficult to monitor because it requires many sensors to map the true temperature gradients. A common approach is to divide the instrument into isothermal regions, but care must be taken to validate this assumption to avoid the contribution of thermal effects on kinetics (see Figure 17). For example, if a sample is held at 77 K, the pressure is the same throughout the system. However, the hydrogen gas density is greater in the fraction of the system at 77 K. The volume fraction at 77 K depends on the system design, the type of sample holder used and the skeletal density of the sample.

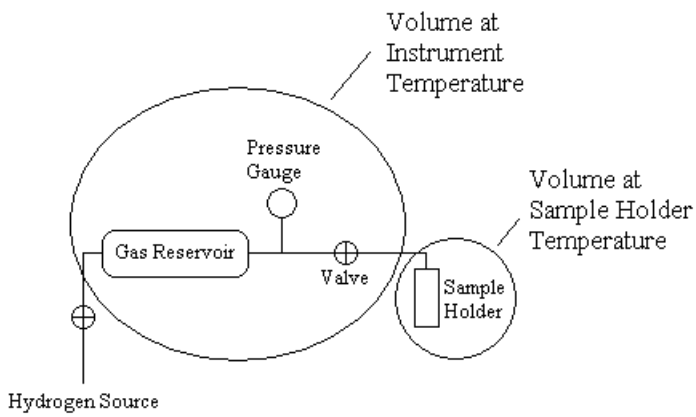

Figure 17. Schematic of temperature regimes in a volumetric instrument. The volume of gas at instrument temperature and at sample holder temperature varies depending on the system design and the type of sample holder used.

There are two data correction methods that can be used to account for temperature and hydrogen (gas) concentration variation in the reservoir/sample holder system; both involve calculating 'apparent' volumes that more closely represent the actual concentration of gas in the system. The apparent volume corrections can be applied to raw data after experimentation.

2.6.2.2.1 Volumetric: Temperature Correction

Temperature corrections use an empirically determined temperature correction factor to calculate the true hydrogen gas content in the system. In practice, a temperature correction factor does not affect the temperatures used in the concentration correlation equation (equation of state) but rather the volume used. It is determined from the volume fraction of the system at non-ambient temperatures and is used to define an apparent volume. This apparent volume is then applied to the equation of state to determine the hydrogen content in the total volume of the system.

The process for applying a temperature correction is straightforward. An inert (non-sorbing) material of similar physical properties is tested at identical conditions to the actual sample experiment. This is done to minimize the number of free variables

associated with the temperature correction factor. For example, if one is investigating the hydrogen storage properties of a sample at 77 K, the inert material should be tested at 77 K with the exact same reservoir volume, tubing and sample holder. It is important the inert material have the *same* skeletal (gas displacement) volume as the sample, as well. Because the temperature correction factor reflects the volume fraction of the system at non-ambient temperatures, it is necessary that the volumes of gas at sample and reservoir temperatures are identical in the inert material and sample experiments. Once volumetric equivalency has been ensured, the inert sample is tested in order to establish a baseline with which to compare the performance of the sample. Theoretically, capacity should be zero at all pressures for the inert material. In practice, this is not the case due to the temperature and concentration variation in the system (see Figure 18).

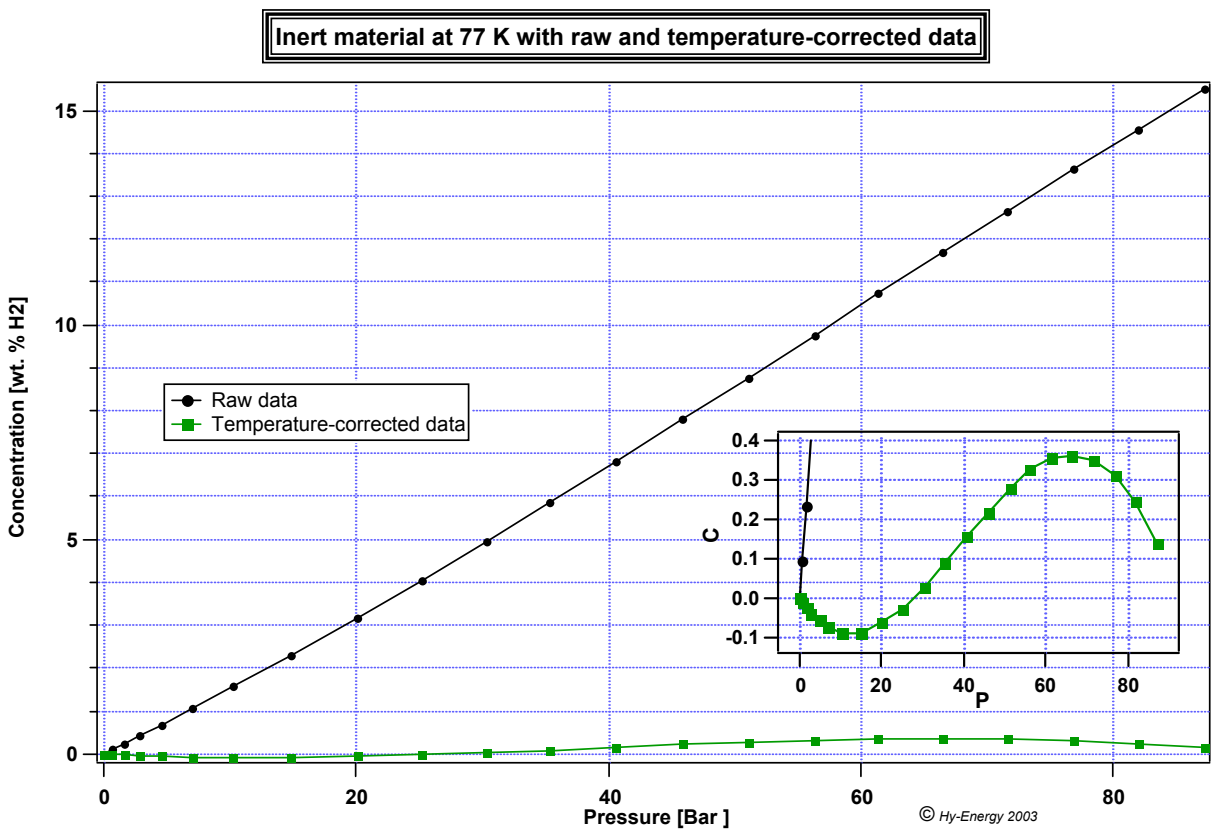

Figure 18. PCT data for inert material. The linear relationship between pressure and sorbed concentration is due to the temperature difference between the reservoir (302 K) and the sample holder (77 K).

A temperature correction factor is then applied to the raw data of the inert material and varied until the associated apparent volume yields zero sorption at all pressures. The temperature correction factor that yields zero sorption for the inert sample is then applied to the raw data of the actual sample. Figure 19 is an extreme example of a low capacity, very low density material (0.1 g/ml) showing raw and temperature corrected

data for a physisorbtion at 77 K. The temperature correction was taken from the data in Figure 18.

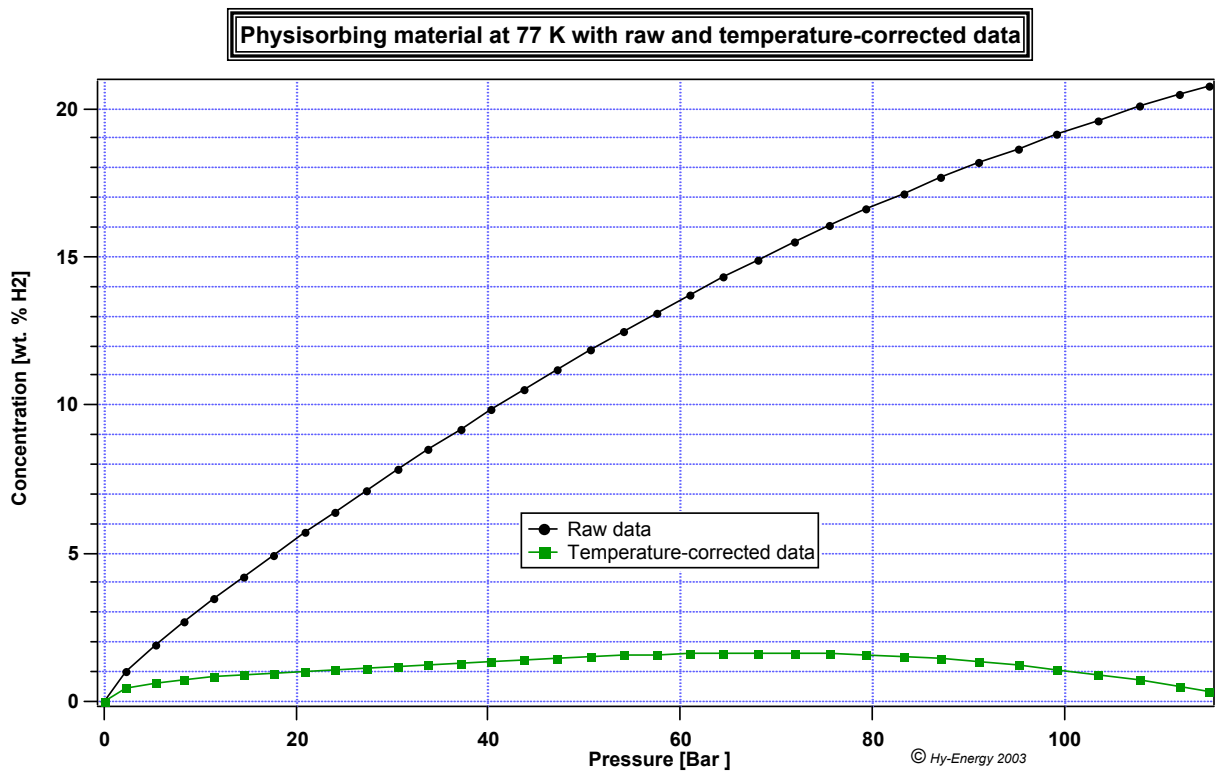

Figure 19. PCT for a physisorbing material at 77 K showing raw and temperature corrected data.[6]

2.6.2.2.2 Volumetric: Volume Correction

A volume correction is an empirical correction for the temperature based gas density gradient based on performing a volume calibration measurement of the sample holder (with sample) at testing temperature. This calibrated volume is the volume at room temperature required to contain the same amount of hydrogen gas as the volume of the sample holder at testing temperature. This simple relationship is defined in Equation 2.

$$n_{SH} = \frac{PV_{SH}}{RT_{SH}} = \frac{PV_{SH,App}}{RT_R} \rightarrow V_{SH,App} = \frac{T_R}{T_{SH}} V_{SH} \qquad \textbf{Equation 2}$$

Where n_{SH} is moles of gas in the sample holder, R is the gas constant, P is the measured pressure, V_{SH} is the volume of the sample holder, $V_{SH,App}$ is the "Apparent volume" of the sample holder, T_{SH} is the temperature of the sample holder, and T_R is the temperature of the reservoir (instrument). To apply an empirical volume correction, use the apparent volume (at testing temperature) along with pressure and *reservoir* temperature data in the concentration correlation. Reservoir temperature data must be used exclusively because the temperature variation in the system is accounted for in the apparent volume correction.

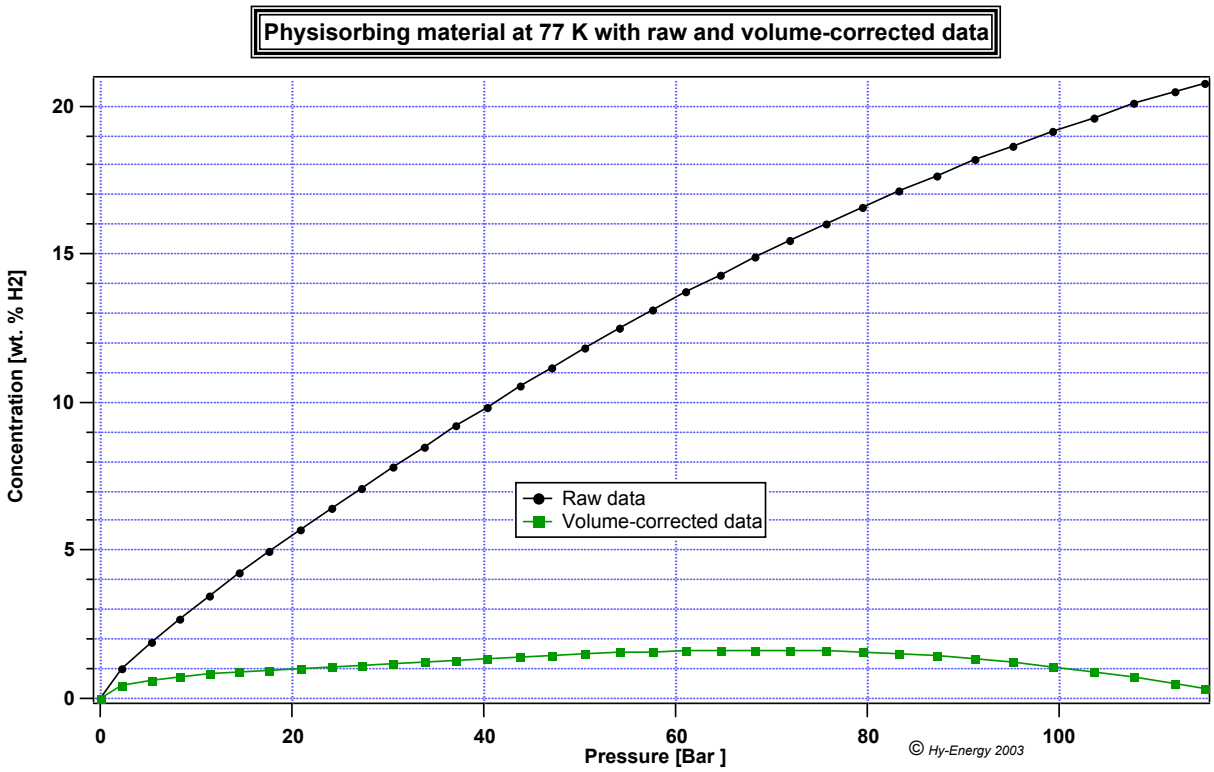

Figure 20. PCT for a physisorbing material at 77 K showing raw and volume corrected data. This is the same raw data that is used in Figure 19.

2.6.2.3Considerations

2.6.2.3.1 Consideration: Compressibility Factor

The volumetric method uses gas laws to determine the number of moles of hydrogen in the system based on pressure, temperature and volume measurements. A gas law can be written in general form as

$$PV = nRTz(P,T) \qquad \textbf{Equation 3}$$

The measurement and sources of error for pressure, temperature and volume are discussed in the variables section. The compressibility factor, z, accounts for the non-ideality of the gas at a given temperature and pressure. For an ideal gas, the compressibility factor is unity and Equation 3 collapses into the familiar ideal gas law. The compressibility factor for hydrogen is taken from compressibility data and applied as a function of the measured pressure and temperature (Figure 21).

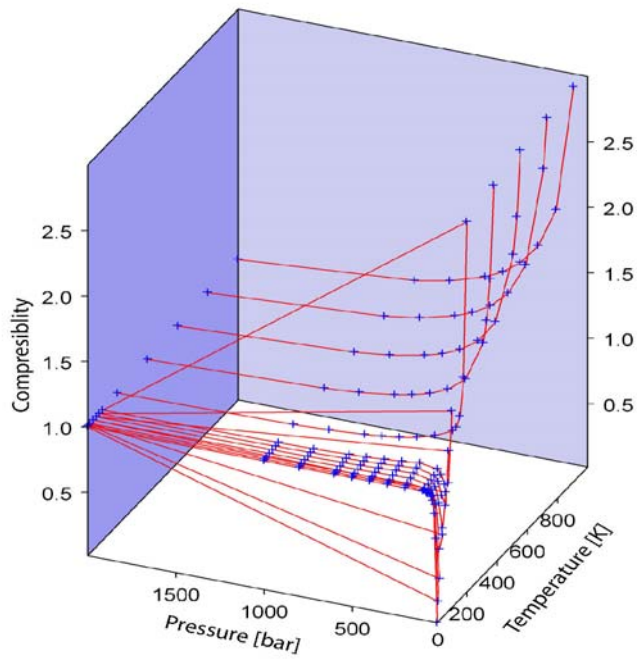

Figure 21. Compressibility factor z for hydrogen as a function of temperature and pressure.

2.6.2.3.2 Consideration: Gas Impurities

Gas impurities can be introduced into a volumetric system through the use of impure hydrogen gas and leaks during desorption experiments. In volumetric measurements the sample's hydrogen storage capacity is determined by measuring pressure drop/increase due to sorption/desorption. Since the partial pressures of any low level impurities are a minute fraction (parts per million to perhaps parts per thousand) of the measured hydrogen pressure, the impact on the total capacity caused by impurities is essentially negligible. In the volumetric method, the impurities may still impact capacity and kinetics through surface effects such as poisoning and retardation; however, the measurement will be truly representative of the material's performance in the presence of impurities.

Poisoning and retardation (see Capacity and Kinetics chapters) occur when gas impurities react with the sample to inhibit the total hydrogen sorbed/desorbed and the rates of reaction, respectively. These effects cause decreases in the measured storage capacity and kinetic activity of the sample material and may incorrectly indicate the sample material is not suitable for hydrogen storage applications. It is important to not eliminate a sample from consideration until gas impurity effects are mitigated.

2.6.2.3.3 Consideration: Instrument Temperature

The temperature of the instrument is an often-overlooked factor in taking accurate measurements. In most volumetric equipment, the dosing volume is inside the body of the instrument and is not in thermal equilibrium with the sample and sample holder. Therefore, knowledge of the instrument temperature and the temperature gradient between the instrument and the sample holder is necessary to accurately relate the

pressure reading on the pressure transducer (inside the instrument) and the equilibrium pressure in the sample holder. Instrument temperature management is most often performed by a temperature control system inside the instrument housing.

2.6.2.3.4 Consideration: Leaks

Hydrogen can be leaked to the environment (external leak) and across valves inside equipment (internal leak) during hydrogen storage testing. Both types of leaks during volumetric testing cause unexpectedly high capacities and strange kinetic behavior. During sorption testing above ambient pressures, gas leaked to the environment is assumed to be sorbed to the sample. Leaks during sub-ambient desorption also affect the capacity by increasing the reading of the amount of gas desorbed. In kinetic testing, leaking sorption/desorption profiles appear linear in time, as opposed to true sorption profiles that have a curved profile and eventually reach an equilibrium pressure. An equilibrium pressure of exactly 1 atmosphere and extraordinarily large hydrogen storage capacities are highly unlikely and should be double checked. Leaks also expose the sample and system to gas impurities that can affect property measurements and compromise samples.

It is advisable to check hydrogen storage testing systems for external and internal leaks every 20-40 experiments by running an empty sample holder. It is also good practice to check for external leaks on exposed tubing and joints using helium leak detection or a hand-held flammable gas detection instruments. These leak precautions apply to both volumetric and gravimetric testing methods.

2.6.2.3.5 Consideration: Reference Point

The volumetric method measures relative changes in hydrogen concentration calculated from changes in pressure in the reservoir/sample holder system. Because only changes in hydrogen concentration can be calculated, volumetric methods require a reference point with which to calculate absolute concentrations. The most obvious and most commonly used reference point is an uncharged sample under vacuum, which corresponds to (0 bar, 0 wt.% H_2). From this reference point, absolute concentration with respect to a indirect variable can be determined.

2.6.2.3.6 Consideration: Reverse Joule-Thompson Heating

An important temperature effect is the reverse Joule-Thompson gas expansion effect. Hydrogen is unusual in that it has a range that exhibits reverse Joule-Thomson behavior depending on the differential pressure. In other words, if the pressure difference is large enough, hydrogen will actually heat up during an expansion. This effect can often be seen in the initial part of a kinetics measurement when hydrogen is dosed at high pressure from a calibrated volume to the sample. There is a small temperature spike in the gas that is seen as a pressure spike and consequently what appears to be initial sorption. The gas expansion effect impacts desorption kinetics measurements in a similar manner: as the hydrogen desorbs from the sample and expands into the vacated volume, the temperature and pressure spike can be mistaken as increased desorption. These transient effects usually last only a few seconds or less depending on the thermal mass and internal surface area of the gas handling system and sample holder. This

effect disappears as the gas comes into thermal equilibrium with its surroundings. One should be careful to not misinterpret this temperature relaxation behavior as gas sorption by the sample. This is one good reason why it may be quite important to have a temperature sensor in close proximity if not intimate contact with the sample. To be able to determine when transient temperature related effects have subsided, one should ideally monitor the samples return to isothermal conditions.

2.6.2.3.7 Consideration: Sample Size

During single-dose measurements, the largest practical calibrated volume available limits the amount of material that can be tested. At a more sophisticated level an automatic volumetric doser with multiple volumes can be used to perform such kinetic measurements on wide range of sample sizes.

Small samples (less than 100 mg) exhibit small pressure changes due to sorption/desorption. It is therefore important to minimize the background pressure noise in order to measure the small pressure changes associated with small sample sorption/desorption. Also, small samples require that the instrument must be capable of high sensitivity both in the pressure sensor itself and the volume size. In particular, volumes should be match in size relative to the sample volume.

2.6.2.3.8 Consideration: Skeletal Density

The low skeletal density of highly-porous materials can cause difficulties in accurately determining hydrogen storage properties. This is primarily due to two factors: first, knowledge of the amount of gas displaced by the sample is required to determine the free volume in the sample holder. This can be difficult to quantify for samples of low skeletal density that have the potential to adsorb helium, the gas commonly used to calibrate volume in a volumetric system. Helium adsorption during volume calibration may lead to unexpectedly large volume calibrations, an effect that becomes especially pronounced at cryogenic temperatures. Second, low skeletal density makes it difficult to test a sufficient mass of sample for an accurate measurement. Insufficient sample mass leads to small pressure changes and, therefore, less accuracy due to pressure transducer sensitivity. It is important to have enough sample mass that pressure changes are significantly above the level of resolution of the pressure transducers.

When the skeletal density of the sample is very low and difficult to determine, the two factors discussed above lead to opposite conclusions regarding the amount of sample necessary for accurate testing. On the one hand, it is desirable to minimize the error associated with the free volume in the sample holder by using a small sample volume compared to the overall volume of the sample holder. This suggests using as small a sample as possible. Recent literature from Gray et al. supports this view and finds that the volume calibration error associated with skeletal density is proportional to the square of the volume of the sample.[10] On the other hand, pressure transducer sensitivity suggests a larger sample will lead to more accurate measurements due to the larger pressure changes associated with sorption and desorption. These opposing conclusions engender a tradeoff between small and large sample sizes in this special

case; one possible solution is to test both small and large amounts of material and compare the results.

2.6.2.3.9 Consideration: Volume Calibration

The effects of mis-calibration of the reference volume and a possible volume change with pressure can contribute error through the volume term; the latter effect is only considered significant in the sensor head, the valves with their accompanying diaphragm or bellows components and changes in the sample volume itself. Pressure-induced volume changes in the tubing, calibration volumes, and gas componentry are generally considered negligible.

2.6.2.3.10 Consideration: Volume Dilatation

Some hydrogen storage materials, especially metal hydrides, undergo volume dilatation and contraction during hydrogen sorption and desorption. The volume of a system (sample, sample holder and appropriate tubing) is typically calibrated using helium before or after experiments are conducted when the sample is in the uncharged state. Because volumetric methods require knowledge of the volume of a system in order to calculate concentration, changes in the volume of the sample during testing are not accounted for in the calculations and have the potential to cause errors in measurement. Volume dilatation and contraction of a sample is often negligible when compared to the overall volume of the system. However, dilatation effects should be considered when testing large quantities of materials that exhibit large volume expansion coefficients.

2.6.3 Gravimetric Method[9]

The gravimetric method of measurement uses weight changes measured on a balance to determine concentration and the storage properties of a material. A schematic of a simple gravimetric system is presented in Figure 22. Note additionally, that gravimetric systems are also often configured as flow-through systems, in which case there is also a gas exit port attached to the chamber through a pressure control device.

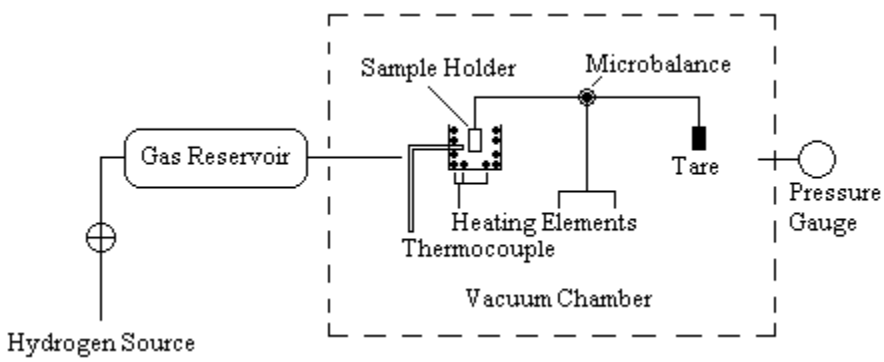

Figure 22. Schematic of counterbalanced gravimetric method system for hydrogen storage testing.

Before gravimetric testing, the weight of the unhydrided sample is measured and the sample is placed on one end of a symmetric microbalance in a sample holder. In more advanced gravimetric systems, an inert tare with the same weight and comparable density to the unhydrided sample is placed on the other end of the microbalance to provide a counterbalance. The tare is designed to minimize the effects of buoyancy caused by the hydrogen gas displaced by the sample volume and must be inert in a hydrogen atmosphere.

After the chamber containing the gravimetric equipment is evacuated, hydrogen from an external hydrogen source enters the chamber and is generally increase in incremental pressure steps as it is sorbed by the sample in the sample holder. The microbalance is typically equipped with an electronic circuit that measures the strain on the balance material that is directly related to the change in weight of the sample. This information combined with pressure and temperature readings provided by a pressure gauge connected to the vacuum chamber and a thermocouple located next to the sample holder can be used to construct various forms of hydrogen storage properties.

Measurements can generally be made under isobaric conditions with no loss of sensitivity and modification of the thermodynamic driving force or altering the kinetics by significant pressure changes. This can be accomplished even in static experiments by providing makeup gas during absorption or bleeding the evolved gas during desorption.

2.6.4Thermal Gravimetric Analysis Method[11]

We make a distinction here between the Gravimetric instruments described above and Thermal Gravimetric Analysis (TGA) in that Gravimetric instruments generally operate under isothermal conditions with a controlled over pressure of gas. Whereas, TGA's typically operate under vacuum or low-pressure flowing gas conditions and ramping temperatures. Some equipment, however, may be setup to operate in all of these modes. TGA is a thermal analysis technique often used in conjunction with DSC to determine the hydrogen storage properties of a sample. The first documented use of TGA was in the study of the efflorescence of hydrated salts in 1912 but it is now traditionally used in the quantitative investigation of decomposition reactions. TGA is experimentally similar to DSC but instead of measuring the heat flow as function of temperature, TGA measures sample weight as a function of time or temperature. This is accomplished by placing the sample in an environment that is heated or cooled at a controlled rate and measuring the weight change.

The equipment necessary to perform TGA consists of an accurate balance, a programmable furnace, a reaction chamber and a data collection system. As the temperature inside the furnace and reaction chamber changes, the balance measures the variation in weight due to various chemical reactions including dehydriding. TGA is affected by many of the same issues as the gravimetric testing method such as buoyancy and mechanical disturbances. The buoyancy force exerted on the sample by the displaced fluid varies with temperature and must be taken into account either during the experiment, e.g. the tare technique in the gravimetric method, or during data

analysis; mechanical disturbances must be minimized through leveling and anti-vibration supports. Another complication TGA shares with the gravimetric method is how to determine the sample temperature. Using a thermocouple to directly measure the temperature affects the weight reading of the sample. Consequently, care must be taken to place the thermocouple in such a way that it accurately reads the sample temperature but does not affect weight readings.

Scanned temperature experiments (TGA) are often done using flowing inert gas, such as argon. Although useful for comparing different materials (catalyzed vs. uncatalyzed, for example), desorption occurs into an essentially H2-free environment, and thus it does not reflect the actual conditions encountered in a real storage system application, where there is always H2 gas present at pressures at or exceeding 1 bar. Interpretation of desorption temperatures thus must be done carefully. For this reason TGA may be used as a screening tool, but not as a technique to rely on for realistic system desorption temperatures. When one really want to know practical desorption temperatures, the experiment must be conducted by flowing H2 gas into the TGA at the particular pressure of interest (say, 1-8 bar).

2.6.4.1Considerations

In addition to the sources of error associated with measuring the weight of a sample (see Weight section in Variables), additional gravimetric method considerations include the effect of gas impurities and heat transfer effects.

2.6.4.1.1 Consideration: Buoyancy

The weight of the fluid displaced by the sample exerts an upward force on the sample holder that can affect the measured weight change appreciably. The degree of the buoyancy effect is proportional to the volume displaced by the sample and the density of the surrounding gas. The upward force due to buoyancy on a symmetric microbalance like that in Figure 22 is

$$F_b = g\rho\Delta V = g\rho\left(\frac{m_s}{\rho_s} - \frac{m_t}{\rho_t}\right) \qquad \textbf{Equation 4}$$

where ρ is the density of the hydrogen gas, m_s and ρ_s are the mass and density of the sample and m_t and ρ_t are the mass and density of the tare which may include terms representing the mass and density of the sample holder (bucket, pan) and the hang-down wires. At elevated pressures ρ is not only a function of pressure and temperature but must also include corrections for non-ideal gas behavior.

2.6.4.1.2 Consideration: Gas Impurities

Gas impurity effects are generally much more severe in gravimetric methods than volumetric methods because samples are much smaller and the total amount of gas surrounding the samples is many orders of magnitude larger than in the volumetric case. This means that even at low impurity levels the relative exposure of the sample to impurities may be orders of magnitude higher. In addition, the weight increase due to

contaminants can not be distinguished from increase due to hydrogen sorption and therefore gas impurities have the potential to greatly affect measurements; in the volumetric system, the partial pressure of contaminants is typically negligible compared to hydrogen and therefore doesn't affect measurements to the same degree. This makes it important to reach relatively high levels of vacuum in order to take accurate measurements.

In contrast to the volumetric method, the effects of gas impurities tend to lead to false positives, measurements that indicate a sample is a better hydrogen storage material than it really is. This is because weight increase due to sorption of impure species is mistaken for hydrogen sorption, although in reality the sorption of hydrogen is decreasing (poisoning). Once again, it is necessary to minimize gas impurity effects during testing in order to gain an understanding of a material's true hydrogen storage properties. When a gravimetric system is used in a flow-through mode, the sample is continuously exposure to fresh source gas, thus impurities in the source gas must be minimized. Use of high purity gas, non-permeable and non-contaminating tubing such as stainless steel, and, if necessary, passing the source gas through water and oxygen scrubbers will mitigate the effect of impurities.

Because gravimetric measurements are much more sensitive to co-generation of other gases (evolved mass, not evolved moles) they often send up warning flags (like when the weight loss exceeds the total hydrogen content) even when the evolved gas is not being monitored.

2.6.4.1.3 Consideration: Heat Transfer

Heat transfer effects are critically important to hydrogen storage measurements and are resolved from temperature data collected by thermocouples. Ideally, the thermocouple measuring the temperature of the sample material and the sample are in perfect thermal contact, allowing the thermocouple to best measure the temperature of the sample. In gravimetric systems, this is not the case. A thermocouple cannot be attached directly to the sample because it will affect the sample's measured weight and is therefore placed near but not touching the sample. This makes it difficult to measure the true temperature of the sample and resolve heat transfer effects. In cases where the thermal gradients in the vicinity of the sample holder are large enough that the temperature reported by the thermocouple does not represent the true temperature at the sample holder, calibration with known temperature standards is necessary. System design that minimizes thermal gradients near the sample is highly desirable.

2.6.4.1.4 Consideration: Leaks

The effects of leaks on the gravimetric method vary widely depending on the type of experiment. One advantage of the gravimetric method is that leaks that occur during sorption testing have little effect on the measurement because the gas lost to the environment is not included in the indirect calculation of concentration like in the volumetric method. However, the flow of gas in the instrument caused by a leak can affect the forces measured by the cantilever. Leaks during gravimetric desorption testing can affect the sample material as well as the measurement. Sub-atmospheric

pressures sometimes used for desorption promote gas contamination and can lead to poisoning, retardation and other issues associated with gas impurities. This is a serious consideration when evacuating the sample holder or degassing a sample at elevated temperatures under vacuum.

2.6.4.1.5 Consideration: Sample Transfer

Some hydrogen storage materials are sensitive to common gases and vapors like those found in the atmosphere. Physisorbing materials readily adsorb atmospheric gases and vapors and must be activated (baked under vacuum) before hydrogen storage testing. Other materials, such as magnesium-nickel metal hydrides, oxidize rapidly and can not be exposed to oxygen. Both cases necessitate 'airless' sample transfer between storage containers and the hydrogen storage instrument. Airless sample transfer is difficult in gravimetric systems because the sample must be loaded onto a microbalance, a process that often exposes the sample to atmosphere. Some gravimetric and volumetric systems offer airless sample transfer devices but the process is typically awkward and while special designs make this manageable, typical systems are prone to mistakes that can compromise a sensitive sample. One approach is to incorporate the entire instrument inside an inert gas glovebox.

2.6.4.1.6 Consideration: Volume Dilatation

Volume dilatation during sorption affects weight measurements in gravimetric systems by changing the buoyancy forces acting on the microbalance. As the volume of the sample increases, the amount of hydrogen displaced by the sample also increases. This increases the buoyancy force acting on the volume that in turn affects the resultant force measure by the microbalance. This is a particularly challenging consideration because tarring the microbalance with an inert material, a common technique used to minimize buoyancy effects, will not account for buoyancy effects due to volume dilatation. If necessary, these can be taken into account by post-data acquisition processing provided a measurement or reasonable estimate of the sample density in the sorbed state is available.

2.6.4.1.7 Consideration: Thermal Gradients and Gas Flow Forces

Thermal gradients in the gas phase inside the chamber cause natural convection currents that can affect the microbalance, leading to noisy weight measurements. Once perturbed, the microbalance can take a long time to stabilize; therefore it is important to heat and cool the system slowly to minimize thermal gradients. Careful system design, including controlled flow channels and baffles to prevent establishing large convective cells, can help mitigate against thermal gas flow noise. In flow-through systems, gas flow drag forces on the sample holder and hang-down wires must be taken into account. These require either running a second, null experiment under identical conditions in the absence of the sample as a baseline for comparison of the sample run, or else calibration of the flow forces under various conditions of flow velocity (which generally changes with the kind of gas, temperature, and pressure).

2.6.5Temperature-Programmed Desorption Method

Temperature-Programmed Desorption (TPD) refers to a wide range of experimental methods that rely on temperature variation and generally include mass spectroscopy to initiate and quantify desorption reactions. The technique can be used for both reversible and irreversible processes, with the latter referred to as Temperature-Programmed Reaction Spectroscopy (TPRS).

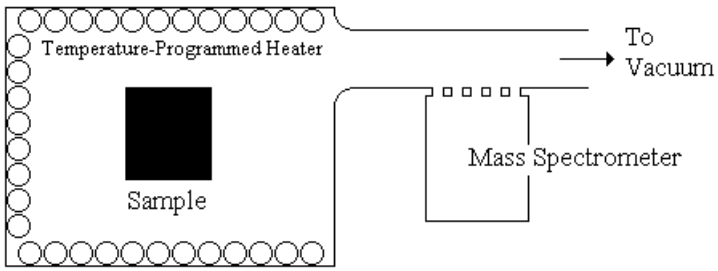

Figure 23. Schematic of typical Temperature-Programmed Desorption experimental set-up.

TPD measurements may be as simple as measuring pressure rise in a volumetric instrument or weight loss in a gravimetric instrument while ramping the sample temperature. However, TPD generally refers to spectroscopic desorption measurements. The basic set-up for TPD techniques is illustrated in Figure 23. The sample is loaded into the experimental apparatus (a temperature-programmed heater contained in a vacuum chamber) and charged with hydrogen until fully loaded. Note that hydrogen loading may also be performed in a separate apparatus prior to putting the sample in the TPD instrument. After the remaining gas has been drawn off, the computer-controlled heater slowly raises the temperature of the sample. This releases hydrogen that is evacuated to vacuum. A mass spectrometer connected to the evacuation line analyzes the relative composition of the desorbed gas and quantifies the amount of hydrogen desorbed by the sample. As with other methods (gravimetric and volumetric) that employ simultaneous mass spectrometry analysis, TPD systems have an advantage, in that it can distinguish between hydrogen and other constituents in the evacuated stream.

Concentration, temperature and time data is obtained through TPD measurements and can be used to determine capacity, kinetic and thermodynamic properties of a material. A common data representation format for TPD experiments is shown in Figure 24.

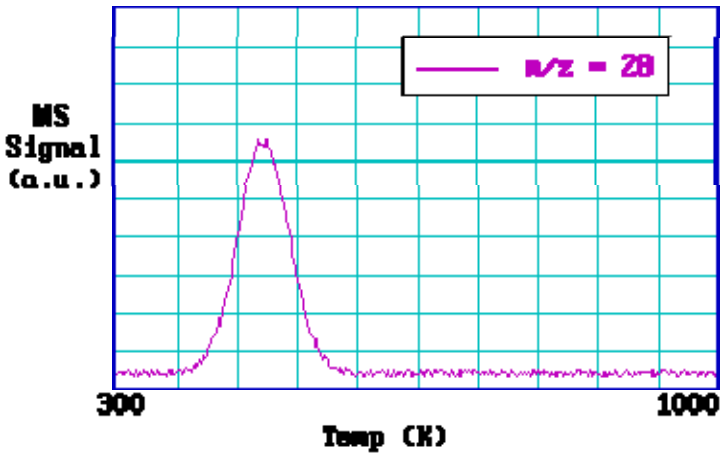

Figure 24. Typical data representation of single-component TPD experiment with CO.[12]

The area under the peak at ~475K in Figure 24 is proportional to the amount originally sorbed to the sample. In the case of full charging, it represents the capacity of the material. Kinetic information is obtained from the contour of the spectroscopic peak and knowledge of the relationship between temperature and time based on the computer program. Lastly, the temperature associated with the peak is related to the reaction enthalpy of hydrogen-substrate desorption. Unfortunately, TPD measurements can only be done at vacuum due to limitations in analytical equipment, effectively limiting the amount of thermodynamic information that can be collected. Quantitative analysis requires accurate calibration of the mass spectrometer against known flow rates. It is also important to understand that TPD or any dynamic type measurement of measurement gives results that is a convolution of both thermodynamic and kinetic properties of the hydrogen storage material. This may lead to miss-interpretation of the results. For example, does a decrease in desorption temperature of a material that is modified through the addition of a dopant mean that the thermodynamics of the host material has been altered? Or, is the dopant acting as a catalyst, or a thermal conductor, or modified the materials morphology such that kinetics are improved, increasing desorption rates at lower temperatures. For the development of new (reversible) materials it is important to have information on both the dynamic and equilibrium hydrogen sorption behavior of the storage material.

2.6.6Differential Scanning Calorimetry Method[13]

Differential Scanning Calorimetry (DSC) is a thermal analysis technique used to investigate the thermodynamic properties of a material by measuring the energy necessary to maintain a sample material and an inert reference material at the same temperature over a range of temperatures. The relative heat flow to the sample material as a function of temperature can be used to determine thermodynamic properties such as specific heat and enthalpy. A typical DSC diagram is shown in Figure 25.

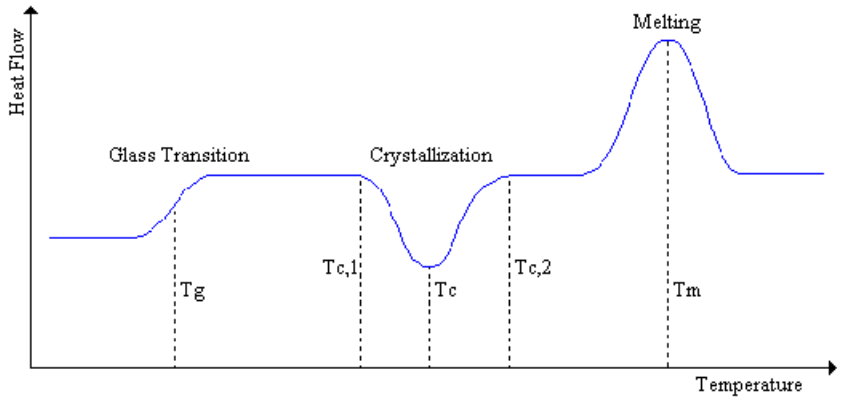

Figure 25. Typical DSC diagram with glass transition, crystallization and melting phase transitions.

Temperature variation in DSC is controlled by a computer and is typically linear in order to simplify calculation, although nonlinear temperature variation can be used as well. The specific heat of the sample material as a function of temperature is determined by the equation

$$c_p(T) = \left(\frac{\partial h}{\partial T}\right)_p = \frac{q(T)}{\frac{dT}{dt}(T)} \qquad \textbf{Equation 5}$$

Where T is temperature, h is energy, q is heat flow and t is time. The heat flow can be taken from the data and the temporal temperature variation is based on the computer program controlling the experiment. In this way, the specific heat as a function temperature can be determined. Furthermore, the enthalpies of reactions can be determined from Figure 25. For example, the enthalpy of crystallization is calculated by integrating the specific heat capacity determined from Equation 5 between the temperatures at which the heat flow varies ($T_{c,1}$ and $T_{c,2}$).

$$\Delta H_{crys} = \int_{T_{c,1}}^{,2} c_p(T)dT \qquad \textbf{Equation 6}$$

The two most commonly used methods for conducting DSC measurements are power-compensation DSC and heat-flux DSC. In the power-compensation method, the sample and reference material are placed in independent, identical furnaces. The furnaces are maintained at the same temperature over a variety of temperatures by varying the power input. The power input and temperature data are used to construct the DSC diagram. The indirect and direct variables in power-compensation DSC are flipped in heat-flux DSC. The sample and the reference material are placed in one furnace and exposed to the same heat flux. The variation in temperature between the sample and reference is used to determine the relationship between heat flux and temperature.

In the context of hydrogen storage, Differential Scanning Calorimetry is primarily used for desorption testing because DSC equipment is not typically designed to handle the high pressures required for sorption with some exceptions. The advantage of DSC over

other methods is that other thermal events such as melting or crystal structure changes may be observed. A significant limitation for testing hydrogen storage using DSC is that there is no way to determine the amount of hydrogen desorbed by a sample, only the total enthalpy of a given reaction. For instance, DSC alone would be unable to distinguish between a material that desorbs 0.1 mol H_2 with an enthalpy of reaction of 30 kJ/mol H2 from one that desorbs 1 mol H_2 with an enthalpy of reaction of 3 kJ/mol H2. It is important to have an understanding of the enthalpy of reaction per mol hydrogen in order to compare thermodynamics across materials. This vital consideration for hydrogen storage should not be overlooked but can be remedied by coupling DSC with quantitative measurements of hydrogen uptake and release.

2.7 Summary

It is our intent that this overview of fundamental processes and measurement considerations will aid research and development of new and better hydrogen storage materials. In particular we hope to have clarified some of the best practices and caveats in performing high-quality experiments to measure the hydrogen storage properties of advanced materials.

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2.9 Disclaimer

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Best Practices for the Characterization of Hydrogen Storage Materials

Kinetics

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National Renewable Energy Laboratory Contract No. 147388
Contract Technical Monitor: Dr. Philip Parilla

DRAFT
V25: June 11, 2008
Comments may be sent to DOE.HydrogenStorage@ee.doe.gov up to August 15, 2008;
Reference "Best Practices

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3 Kinetics

Measurement of hydrogen sorption and desorption kinetics is important for practical hydrogen storage system performance, advanced materials development and fundamental research on the mechanisms of hydrogen uptake and release.

In this chapter we will provide an overview of the purpose of kinetics measurements, introduce some modeling of kinetic mechanisms, discuss important considerations that affect kinetics measurements, and present some methods to improve kinetics.

The proper characterization of hydrogen storage properties is one of the most crucial and time-consuming steps on the road to the discovery and development of advanced and practical materials. Because of this, it is important that measurements, including kinetics measurements, are informative, reliable and consistent with accepted standards. The intent of this chapter is to describe some common practices accepted in the field of hydrogen storage and to highlight important considerations both positive and negative that can have a strong impact on kinetics measurements.

3.1 Recommended Reading

This document is not meant to be a thorough review of the leading work in this field, but rather an overview and series of instructive examples of important issues concerning the measurement of the kinetic properties of hydrogen storage materials. The following resources are a good place to find more detailed information on the key topics.

3.1.1 Kinetics

The book "Basic Chemical Kinetics" by Eyring, Lin and Lin.[1]
The book "Chemical Kinetics and Reaction Mechanisms" by Espenson.[2]

3.1.2 Hydrogen Storage

The book "Hydrogen Storage Materials (Materials Science Forum)" edited by Barnes.[3]
The review article "Hydrogen-storage materials for mobile applications" by Schlapbach and Züttel.[4]

3.1.3 Hydrides

The book "Hydrides" by Wiberg and Amberger.[5]
The review article "A panoramic overview of hydrogen storage alloys from a gas reaction point of view" by Sandrock.[6]

3.1.4 Metal Hydrides

The book "Metal Hydrides" by Muller, Blackledge, and Libowitz.[7]
The book "Transition Metal Hydrides" edited by Dedieu.[8]

3.1.5 Physisorption Storage

The review article "Review of hydrogen storage by adsorption in carbon nanotubes" by Darkrim, Malbrunot and Tartaglia.[9]
The journal article "Hydrogen Storage in Microporous Metal-Organic Frameworks" by Rosi et al.[10]

3.2 Introduction

As an introduction, we will briefly review chemical kinetics in general and then discuss kinetics as it pertains to hydrogen storage materials.

3.2.1 Chemical Kinetics

The following definition of kinetics is from the "Chemical Kinetics" article on Wikipedia, the wiki encyclopedia.[11] Please note that due to its open-source format, the exact text from the Wikipedia article may be different depending on when the article is accessed. The presented text was taken on January 8, 2008. The presented text has also been reviewed for accuracy.

> "Chemical kinetics, also known as reaction kinetics, is the study of rates of chemical processes. Chemical kinetics includes investigations of how different experimental conditions can influence the speed of a chemical reaction and yield information about the reaction's mechanism and transition states. In 1864, Peter Waage and Cato Guldberg pioneered the development of chemical kinetics by formulating the law of mass action, which states that the speed of a chemical reaction is proportional to the quantity of the reacting substances.
>
> Chemical kinetics deals with the experimental determination of reaction rates from which rate laws and rate constants are derived. Relatively simple rate laws exist for zero order reactions (for which reaction rates are independent of concentration), first order reactions, and second order reactions, and can be derived for others. In consecutive reactions the rate-determining step often determines the kinetics. In consecutive first order reactions, a steady state approximation can simplify the rate law. The activation energy for a reaction is experimentally determined through the Arrhenius equation and the Eyring equation. The main factors that influence the reaction rate include: the physical state of the reactants, the concentrations of the reactants, the temperature at which the reaction occurs, and whether or not any catalysts are present in the reaction.

3.2.1.1 Factors Affecting Reaction Rate

3.2.1.1.1 Nature of the Reactants

Depending upon what substances are reacting, the reaction rate varies. Acid reactions, the formation of salts, and ion exchange are fast reactions. When covalent bond formation takes place between the molecules and when large molecules are formed, the reactions tend to be very slow.

3.2.1.1.2 Physical State

The physical state (solid, liquid, or gas) of a reactant is also an important factor of the rate of change. When reactants are in the same phase, as in aqueous

solution, thermal motion brings them into contact. However, when they are in different phases, the reaction is limited to the interface between the reactants. Reaction can only occur at their area of contact; in the case of a liquid and a gas, at the surface of the liquid. Vigorous shaking and stirring may be needed to bring the reaction to completion. This means that the more finely divided a solid or liquid reactant, the greater its surface area per unit volume, and the more contact it makes with the other reactant, thus the faster the reaction. To make an analogy, when you start a fire, first you use wood chips and small branches that have high specific surface areas, you don't start with big logs. In organic chemistry, 'On water' reactions are the exception to the rule that homogeneous reactions take place faster than heterogeneous reactions.

3.2.1.1.3 Concentration

Concentration plays an important role in reactions. According to the collision theory of chemical reactions, this is because molecules must collide in order to react together. As the concentration of the reactants increases, the frequency of the molecules colliding increases, striking each other more often by being in closer contact at any given point in time. Imagine two reactants in a closed container. All the molecules contained within are colliding constantly. By increasing the amount of one or more of the reactants you cause these collisions to happen more often, increasing the reaction rate.

3.2.1.1.4 Temperature

Temperature usually has a major effect on the speed of a reaction. Molecules at a higher temperature have more thermal energy. When reactants in a chemical reaction are heated, the more energetic atoms or molecules have a greater probability of colliding with one another. Thus, more collisions occur at a higher temperature, yielding more product in a chemical reaction. More importantly however, is the fact that at higher temperatures molecules have more vibrational energy; that is, atoms are vibrating much more violently, so raising the temperature not only increases the number of collisions but also collisions that can result in rearrangement of atoms within the reactant molecules. For example, a refrigerator slows down the speed of the rate of reaction since it cools the food molecules. On the other hand, an oven gives heat (energy) to the food molecules, which in turn speeds up the rate of reaction, cooking the food faster.

A reaction's kinetics can also be studied with a temperature jump approach. This involves using a sharp rise in temperature and observing the relaxation rate of an equilibrium process.

3.2.1.1.5 Catalysts

A catalyst is a substance that accelerates the rate of a chemical reaction but remains chemically unchanged afterwards. The catalyst increases reaction rate by providing a different reaction mechanism to occur with a lower activation

energy. In autocatalysis a reaction product is itself a catalyst for the reaction that created it, leading to positive feedback. Proteins that act as catalysts in biochemical reactions are called enzymes. Michaelis-Menten kinetics describes the rate of enzyme-mediated reactions.

In certain organic molecules specific substituents can have an influence on reaction rates in neighboring group participation.

Agitating or mixing a solution will also accelerate the rate of a chemical reaction, as this gives the particles greater kinetic energy, increasing the number of collisions between reactants and therefore the possibility of successful collisions.

Increasing the pressure in a gaseous reaction will increase the number of collisions between reactants, increasing the rate of reaction. This is because the activity of a gas is directly proportional to the partial pressure of the gas. This is similar to the effect of increasing the concentration of a solution.

3.2.1.1.6 Equilibria

While chemical kinetics is concerned with the rate of a chemical reaction, thermodynamics determines the extent to which reactions occur. In a reversible reaction, chemical equilibrium is reached when the rates of the forward and reverse reactions are equal and the concentrations of the reactants and products no longer change. This is demonstrated by, for example, the Haber-Bosch process for combining nitrogen and hydrogen to produce ammonia. Chemical clock reactions such as the Belousov-Zhabotinsky reaction demonstrate that component concentrations can oscillate for a long time before finally reaching equilibrium.

3.2.1.1.7 Free Energy

In general terms, the free energy change (ΔG) of a reaction determines if a chemical change will take place, but kinetics describes how fast the reaction occurs. A reaction can be very exothermic but will not happen in practice if the reaction is too slow. If a reactant can produce two different products, the most thermodynamically stable product will generally form except in special circumstances when the reaction is said to be under kinetic reaction control. The Curtin-Hammett principle applies when determining the product ratio for two reactants interconverting rapidly, each going to a different product. It is possible to make predictions about reaction rate constants for a reaction from free-energy relationships."

3.2.2Kinetics in Hydrogen Storage

For hydrogen storage, kinetics is generally taken to mean the dynamic rates at which hydrogen sorption and desorption from a storage material occur in time. A primary distinction between capacity and kinetics is that capacity measurements are

theoretically taken at thermodynamic equilibrium, independent of the time required to reach equilibrium, while kinetics investigates how the material approaches equilibrium and what influences this approach. The availability of hydrogen in a storage material is dependent on the kinetics of the material under the system operating conditions. While a material might demonstrate high hydrogen storage capacity, the true amount of hydrogen practically available may be significantly less depending on the material's intrinsic kinetics. A number of different intrinsic properties of a storage material may control kinetics including surface interactions, transport phenomena, hydrogen-substrate storage mechanisms and phase change.[12] External factors such as temperature and pressure also have a profound effect on hydrogen sorption and desorption kinetics.

In its most simple form, a kinetics experiment provides a useful measure of the rate of hydrogen uptake or release from a storage material. Unfortunately, comparing kinetics across materials and experimental setups can be complicated. For example, one way to compare kinetics is to consider average rates. A common practice is to define the average kinetic rate as the time to reach 95% of the full capacity. However, as is demonstrated in Figure 1, it is possible to derive the same average sorption rate for materials that, in fact, exhibit very different kinetic character. Thus, it is important not only to compare average rates but also to compare the shape of the kinetic curves. Factors that can influence the experimental rates are discussed in the section on experimental and analysis considerations.

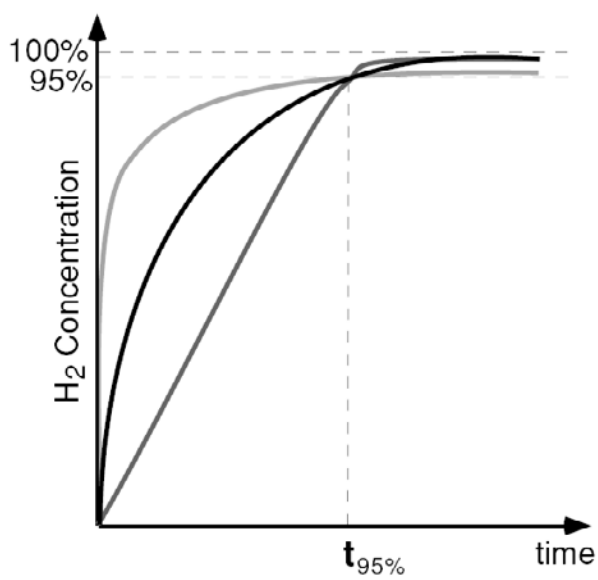

Figure 1. Hypothetical concentration versus time curves showing 3 different kinetic behaviors that have the same average rate at t_{95}%.

3.2.3 Impact of Heat Transfer

Kinetics measurements are conducted to quantify the kinetic performance of hydrogen storage materials and identify the intrinsic mechanisms controlling hydrogen uptake and release. Identification of the kinetic mechanisms, most specifically the rate-controlling mechanism, is instrumental in developing materials with improved kinetic properties. It is not easy to perform measurements to accurately determine the intrinsic rate-controlling mechanism however. Early in hydrogen storage research, intrinsic material properties like surface effects, mass transport and storage mechanisms were generally assumed to be the rate-controlling mechanisms. In reality, heat transfer and other thermal effects dominate kinetic rates for nearly all reactions in hydrogen storage systems and measurements.[13]

In taking kinetics measurements, heat transfer is the most important effect for which researchers must account. The temperature of sorption/desorption is the most influential variable in hydrogen storage kinetics for both chemisorbing and physisorbing materials. It is imperative that measurements are taken under isothermal conditions in order to minimize the effects of heat transfer and identify the intrinsic kinetic mechanisms. Isothermal measurements are difficult in systems with poor heat transfer and fast intrinsic kinetics because the heat generated or taken up during hydrogen-substrate interactions can cause local temperature excursions that profoundly affect kinetic rates. All too often, kinetic rates reported in literature are in fact heat transfer rates because the sorption/desorption process is limited by an experiment's ability to supply or dissipate energy. Heat transfer-limited kinetics measurements occur primarily because of improper equipment design and errors in experimental protocol. The effect of heat transfer on kinetics measurements is underscored by Dantzer in 1997: with regard to kinetic measurements on hydrogen sorption in $LaNi_5$, before 1983-1985, attempts to interpret data in terms of a microscopic [kinetics] model are questionable since no proof is provided on the isothermal conditions of the experiments.[14] The effects of heat transfer are addressed often to reinforce their importance to the field. Further discussion on steps that can be taken to minimize the effects of heat transfer can be found in the experimental and analysis considerations section of this chapter.

3.3 Purpose of Measurements

Perhaps more than any other type of measurement, the manner in which kinetics measurements are performed will greatly depend on the purpose of the measurement. The purpose of measurements is the deciding factor in determining the measurement method to be used and ultimately the size of the sample and the design of the containment. This section will provide some guidelines to help the reader understand the purpose of kinetics measurements at the different levels of research and highlight considerations associated with measurements at each level.

3.3.1 Purpose: System Performance

The kinetic rates of a hydrogen storage system are determined by a number of factors in addition to the intrinsic kinetic properties of the storage material. Some of the factors that affect kinetic rates at the system level include heat transfer between the storage material, material housing and environment, the operating over- or under-pressure relative to thermodynamic equilibrium and the packing density of the storage material. Heat transfer plays an important role in the kinetic performance of storage systems because some materials require the delivery and dissipation of significant amounts of energy during charging and discharging. Dedrick presents an example of the extreme energy releases characteristic of some metal hydrides upon charging: hydriding 5 kg of sodium alanate storage material in 2.5 min releases an average of 668 kW. The total heat released is enough to boil 64 gallons of water.[15] The ability to handle sorption/desorption energy loads such as those for sodium alanate necessitates the use of sophisticated thermal management systems such as internal plates, fins and tubing in system performance measurements.[16] System-level considerations like thermal management devices must be included in the design and evaluation of the kinetic performance of a storage system.

3.3.2 Purpose: Materials Development

Kinetics measurements for materials development must focus on the intrinsic kinetics of the storage material in order to effectively compare materials. This can be difficult for materials with highly exothermic or endothermic reactions and good intrinsic kinetics because heat transfer often masks the intrinsic kinetic character of the materials. Intrinsic kinetics testing emphasizes testing at isothermal conditions and conducting measurements under identical conditions (pressure, temperature, sample size etc.) using identical measuring equipment in order to minimize the effects of heat transfer. The importance of testing kinetics under identical conditions using identical measuring equipment and setup is illustrated in the many dozens of papers before 1982 reporting absolute absorption and desorption rates for $LaNi_5$. Reported kinetics rates at half capacity varied between < .01 min^{-1} to 35 min^{-1} at 5 atm and 298 K.[17] The measurements in the review were performed with different quantities of material on completely different equipment without special considerations for heat transfer. Therefore conclusions drawn from these measurements concerning intrinsic kinetics are questionable at best. There are a few special instances when non-isothermal kinetics measurements are informative, particularly when applied to developing functional hydrogen storage applications.

3.3.3 Purpose: Fundamental Mechanisms

Fundamental mechanism studies look to identify and understand intrinsic kinetic phenomena. Like those for materials development, fundamental investigations require isothermal conditions in order to eliminate the effects of heat transfer. Investigation of hydrogen diffusion mechanisms, the effects of catalysts on hydrogen dissociation, and the nature of hydrogen/sample material interaction are examples of research at the fundamental level. If the purpose of a kinetics measurement is to study intrinsic

mechanisms, it is absolutely necessary to design the experimental measurement equipment to achieve essentially isothermal conditions.

3.4 Kinetic Theory

This section is designed to familiarize the reader with knowledge of the fundamental mechanisms of hydrogen storage kinetics. It will also briefly review the process used to identify rate-limiting mechanisms through mathematical modeling.

Kinetic theory is a complicated and heavily researched field and a complete review of its content is beyond the scope of this work as an introductory document on hydrogen storage properties and testing. Accordingly, the kinetic theory section is restricted to a brief overview. The authors will use references extensively in order to both summarize information and provide the reader with avenues for further inquiry into the subject of kinetic theory.

3.4.1 Fundamental Mechanisms of Kinetics

In order to improve the kinetic properties and performance of potential hydrogen storage materials, it is important to gain a fundamental understanding of the underlying rate-controlling mechanisms. The sorption and desorption of hydrogen by a material involves a number of important steps that occur in series and in parallel. For different sorption and desorption processes as well as for different hydrogen storage materials, the mechanisms controlling these steps differ. In general, there are three broad categories of kinetic mechanisms: surface interactions, mass (hydrogen, potentially the host elements) and energy transport (heat transfer), and binding mechanisms. Surface interactions, mass and energy transport and binding mechanisms are considered intrinsic processes. Mass and energy transport also depend on a number of extrinsic considerations including the particle size, packing density, the shape of the sample and sample holder, the thermal contact between the sample and sample holder, and the mobility and pressure of the gas. Any one mechanism may be the slowest, rate-controlling mechanism, although heat transfer is often the rate-controlling mechanism in practical application. Moreover, for reversible storage materials, the rate-controlling mechanisms may not necessarily be the same for sorption and desorption. It is generally difficult to differentiate experimentally between sorption and desorption mechanisms without careful experimental control.[16]

Sorption and desorption in physisorbing materials is a two-step process consisting of mass and energy transport and surface interactions/binding mechanisms. Hydrogen is only transported through the void volume of the material and physisorption storage occurs at the surface of the skeletal material with minimal effect on the structure of the material. In this sense, surface interactions/binding mechanisms can be considered equivalent phenomena in physisorbing material and will be addressed in the physisorption binding mechanisms section. In chemisorbing media, surface interactions and bulk diffusion present distinct steps in the process of hydrogen storage and one or both may play the key role in hydrogen storage kinetics. The following section on surface interactions will discuss the various surface interactions that affect hydrogen storage kinetics in chemisorbing media.

3.4.1.1 Surface Interactions in Chemisorbing Media

Hydrogen can be stored on the surface (adsorption) and in the bulk (absorption) of chemisorbing materials. For superficial chemisorption, hydrogen is electrochemically bound to the host's surface. For bulk chemisorption, only atomic hydrogen can pass through the surface layers and be transported into and out of the bulk. Therefore, the surfaces of chemisorbing materials must split hydrogen gas into atomic hydrogen for storage. This is accomplished by the dissociation of H_2 via the transfer of electrons to the sample material. Hydrogen dissociation on the surface of a metal hydride is shown in Figure 2. Hydrogen exists as a diatomic molecule before interacting with the surface of the material (left side of the figure), dissociates at the surface into two atomic hydrogen atoms, and diffuses into the bulk of the material (small molecules in the lattice). Doping with metal catalysts is a common technique used to increase the efficiency of hydrogen dissociation at the surface of chemisorbing materials. A considerable number of investigations at the materials development and fundamental mechanism levels seek to maximize the ability of a material to dissociate hydrogen through doping and surface texturing.[18] [19]

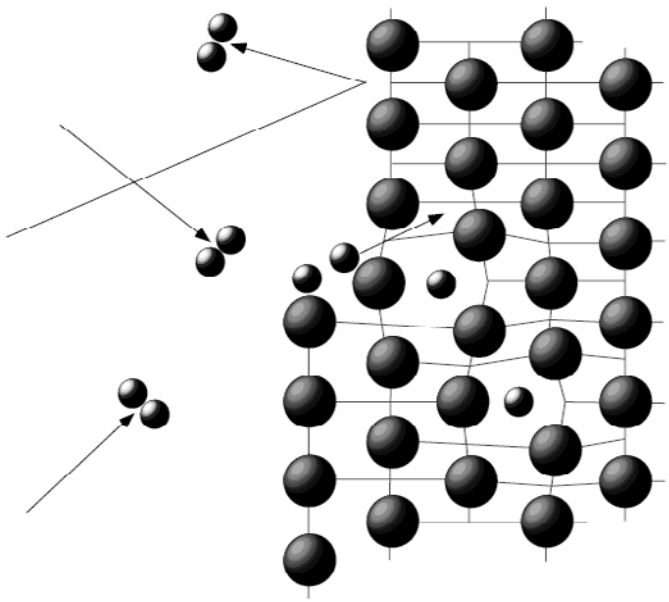

Figure 2. Schematic representation of the interaction of hydrogen with a clean crystalline surface.[20]

The interaction of hydrogen with the surface of a chemisorbing material is complicated by the fact that the surface or interfacial properties of the material may be substantially different than those of the bulk. The crystal structure, electronic, magnetic and dynamic properties, as well as the chemical composition of a material can be dramatically altered near the surface due to the discontinuity of the surface. By definition then, the surface layer consists of the atomic region that shows different properties from those of the bulk. For a clean single crystal, the surface layer is generally no thicker than the first few

monolayers. Oxidized, contaminated, or multiphase materials may have a surface layer as thick as 10 nm. From the crystal structure point of view, atoms in the surface layer may relax or reconstruct. Surface relaxation may involve changes in the lattice dimensions and inter-atomic distances in the first few layers. Reconstruction consists of a rearrangement of atoms in the top atomic layers and often results in a loss or change of symmetry. Electronic states are also altered in the surface layer.

3.4.1.1.1 Surface Energetics

Surface energetics governs the dissociative chemisorption of hydrogen in the surface layer. The potential energy of the interaction of gaseous hydrogen with a surface can be depicted using a simple two-dimensional set of potential energy curves (Figure 3). (Complex hydrides do not fit into this simple picture, since the absorption and desorption of hydrogen involve structural phase transitions.) Away from the surface the two curves are separated by the heat of dissociation, E_D = 218 kJ/molH, which represents the amount of energy required to split H_2 into two hydrogen molecules. The interaction of gaseous hydrogen with the metal to form a stable solid solution or intermetallic is described by following the H_2 + M potential from its minimum (E_P) to its intersection with the 2H + M potential in the surface layer. If the potential energy curves intersect above the zero energy level, positive activation energy E_A is required for hydrogen dissociation; if the curves intersect below zero, dissociation is energetically favorable ($E_{NA} < 0$) and occurs spontaneously. After the curves intersect, dissociation occurs and the potential continues along the 2H + M curve as atomic hydrogen is transported into the bulk. The potential energy of hydrogen in the material reaches a deep minimum on the 2H + M potential (the heat of chemisorption, $E_C \approx$ 50kJ/molH) close to the surface/bulk interface, which dictates that only atomic hydrogen transports through the bulk of metal hydrides.

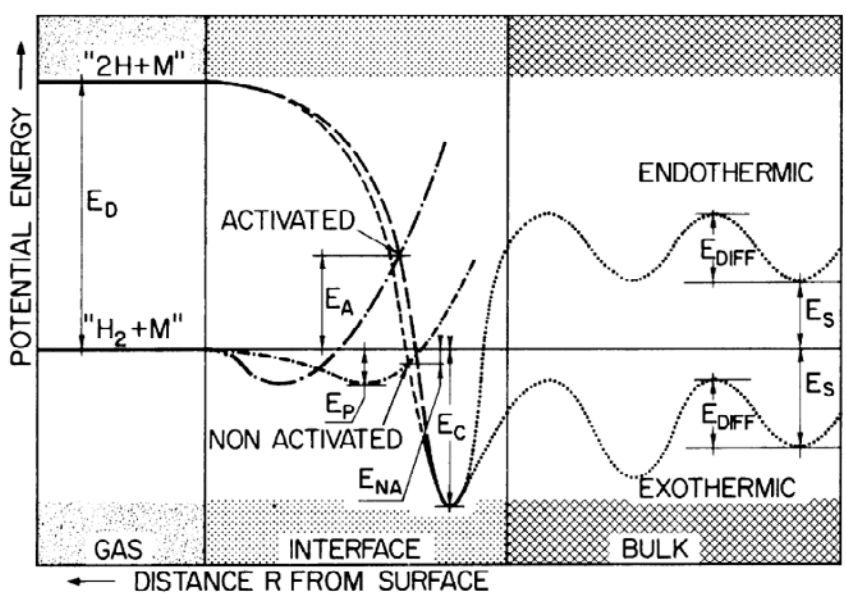

Figure 3. Potential energy curves for the activated or non-activated dissociation and chemisorption of hydrogen on a clean metal surface, followed by the endothermic or exothermic solution of atomic hydrogen into the bulk.[21]

For chemisorption, some surface properties that can limit the overall hydrogen sorption rates (such as E_C and the sticking probability) become concentration dependent as the surface coverage of atomic hydrogen increases. The coverage, in turn, depends on the mobility of atomic hydrogen on the surface and into the bulk. Perhaps most importantly, diffusion from the very stable superficial chemisorption sites (E_C) into the bulk absorption sites (E_S) may be a rate-limiting step and is usually closely linked to surface structure. Thus, kinetics may be influenced by a feedback loop between concentration and surface interactions.

3.4.1.1.2 Surface Contamination

So far, the interaction of hydrogen with metals has been described by the ideal case of a clean elemental metal surface. Clearly, this model does not describe the real surface environment found on most samples. Elemental metals generally have surfaces that have been passivated by oxygen, thus preventing the dissociation reaction and the diffusion of atomic hydrogen into the bulk (Figure 4).

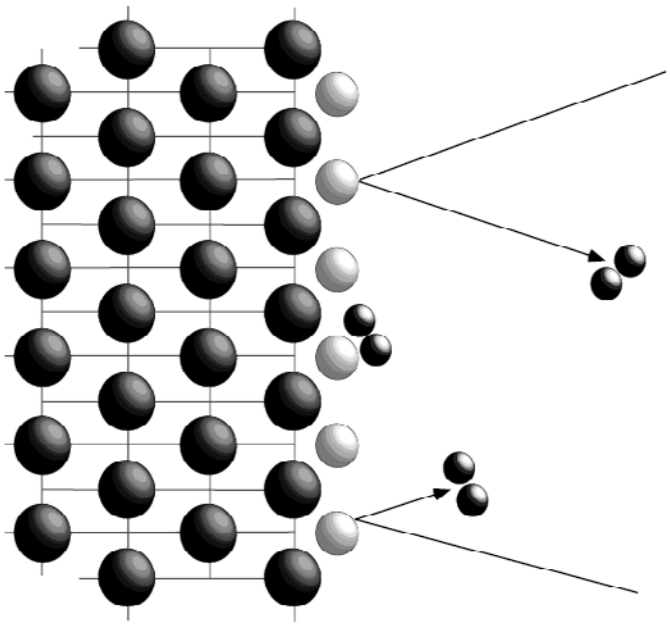

Figure 4. A schematic representation of the passivation of a surface hindering the hydrogen dissociation reaction. The light-colored spheres represent oxygen occluding the surface of the material.[20]

Intermetallic compounds, on the other hand, often show highly reactive surfaces even after exposure to oxygen or other contaminants (H_2O, N_2, CO, CO_2, etc.). This is due to reorganization in the chemical composition of the surface to minimize the surface energy. This form of surface segregation is an intrinsic property of alloys.

Schlapbach et al. showed that surface segregation can be caused by selective oxidation of certain elements in the alloy.[22] In the case of $LaNi_5$, they found that the selective oxidation of La prevents the surface from becoming passivated. Using depth profiling by

combining photoelectron spectroscopy and sputtering, they demonstrated that there was a surface enrichment of La, as well as the precipitation of metallic Ni in the subsurface. This suggests that the decomposed surface layer is permeable to molecular hydrogen that may dissociate in the subsurface on active Ni precipitates and on the un-oxidized host alloy (Figure 5). Surface segregation at room temperature has also been observed in many other hydride-forming intermetallic compounds such as ErFe, $ZrMn_2$, $TiMn_2$, $CeRu_2$, and Th_7Fe_3, and at elevated temperatures for the hydrogen storage compounds FeTi and Mg_2Ni.

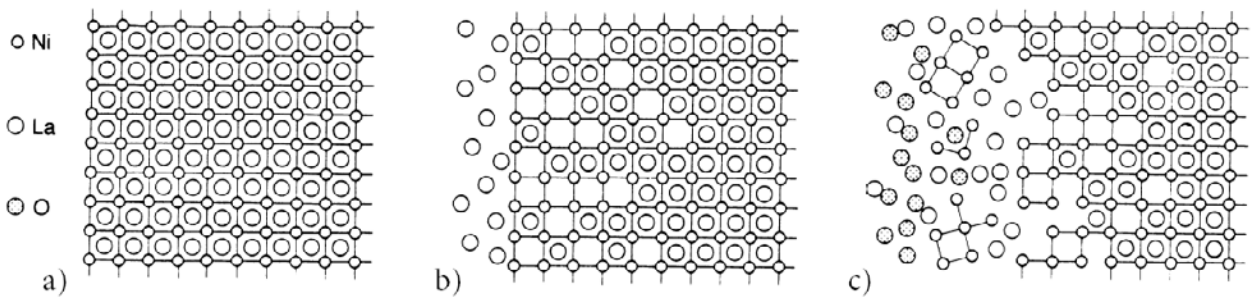

Figure 5. Surface segregation in the $LaNi_5$ system. a) fresh surface, b) surface enrichment of La lowering the surface energy, and c) selective oxidation of La and formation of Ni precipitates at the surface.[23]

An active surface does not necessarily guarantee rapid kinetics. FeTi provides a good example. This compound requires activation at high pressures and temperatures to absorb hydrogen. Yet, the detection of HD molecular species created through H_2–D_2 exchange interactions at the surface showed that this compound actually has an active surface even at room temperature. It is thought that the difficult activation is due to bulk diffusion properties.[24]

3.4.1.1.3 Surface Hydriding

Hydride formation that occurs at the surface of the material can hinder the further transport of hydrogen into the bulk.[25] [26] This phenomenon is depicted in Figure 6. When hydrogen dissociates at the superficial layer, it must be transported away from the surface through the first several monolayers of material. If the hydrogen transport properties of the material are poor, the hydrogen and substrate will react to form an intermetallic at the surface. The intermetallic acts as a barrier to further hydrogen transport into the bulk and can significantly affect kinetic performance. The sorption rate eventually becomes limited by the diffusion of hydrogen through this intermetallic layer.

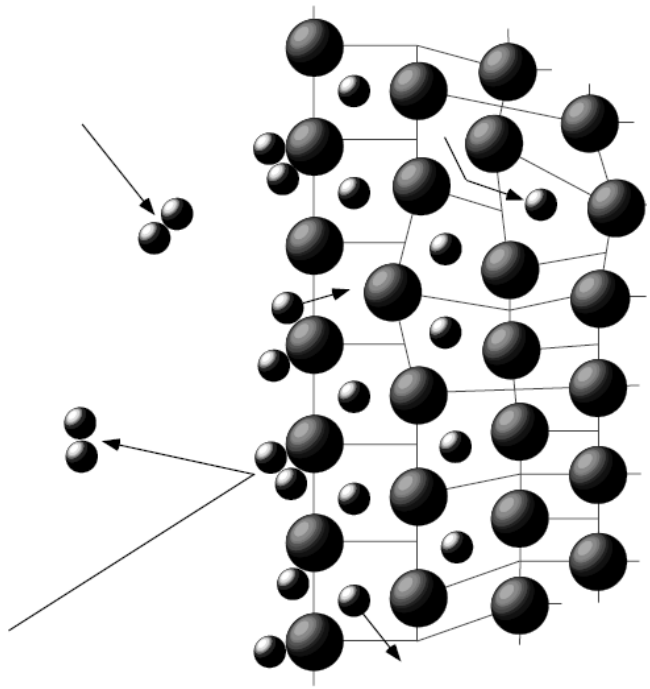

Figure 6. A schematic representation of the formation of a surface hydride which creates a diffusion barrier blocking the transport of atomic hydrogen into the bulk.[20]

3.4.1.2Binding Mechanisms

The mechanisms that store hydrogen differ for physisorbing and chemisorbing media. The relative strength of the bonds greatly influences the kinetics and thermodynamics of the hydrogen storage material.

3.4.1.2.1 Physisorption

For physisorption, molecular hydrogen bonds to the surface via van der Waals forces and remains in molecular form, H_2. Storage through physisorption is primarily limited to porous and nano-structured materials, where high surface area-to-volume ratios allow the physisorption mechanism to contribute significantly to storage capacity. In these types of materials, the external surface dictates the accessibility of the internal pore structure and the internal surface area dictates the degree of physisorption. Bonding can occur through dipole-induced dipole and induced dipole-induced dipole interactions (Figure 7), with heats of adsorption (physisorption) ranging from 4-6 kJ/mol depending on the nature of interaction.[27] In Figure 3, the heat of adsorption is shown on the H_2 + M potential energy curve as E_P. Van der Waals forces dominate kinetic forces at low temperatures because molecules have relatively low kinetic energy under these conditions, allowing weak intermolecular forces to bond hydrogen to a substrate.

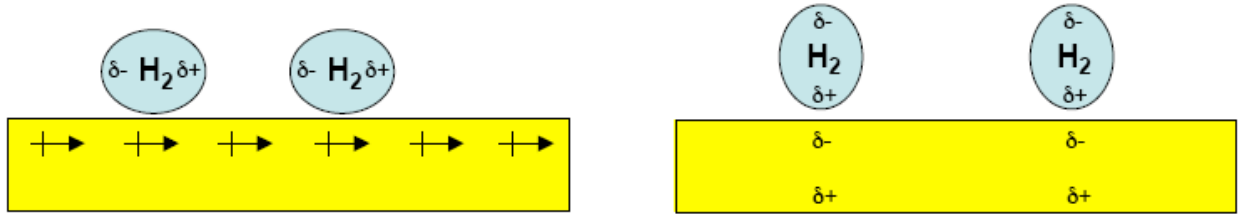

Figure 7. l) Dipole-induced dipole van der Waals interactions. r) Induced dipole-induced dipole van der Waals interactions.[27]

3.4.1.2.2 Chemisorption

The dissociation of hydrogen and the subsequent formation of one or more hydrides with a hydrogen storage material forms the basis of chemisorption hydrogen storage. Depending on the type of hydride bond formed, hydrides may be classified as ionic, metallic or covalent hydrides. A thorough review of the chemistry of hydrides can be found in the book "Hydrides" by Wiberg and Amberger and in particular on metal hydrides in the book "Metal Hydrides" by Muller, Blackledge, and Libowitz.[5] [7] The important point is that the kinetics of hydrogen uptake and release may involve many complex steps including adsorption, dissociation, surface diffusion, bulk hydrogen diffusion, hydride formation, reactant diffusion, phase separation, etc.

3.4.1.3Mass Transport

The kinetics of hydrogen storage is strongly influenced by the mobility of hydrogen and potentially the storage material itself and the transport of energy through the storage media (material and gas). The mobility of hydrogen, reactants, and energy within the storage media involve a wide range of transport properties. For simplicity we have divided the discussion of transport mechanisms into physisorbing and chemisorbing storage media.

3.4.1.3.1 Physisorption

For porous materials, molecular hydrogen easily passes through macroscopic boundaries and is transported through the network of pores to the internal surfaces of the material. Transport through the internal networks is governed by porous media-specific transport laws. Darcy's Law is a well-known momentum transport constitutive equation in porous media that relates the velocity with respect to the porous media ν to the viscosity of the fluid (hydrogen in this case) μ, the diagonal permeability tensor K, and the piezometric pressure, P.[28]

$$\langle v \rangle = -\frac{1}{\mu}\left[\underline{K} \cdot \nabla \langle P \rangle\right] \qquad \textbf{Equation 1}$$

Transport of fluids in porous media is the subject of extensive study and the reader is encouraged to review several books on the subject.[29] [30]

3.4.1.3.2 Chemisorption

For chemisorption in metal hydrides, hydrogen transport in the bulk occurs via atomic diffusion through the interstitial sites of the host metal structure. The dynamics of interstitial motion cover a wide range of time scales, from 10^{14} Hz for vibrational motion

to 10^{10} Hz for collective long-range diffusion. The mechanisms controlling local diffusion in chemisorbing materials are highly temperature dependent. Values measured for long-range diffusion can vary over 12 orders of magnitude for different samples at different temperatures.[31] In the high-temperature region of practical interest to chemisorption hydrogen storage research, a classic barrier-hopping model can be used to describe the diffusion of hydrogen through a metal hydride. The temperature dependence of the diffusion rate can be expressed by the relation

$$D = D_0 e^{\frac{-E_A}{k_B T}}$$ **Equation 2**

where D is the number of successful jumps per unit time, D_0 is the number of vibrations or attempts per unit time, k_B is the Boltzmann constant and E_A is the activation energy. At lower temperatures, quantum tunneling effects of hydrogen atoms become dominant.[32]

3.4.1.4Heat Transfer

Because of the exothermic nature of most hydrogen storage materials, heat transfer often plays the most critical role in the kinetics of hydrogen sorption and desorption.

Heat transfer in porous media occurs through the internal pore network and the material itself. Heat transfer performance is generally dictated by the pore size distribution relative to the mean free path of the hydrogen molecule at various temperatures and the structure (e.g. characteristic dimension, linkage) of the skeletal material.[33] [34]

At first glance, heat transfer in chemisorbing materials would seem to be governed by thermal conduction through the storage material itself. However, with few exceptions, chemisorption materials are often powders with limited particle-to-particle contact. Thus, heat transfer is generally governed by many of the same principles as porous media. For example, the large lattice expansion that occurs in hydriding metals and intermetallic compounds creates enough internal stress within the crystal lattice and grain boundaries that bulk samples will turn to powders on hydriding. With cycling these powders will break down into smaller and smaller particles. This is referred to as decrepitation. This process itself will change the thermal conductivity of the storage material. Thus, the repeated process of hydrogen sorption and release can have a strong influence on the kinetic behavior of the storage material system with cycling. Heat transfer in other chemisorption materials such as alanates and amides as well as nano-materials of any kind may also be affected by mass transport of the reactants and grain growth.

Over the years, a great amount of effort has been put into the design and development of materials and devices optimized for controlling material mobility and heat transfer in hydrogen storage systems.[35]

3.4.2Kinetics Modeling

Mathematical models are used to provide insight into the rate controlling mechanisms of a material's hydrogen uptake and release. The model that best fits experimental observation is typically assumed to be the rate-limiting mechanism.

The kinetics modeling section will be structured around models for metal hydrides to illustrate the process of determining sorption mechanisms. Kinetics in metal hydrides can be mathematically modeled by the general relationship

$$\frac{dC}{dt} = K(T)F(C,P) \qquad \textbf{Equation 3}$$

where K(T) is the temperature-dependent rate constant and F(C,P) is a function dependent on the hydrogen concentration in the material C and gas pressure P. A brief introduction will be given on the rate constant K(T) and how it is determined followed by a more in-depth discussion on modeling the hydrogen concentration function.

3.4.2.1.1 Temperature Dependence

When kinetics measurements are made at different temperatures, it is generally found that gas sorption and desorption rates are highly dependent on temperature. This is indicated in the temperature dependence of the rate constant K in Equation 3. In 1889, Arrhenius recognized that most chemical reactions occur at rates that increase exponentially with temperature. This empirical observation is valid in metal hydrides and can be conveniently written as

$$K(T) = Ae^{\frac{-E_A}{k_B T}} \qquad \textbf{Equation 4}$$

where A is the frequency factor, E_A is the activation energy, k_B is the Boltzmann constant and T is the temperature. From Equation 4 we find that the activation energy E_A is given by

$$E_A = -k_B T \ln(K) \qquad \textbf{Equation 5}$$

The activation energy of a reaction can be determined by measuring the rate constant K(T) at several different temperatures and then plotting ln(K) versus 1/T. This is known as an Arrhenius plot.

An example of such an Arrhenius plot is shown in Figure 8. This plot presents data for the same La_2Mg_{17} sample given in the example in the following section.[20] The rate constants were determined from a series of absorption measurements at different temperatures using the same pressure-dependent curve fitting approach as in Figure 10. A line was then fit to the Arrhenius data in Figure 8. The activation energy for the hydride formation reaction can be obtained from the slope of this ln(K) versus 1/T plot. The activation energy calculated from these measurements is 63.7 kJ/mole.

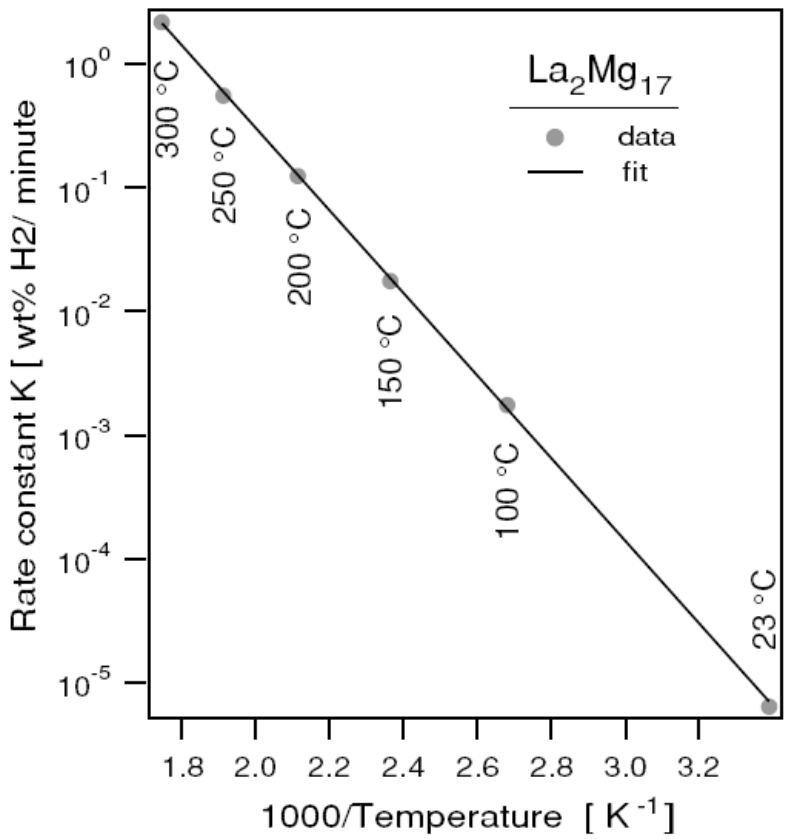

Figure 8. Arrhenius plot of rate coefficients K versus 1/T, for hydrogen absorption by La_2Mg_{17}.[20]

3.4.2.2Concentration Dependence

The rate of adsorption and desorption is dependent on the availability of hydrogen in the sample. The hydrogen concentration function is used to model this availability and is often normalized to allow different kinetics measurements to be compared on the same plot. The functional dependence of concentration is modeled non-dimensionally as

$$F(\alpha) = \kappa \frac{t}{t_{\frac{1}{2}}} \qquad \textbf{Equation 6}$$

where the reacted fraction α is the concentration C normalized by the final concentration C_0, κ is an empirically-determined rate constant, and t is the time normalized by $t_{1/2}$, the time at half concentration ($C_0/2$).[36] The following is a series of models that have been derived for different hydrogen transport mechanisms and geometries. The nine models presented, divided by mechanistic category, are compared to experimental data in Figure 9 to determine the rate-limiting concentration mechanism of the tested material. The subscripts of the equations denote the kinetics profile they describe in Figure 9.

3.4.2.2.1 Diffusion Models

Diffusion models can be used to describe one-, two-, and three-dimensional diffusion processes in several coordinate systems. A simple one-dimensional diffusion process with a constant diffusion coefficient can be described by

$$D_1(\alpha) = \alpha^2 = .2500\left(\frac{t}{t_{\frac{1}{2}}}\right) \qquad \textbf{Equation 7}$$

Two-dimensional diffusion into a cylindrical body gives

$$D_2(\alpha) = (1-\alpha)\ln(1-\alpha) + \alpha = .0426\left(\frac{t}{t_{\frac{1}{2}}}\right) \qquad \textbf{Equation 8}$$

Diffusion from the surface towards the center of a sphere is[37]

$$D_3(\alpha) = \left(1-(1-\alpha)^{\frac{1}{3}}\right)^2 = .0426\left(\frac{t}{t_{\frac{1}{2}}}\right) \qquad \textbf{Equation 9}$$

Another well-know model for a spherical body is[38]

$$D_4(\alpha) = \left(1-\frac{2\alpha}{3}\right) - (1-\alpha)^{\frac{2}{3}} = .0367\left(\frac{t}{t_{\frac{1}{2}}}\right) \qquad \textbf{Equation 10}$$

3.4.2.2.2 Reaction Models

Kinetics may be limited by the chemical reaction rate i.e. the rate of transition from solid solution to intermetallic. This mechanism can be modeled by

$$\frac{d\alpha}{dt} = \kappa(1-\alpha)^n \qquad \textbf{Equation 11}$$

where n is the order of the reaction.[36] In some cases, solid-state reactions appear to follow first order kinetics

$$R_5(\alpha) = \ln(1-\alpha) = -.6931\left(\frac{t}{t_{\frac{1}{2}}}\right) \qquad \textbf{Equation 12}$$

If kinetics are controlled by a constant velocity propagation of the phase transition boundary, then useful relationships can be derived from Equation 11. The case of a cylinder, n = 1/2, gives

$$R_6(\alpha) = 1-(1-\alpha)^{\frac{1}{2}} = .2929\left(\frac{t}{t_{\frac{1}{2}}}\right) \qquad \textbf{Equation 13}$$

For a sphere of radius r in which the reaction proceeds from the surface towards the center with n = 2/3,

$$R_7(\alpha) = 1 - (1-\alpha)^{\frac{1}{3}} = .2063\left(\frac{t}{t_{\frac{1}{2}}}\right) \qquad \textbf{Equation 14}$$

The above models of phase boundary propagation assume a virtually instantaneous and homogeneous nucleation of the product phase. In such a case the surface of a material is quickly covered by a hydride layer and the kinetics are described by the propagation of the phase boundary towards the center of the material. However, this is generally not how a hydride is formed. Typically the hydride phase nucleates at discrete locations in the bulk and grows outward. Hydride domains come into contact with each other as they grow and growth continues along the remaining reactant-product boundaries, eventually consuming the entire material. This process of nucleation and growth can be described by the following equations derived by Avrami and Erofe'ev[39 40]

$$A_8(\alpha) = (-\ln(1-\alpha))^{\frac{1}{2}} = .8362\left(\frac{t}{t_{\frac{1}{2}}}\right) \qquad \textbf{Equation 15}$$

$$A_9(\alpha) = (-\ln(1-\alpha))^{\frac{1}{3}} = .8850\left(\frac{t}{t_{\frac{1}{2}}}\right) \qquad \textbf{Equation 16}$$

3.4.2.3Determination of the Rate-Controlling Mechanism

In order to determine the rate-controlling mechanism the metal hydride sample in Figure 9, the nine models described above are plotted along with the sorption data. The models are shown in Figure 9 on a plot of α versus $t/t_{1/2}$. At low concentrations, it is clear that diffusion (Equation 7 through Equation 10, 1-4 in Figure 9) is the rate-controlling mechanism, although it is difficult to distinguish between the different diffusion models. However, this distinction becomes more obvious at higher hydrogen concentrations. The experimental data best fits curve 3, which describes diffusion from the surface to the center of a sphere. Therefore, this diffusion process is the mechanism that controls the rate of hydrogen sorption in the metal hydride in question. Once again, it is important to remember that it is very difficult to accurately determine the intrinsic mechanisms of hydrogen sorption/desorption due to thermal effects. Heat transfer effects dominate kinetics for most measurements. Therefore, conclusions drawn from modeling must be kept in perspective when analyzing sorption/desorption mechanisms.

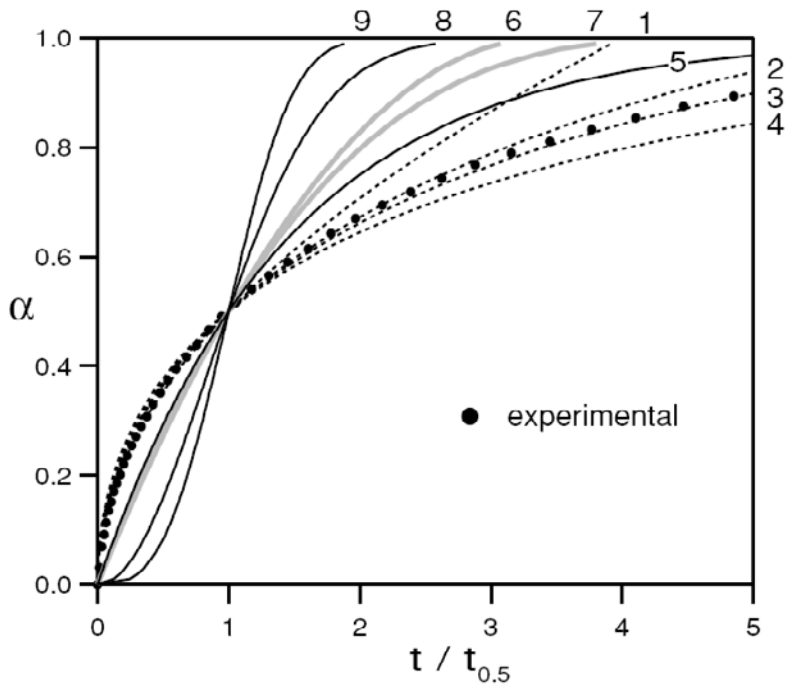

Figure 9. Various solid-state kinetics models.[36] 1) One-dimensional diffusion, 2) diffusion in a cylinder, 3+4) diffusion in a sphere, 5) 1st-order phase transformation, 6) constant velocity phase-boundary propagation in a cylinder, 7) constant velocity phase-boundary propagation in a sphere, 8+9) nucleation and growth.

3.4.2.3.1 Pressure Dependence

The volumetric method commonly used for measuring kinetics is not done at a constant pressure. Therefore, the pressure term in Equation 3 must be included to account for the effect that the changing potential energy of the surrounding gas will have on sorption kinetics. The following set of equations were proposed by Wang and Suda[41] for the sorption kinetics of the hydride phase transition:

$$\frac{dC}{dt} = K_h F_h(P,C) \qquad \textbf{Equation 17}$$

$$K_h = Ae^{\frac{-E_h}{k_B T}}, F_h(P,C) = \left(\frac{P}{P_{eh}}\right)^a \left[1 - \left(\frac{P_f}{P}\right)^a \left(\frac{C}{C_f}\right)^b\right] \qquad \textbf{Equation 18}$$

$$\frac{dC}{dt} = K_d F_d(P,C) \qquad \textbf{Equation 19}$$

$$K_d = Ae^{\frac{-E_d}{k_B T}}, F_d(P,C) = \left(\frac{P}{P_{ed}}\right)^b \left[1 - \left(\frac{P}{P_f}\right)^a \left(\frac{C_f}{C}\right)^b\right] \qquad \textbf{Equation 20}$$

K_h and K_d are the absorption and desorption rate constants, P_{eh} and P_{ed} are the equilibrium plateau pressures, Pf and Cf are the final pressure and concentration, and a

and b are the orders of the relationships between the sorption rates and pressure and concentration, respectively.

As an example of relationships given in Equation 17 through Equation 20, experimental measurements of the hydrogen absorption kinetics of the intermetallic compound La_2Mg_{17} at 300°C are presented in Figure 10. The most linear behavior was found for reaction orders a = 2 and b = 1. This relationship proves to be valid for up to 95% of the absorbed capacity. The slow non-linear residual absorption at the bottom of the plot is most likely due to reestablishing thermal equilibrium after initial fluctuations in temperature caused by the exothermic hydriding reaction. The rate constant K_h from Equation 18 was determined from the slope of a linear fit of the upper part of the data.

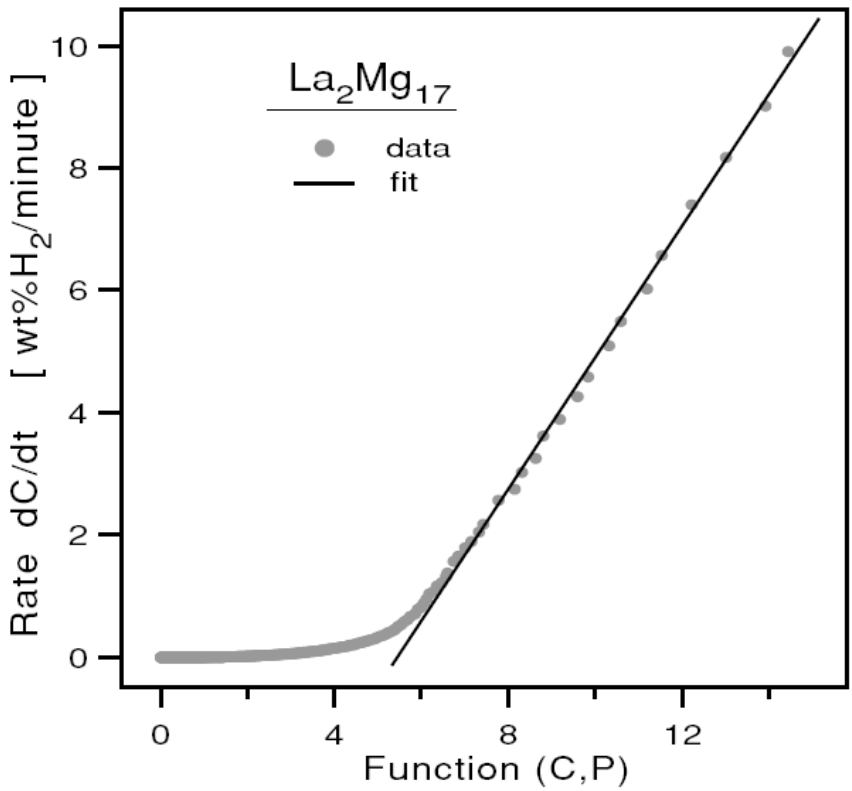

Figure 10. Linear fit to the rate dC/dt versus F(C,P) for hydrogen absorption of La_2Mg_{17} at 300°C. The rate coefficient K is found from the slope of the fit.[20]

3.5 Experimental and Analysis Considerations

Measured sorption and desorption rates are dependent on experimental and data analysis considerations as well as intrinsic material properties. As a consequence, experimental conditions and procedures that vary from system to system and from researcher to researcher can have a tremendous effect on measurements and the conclusions drawn from them. This makes comparisons between measurements with experimental equipment, different experimental conditions, different sample shapes, sizes, morphology and composition difficult if not impossible. Considerations that can have a significant effect on kinetics measurements will be discussed in this section along with suggestions to minimize their impact.

This section will rely heavily on examples from literature to support and illustrate the effects of various kinetics considerations. For more detailed information on specific considerations, refer to the reference of the cited example.

3.5.1 The Limitations of Kinetics Measurements

While a great deal can be learned from a good set of sorption and desorption kinetics measurements, from a materials discovery perspective, it is critical that the underlying hydrogen sorption process that is occurring is well understood. Unfortunately, kinetics measurements themselves often give very little direct information about these processes. In many ways kinetics plots look similar to each other. For that reason, basic sorption and desorption measurements should be complemented by a reliable set of supporting measurements. These may include characterization by PCT isotherm, TPD, X-ray and neutron diffraction, NMR, FTIR and Raman measurements among others.

To give an example, the measurement of hydrogen uptake or release (kinetics) may appear quite similar for extremely dissimilar chemical processes. Two examples are presented to show how desorption measurements from two different types of hydrogen storage materials can look quite similar (no distinguishing features other than being measured at different temperatures and showing differing overall rates) even though the mechanisms of hydrogen uptake and release are very different.

In the first example, the room temperature release of hydrogen from a classic AB5 (LaNi5-based) intermetallic hydride is shown in the kinetics measurement of Figure 11.

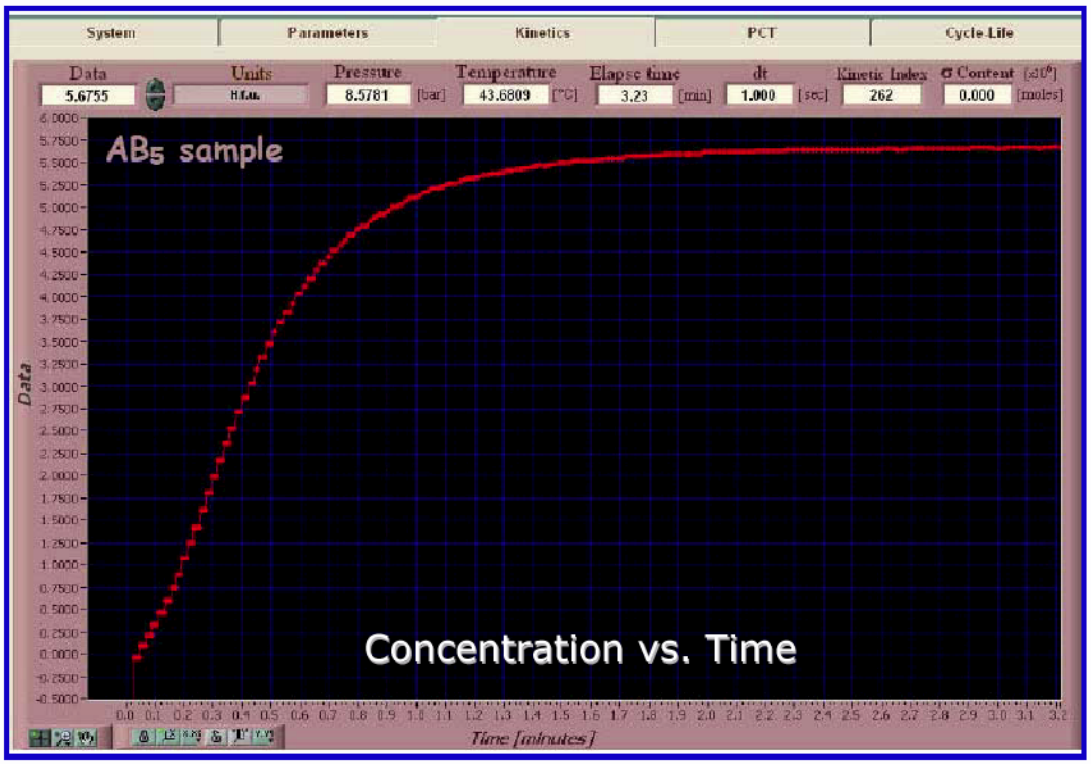

Figure 11. Kinetics measurement of $LaNi_5$ Intermetallic compound with a single phase transition. The experiment was conducted under isothermal conditions at room temperature. Units in H per formula unit released.[42]

Figure 11 was made by measuring the increase in pressure using a calibrated volumetric instrument as a sample of approximately 5 g desorbed hydrogen. For the most part, this material exhibits the classic kinetics profile of a single phase-transition from the intermetallic hydride compound to a metal alloy with some hydrogen in solid solution (commonly referred to as beta and alpha phases, respectively). An intermediate crystal structure transition is known to occur (gamma phase), but for current illustrative purposes the kinetics can be considered as a single chemical reaction. Atomic hydrogen is released from its interstitial binding site in the host metal's lattice, diffuses to the surface and combines with another hydrogen to form gaseous hydrogen, which gives rise to the measured increase in pressure.

The capacity change as a function of time represents the material's total hydrogen content change (in H per $LaNi_5$) during the desorption transition from $LaNi_5H_6$ to $LaNi_5$. This does not mean that the concentration of hydrogen in the hydride is changing but rather that the sample's total composition of the two phases is changing with time. The sample's total composition at any one time is:

$$(1 - X(t))LaNi_5H_6 + X(t)LaNi_5 \qquad \textbf{Equation 21}$$

with boundary conditions X(t=0) = 0 and X(t=∞) = 1.

This transition from solid solution α-phase through the γ-hydride phase to the β-hydride phase in $LaNi_5$ is best observed by performing a series of equilibrium PCT measurements (Figure 12). Absorptions are shown for increasing temperatures in purple to red and desorptions at the same set of temperatures in blue. The flat portion (plateau region) of each measurement is present because of the equilibrium coexistence of the α-phase and β-phases (or γ-phase as the case may be). On moving from left to right along an absorption plateau the measured sample is being transformed, gas aliquot by gas aliquot, from the α-phase intermetallic alloy to the β-phase hydride. The reverse is true going from right to left across the desorption plateau.

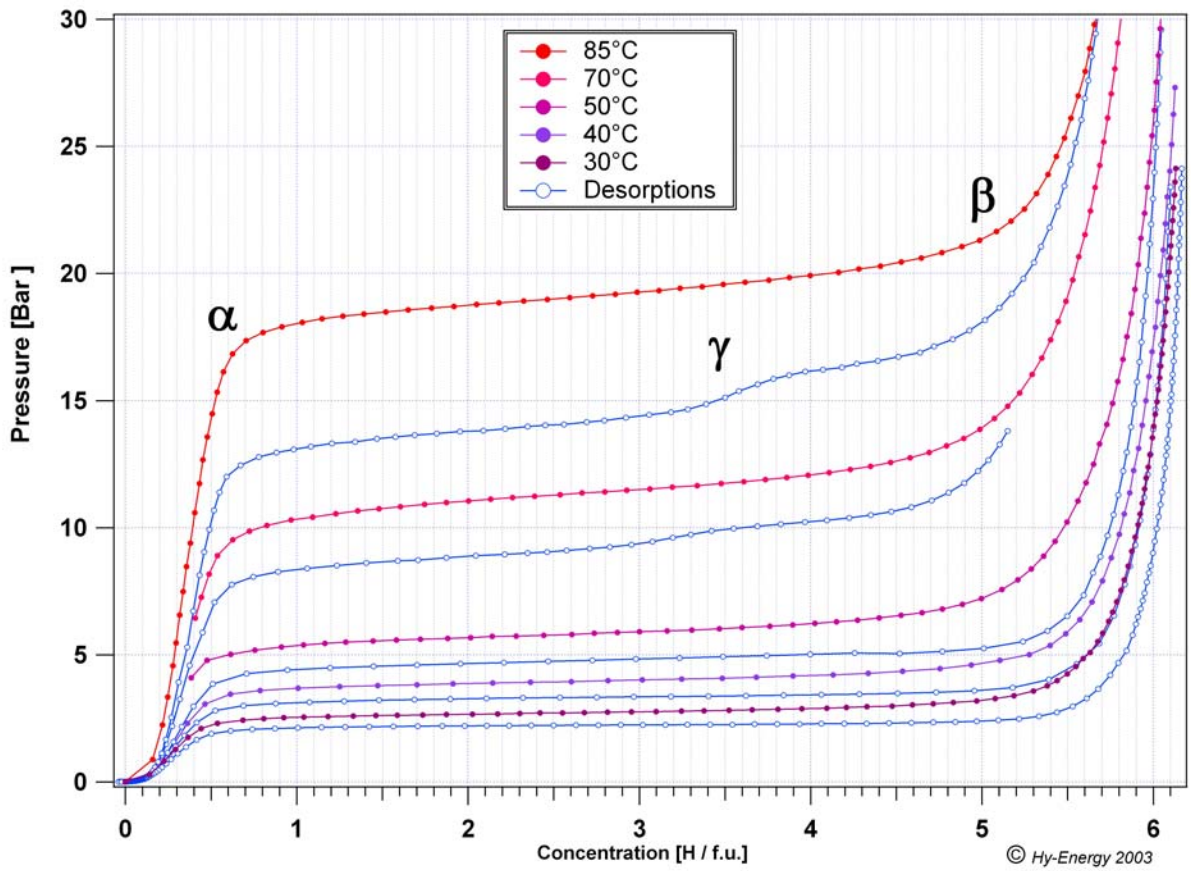

Figure 12. PCT measurements of $LaNi_5$, a classic metal hydride. The transition pressure at various temperatures illustrates the thermodynamic dependence of transition between the solid solution and intermetallic hydride phases.[42]

Hydrogen sorption through a single gas-solid phase transition such as the one above represents the ideal case for studying the mechanisms of hydrogen sorption kinetics. However, today's advanced hydrogen storage materials are becoming increasingly complex. They can consist of materials that undergo multiple hydriding reactions, complete structural decompositions and potentially the long-range transport of reactants

other than hydrogen. And yet, these complex processes may present absorption and desorption kinetics that are quite similar at first glance to a classic hydride.

Our second example shows the measurement of the third cycle of gas desorption from titanium-doped alanate-amide mixture with a starting composition of

$$LiH + Al + 2LiNH_2 + Mg + TiF_3 \qquad \textbf{Equation 22}$$

It should be noted that, unlike the intermetallic hydride example above, this is not an isothermal measurement but rather a ramp and soak-style TPD measurement. However, within the isothermal portion of the measurement at t > 0.4 hours, the desorption resembles the classic kinetics curve of Figure 11 to a large extent.

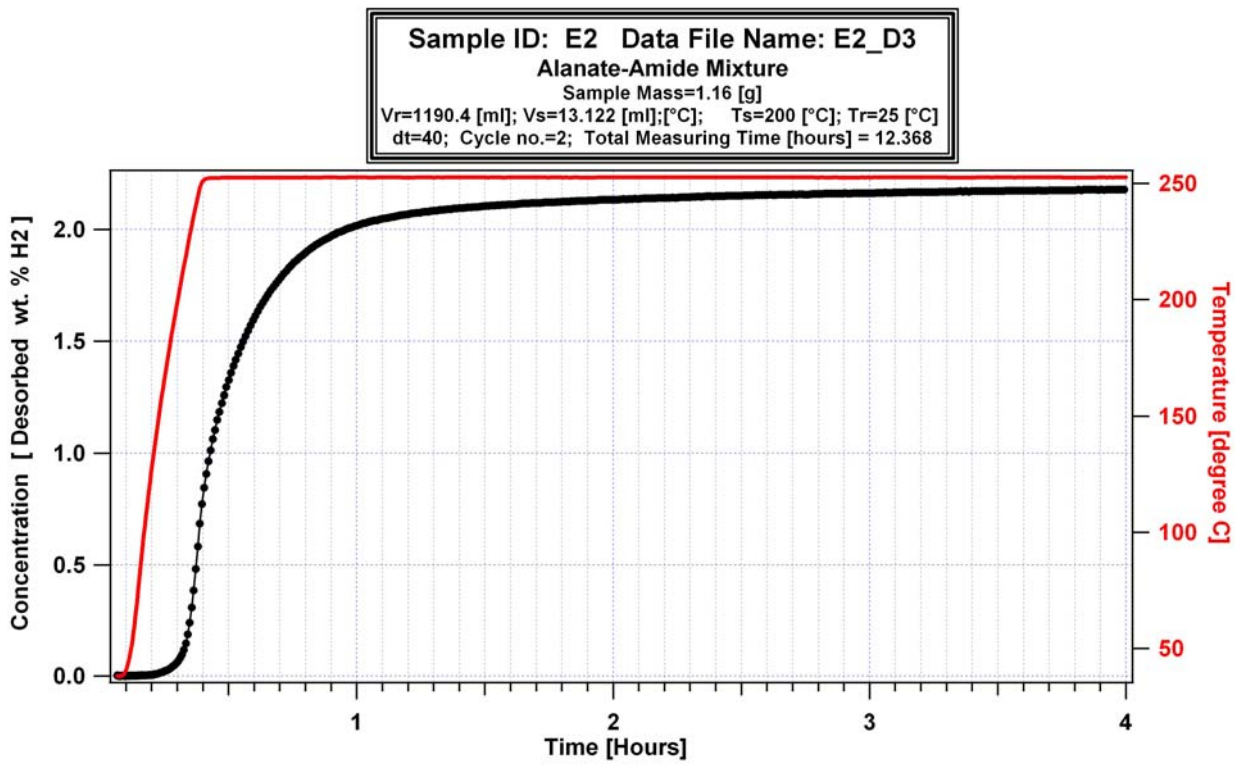

Figure 13. TPD measurement of the alanate-amide mixture described in Equation 22.[43]

Without doing a more detailed PCT isotherm, it may be incorrectly assumed by looking only at the kinetics measurement that the desorption involves a single reaction. By performing an equilibrium desorption PCT measurement of the same sample (Figure 14) in the fourth cycle makes it clear that the continuous evolution of gas observed in the kinetics measurement of Figure 13 is the result of a complex series of chemical reactions instead of the single phase-transition as in classic hydrides.

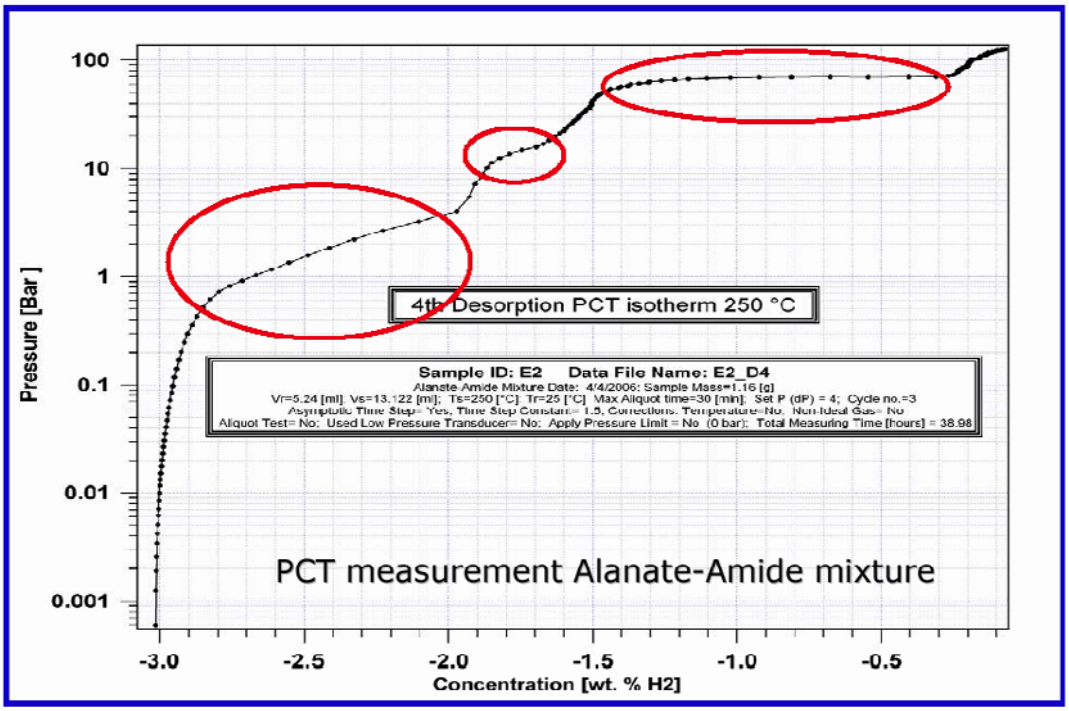

Figure 14. PCT diagram of the alanate-amide mixture described in Equation 22.[43]

Each of the three distinct plateaus corresponds to a different chemical transition within the material. This complex system has not been optimized or fully characterized by any means, but from what is known of its complex hydride and amide precursors, these reactions undoubtedly involve chemical decomposition and re-formation reactions. For hydride and amide products to form, this necessitates the long-range transport, not only of hydrogen, but also of other reactants including one or more species of Li, Al, and N. Later studies that coupled a high-pressure mass spectrometer to these same experiments showed the presence of ammonia in the evolved gas, adding additional complexity to the gas-solid system.[43]

3.5.2Discrete Kinetics Measurements

In the opening paragraph of Kinetics, it is noted that the difference between kinetics and capacity is that kinetics are inherently dynamic while capacity measurements are taken at thermodynamic equilibrium. However, in principal, each data point on a PCT isotherm is the equilibrium concentration after the gas/material system has been perturbed from equilibrium. In fact, a volumetric PCT measurement consists of a series of small doses which, when measured with respect to time, individually represent measurements of kinetic properties. More precisely, with each dose (or aliquot of gas), a specified over-pressure (or under-pressure) is applied to the sample and the system is allowed to reach equilibrium through a dynamic process. The last data point of each kinetics measurement, which is assumed to represent equilibrium in composition, pressure and temperature, provides a single point on the PCT curve. This process is performed

repeatedly until there are enough equilibrium data points collected to construct a full PCT diagram.

In a volumetric measurement where the quantity of gas is controlled (and thus the reactions are controlled), each dose is performed within a narrow band of concentration and pressure. In this sense the time-resolved data of a PCT measurement can be thought of as a series of mini-kinetics measurements that can separate different portions of the overall sorption process. This is demonstrated using the same PCT isotherm measurement of the second example above. Figure 15 presents the pressure time plot of what was used to create the PCT isotherm of Figure 14.

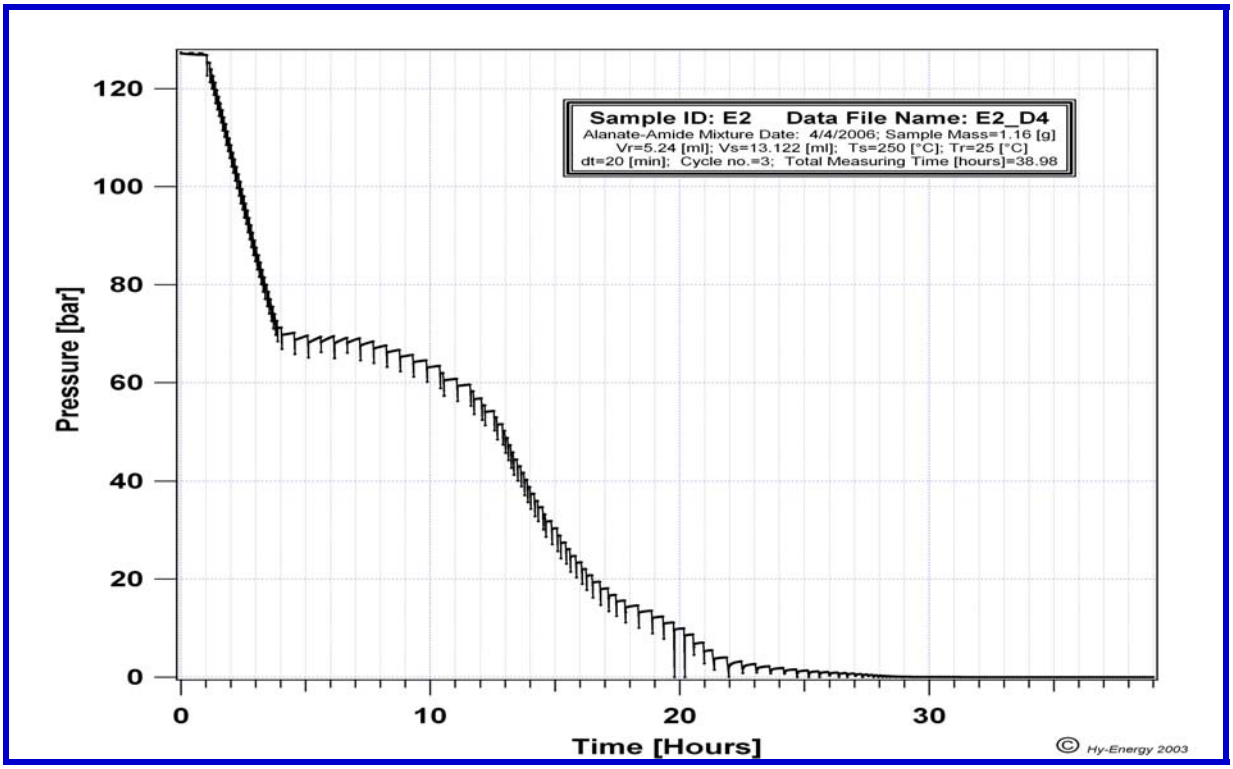

Figure 15. Pressure versus time plot of data used to create the PCT diagram of alanate-amide mixture in Figure 4.[43]

By controlling the dosing pressure so that only one reaction occurs at a time, it is possible to determine relative reaction rates of each independent reaction. Indeed with the same applied pressure differential of 2 bar, the desorption rates for the three observed reactions from the highest to the lowest pressure plateaus are 0.29, 0.10 and 0.15 wt.%/hr. Note that such data is not only useful for determining the kinetics of individual reactions, but it also demonstrates that due to poor kinetics the final PCT isotherm was derived from relatively non-equilibrium conditions.

These examples serve not only to demonstrate the wide range of complexity encountered in the development of advanced storage materials, but also point to the importance of utilizing multiple methods of characterization in evaluating what may at

first appear to be a simple sorption process. Given limited time and resources, the ability to perform different measurements simultaneously in a single experiment becomes a real advantage in understanding complex systems.

3.5.3 Matching Experimental Setup to the Measurement Purpose

From the system performance, materials discovery and development, and fundamental mechanisms perspectives, the process that occurs during the uptake and release of hydrogen is of paramount importance. The key is to gain insight into these processes by designing the experiment or a series of experiments to provide clear and accurate information about the processes involved.

3.5.3.1.1 Experiments for System Performance

For a system level understanding, this may mean, for example, designing experiments to be able to examine material from different sections of a test bed after performing kinetics measurements under a different set of charging or discharge conditions. In such a case, being able to access the material multiple times would be important. Or perhaps it is the heat produced and heat transfer that is the focus of interest. Then one may want to instrument a test bed with multiple temperature sensors at different position in the material and then to run a series of kinetics measurements under different test conditions.

To gain useful system performance information, enough material should be tested to provide results representative of the material's behavior in a full-sized operating storage system. In general, this means between 10 grams and 1 kilogram of storage material. 100 grams is probably a good tradeoff between the practical issues of synthesis and handling of the materials and a characteristic, uninterrupted volume of material that would be found in a large-scale system. For kinetics measurements it will be important to be able to measure hydrogen flow rates into or out of the test bed. If the material performance is already fairly well characterized, it may be possible to use flow meters to study sorption/desorption rates at a system level. However, with the exception of Coriolis-based flow measurement devices that maintain accuracy over two decades, conventional flow meters generally have fairly narrow dynamic measurement ranges (often less than one decade). This is a severe limitation when sorption/desorption rates may vary over several orders of magnitude depending on state of charge, temperature and pressure.

Mass change measurements on a system scale are also possible, but complicated by the connections between the system on a balance and the need for hydrogen transfer and potential heating or cooling. System scale kinetics measurements are most easily performed volumetrically using a normal regulator for sorption and a backflow regulator for desorption to maintain a constant or simulated pressure profile on the storage system. In its most simple form the amount of material is limited by the largest practical calibrated volume for a single desorption dose.

One example of scale up measurements were the experiments performed by Gary Sandrock on Ti-doped alanates.[44] Hydrogen absorption/desorption studies were performed on a simple high-pressure cylindrical vessel shown in Figure 16 designed to simulate the heat transfer and gas impedance conditions of a larger bed. This 316 SS reactor has a 4.6cm OD, 0.38cm wall thickness, about 11.4cm internal length and was pressure rated to 3000 psia (204 atm) at 350˚C. It was loaded with about 100 g of bicatalyzed $NaAlH_4$ (78 g of $NaAlH_4$ and 22 g of $Ti(OBu^n)_4$ + $Zr(OPr)_4$). The reactor had internal thermocouples but no internal heat exchange structure. The reactor was heated within an air furnace. Absorption kinetics and capacity were measured volumetrically and desorption measured with flow meters backed up by a wet test meter (A device to measure gas flow by counting the revolutions of a shaft upon which water-sealed, gas-carrying cups of fixed capacity are mounted).

Figure 16. Scaleup (100 g) reactor with end cap removed in Ar-glovebox to show catalyzed alanate.[44]

The higher than expected initial charging kinetics, combined with limited heat transfer, results in exothermic temperature excursions, as is common with hydrides. An example is shown in Figure 17 for the 4th hydrogen absorption. The fully dehydrided bed was heated to 155˚C and then charged with hydrogen at 172 atm. Within one minute, the exothermic hydriding reaction resulted in an internal temperature of 234˚C. This is essentially the van't Hoff temperature for $NaAlH_4$ at this applied pressure. However, the melting point of $NaAlH_4$ is only 182˚C; thus, any $NaAlH_4$ formed during the first 0.5 hr of Figure 17 would do so directly into the liquid phase. As one can see in the figure, a thermal arrest occurs at 182˚C due to solidification during cooling (about t = 0.6-0.8 hr). This is precisely as expected and shows that liquid $NaAlH_4$ was formed during the exothermic temperature excursion associated with the rapid initial charge.

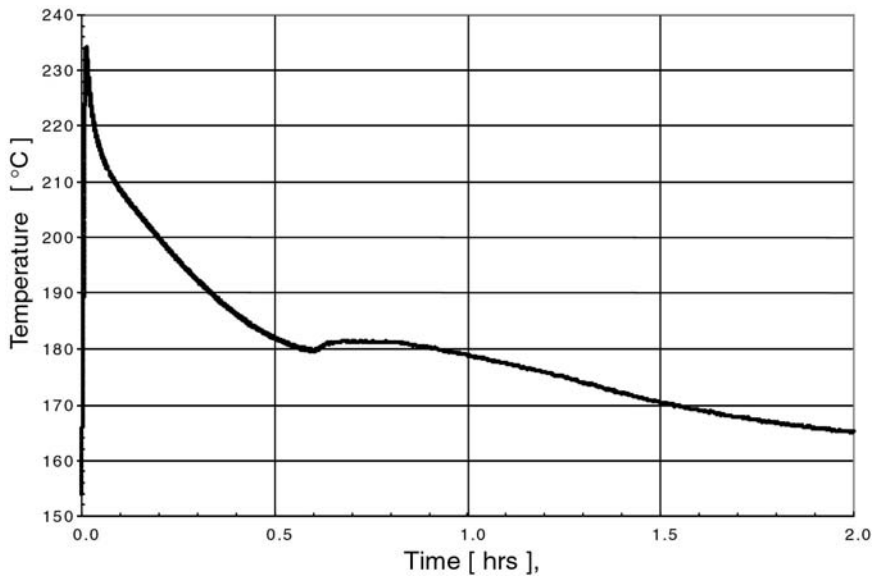

Figure 17. Exothermic temperature excursion during scaleup bed charge half-cycle 4A (Pi = 172 atm, Ti = 155˚C).[44]

It is natural to ask if such melting could be detrimental to the subsequent performance of the alanate bed. From subsequent absorption and desorption measurements, the answer seems to be "no" or at least "not much". In fact that series of scale up experiments pointed to a possible benefit of partial melting. When the reactor was opened between cycles 4 and 5 (photograph shown in Figure 16) the material in the bed was found to be sintered into a porous, solid mass. Such a structure may have distinct advantages for actual applications. In particular, such a sintered structure should reduce particulate migration, increase packing densities, allow expansion, and provide a constant internal gas impedance and enhanced safety.

Later, a more advanced test bed (Figure 18) was developed which had thermocouples placed at regular radial spacings and at different depths within the bed to examine heat transfer properties of the material during charge and discharge measurements.[45]

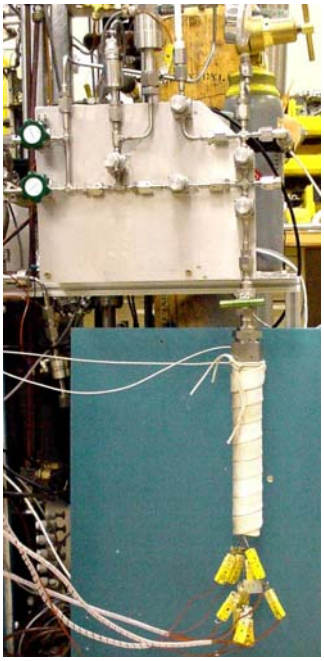

Figure 18. Image of scaled up Alanate test bed with series of internal and external thermocouples.[45]

3.5.3.2Experiments for Materials Development

For materials development, a good approach is to run a series of comparative measurements on different samples while ensuring that all other material properties (sample size, packing density, purity…) and measuring conditions remain as consistent as possible. The experimental setup, sample size and measurement technique should be centered on simplicity and the ability to make comparative measurements as efficiently as possible.

Heat transfer and measurement of the true sample temperature at low gas pressures, in addition to buoyancy corrections at high gas pressures, make kinetics measurements by gravimetric methods difficult if not impractical. These complications are due to the limitation that the sample in a gravimetric analysis system cannot make physical contact with a thermal mass for heat exchange. This can be accommodated by reducing sample size or, in the case of desorption, by using a carrier gas in flow through mode to maintain the sample temperature. Volumetric kinetics measurements on samples ranging in size from a few milligrams to a couple of grams are quite straightforward. A major consideration is that, in particular for materials with elevated enthalpies of formation (> 10 KJ/mol H_2) and good intrinsic kinetics, sorption/desorption rates may be limited more by heat transfer in the measuring equipment than by physical or chemical sorption mechanisms. The flexibility in sample holder design and sample compositions (addition of thermal ballasts) can overcome this problem. With this in mind, it is still very relevant to measure sorption rates under imperfect (non-isothermal) conditions in order to obtain relative hydrogen uptake and release rates and to develop modified materials

with improved kinetic performance. However, it is exceptionally important that materials are measured under essentially the same conditions (pressure, temperature, sample size, perhaps sample packing density) using identical measuring equipment and setup to be able to make quantitative and even qualitative comparisons between materials. Comparison of the intrinsic kinetic properties under the aforementioned instrumental limitations can be further qualified by considering or measuring, for example, differences in the isobaric heat capacity and thermal conductivity among the materials under investigation.

A classic example of such a successful comparative analysis with the goal of developing optimized hydrogen storage materials was the systematic study of increasing levels of $TiCl_3$ additives in $NaAlH_4$. By performing these measurements under identical conditions a clear trend in kinetic performance was observed ultimately leading to key findings in understanding the effect of Ti additives on alanates. Another example of comparative measurements for improved performance of storage materials was through the investigations of many different types of alanate additives by Anton et al.

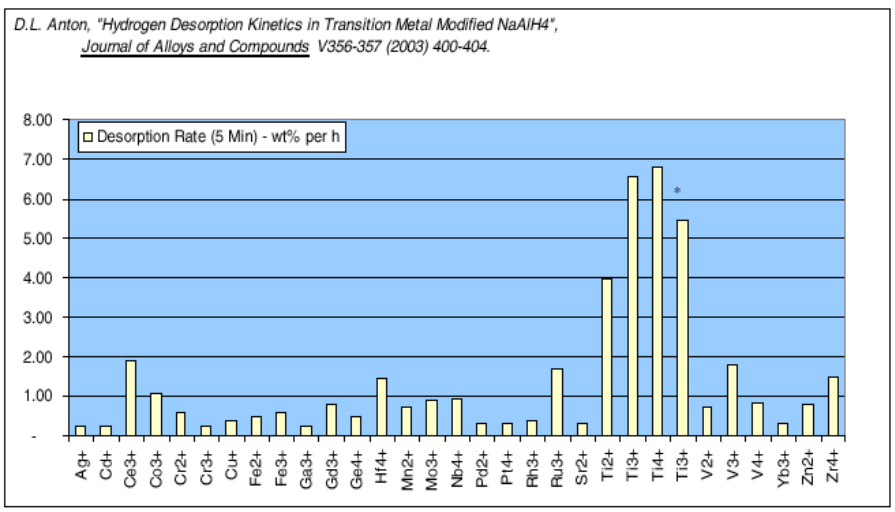

Figure 19. Investigation of different additives for improvement of kinetics of $NaAlH_4$. Dopants are transition metals and rare earth ions.[19]

3.5.3.3Experiments for Fundamental Studies

For basic science experiments, simplicity (reducing the number of free experimental parameters) is key. While it may not be possible to determine rate-limiting mechanisms without specially designed sample cells, sorption and desorption kinetics measurements on standard equipment and laboratory scale samples (e.g. 1 gram) can provide not only relative measurements for materials optimization but also some fundamental insight into sorption processes. Gary Sandrock's work on Ti doping in sodium alanates provides a good example of how detailed kinetics measurements and the determination of activation energies have been employed for improved understanding and development of better hydrogen storage materials.[46] Hydrogen desorption rates were measured at several temperatures for the decomposition of $NaAlH_4$. For convenience, these rates

were determined using a linear fit to the initial portion of each desorption kinetics measurement. The desorption rates for both undoped and 4 mol.% $TiCl_3$-doped $NaAlH_4$ are plotted on a log scale versus 1/T in Figure 20. This is essentially an Arrhenius plot. The effect that Ti doping has on the desorption behavior of $NaAlH_4$ is apparent from these measurements.

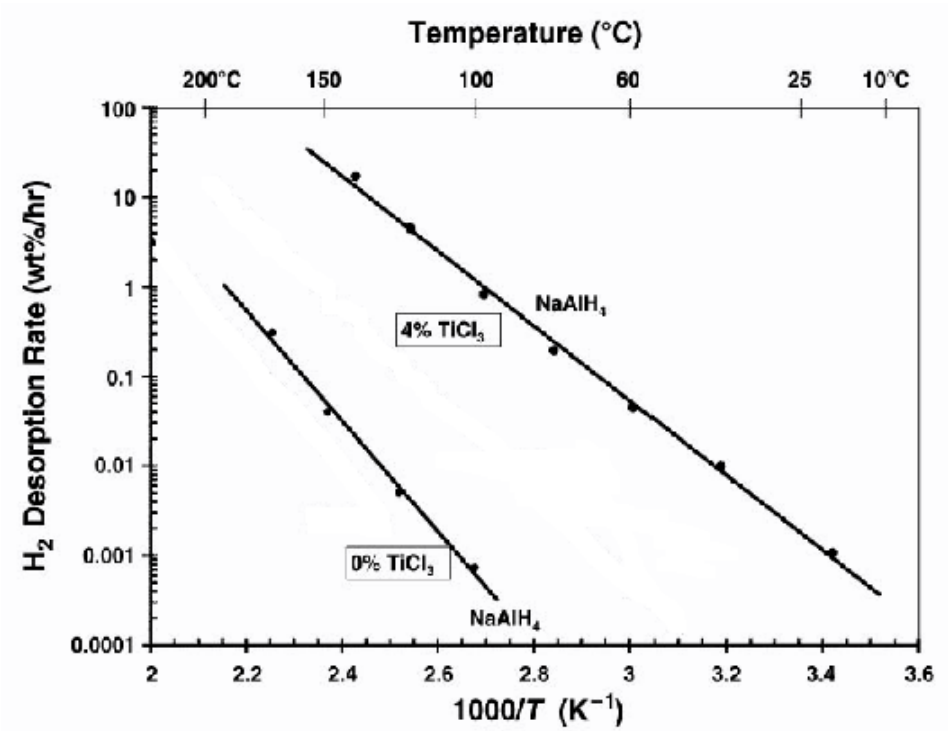

Figure 20. Log desorption rates versus inverse temperature plotted for $NaAlH_4$ with no $TiCl_3$ and 4 mol% added $TiCl_3$ [Original plot modified for simplicity, Na_3AlH_6 removed from figure].[46]

The activation energies calculated from this plot as well as other Ti doping levels are presented in Figure 21. This series of kinetics measurements demonstrate that adding only small amounts of $TiCl_3$ to the alanates significantly reduces the activation energy for hydrogen desorption. It is interesting to note from Figure 21 that increasing the level of $TiCl_3$ in $NaAlH_4$ shows little change in the activation energy. Thus, the chemistry of the Ti-enhanced kinetics is unchanged with Ti concentration. Further improvement in the desorption rates by increased $TiCl_3$ doping is observed through an increase in the pre-exponential factor *A* of Equation 19. This indicates that performance is improved by the increased distribution and access to titanium in the material.

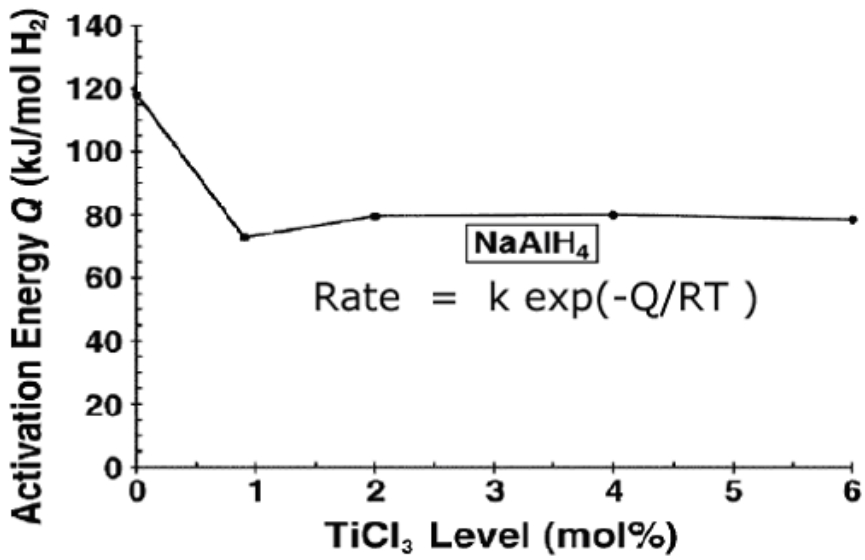

Figure 21. Activation energies Q (= E_A) for $NaAlH_4$ decompositions as a function of added $TiCl_3$ [modified for simplicity, Na_3AlH_6 removed from figure].[46]

If the purpose of the kinetics measurements are indeed to study fundamental mechanisms then it is absolutely necessary to design the experimental measurement equipment to achieve essentially isothermal conditions and at an even higher level of precision, isobaric measurements. This was in fact done with painstaking detail by Goodell et al. for hydrogen absorption and desorption in $LaNi_5$. Their thermal ballast technique is described in detail in the Thermal Effects section of Considerations.

3.5.4Consideration: Efficient Testing

Evolution of hydrogen storage material discovery, development and characterization is directly dependent on the ability to conduct measurements with speed and efficiency. Kinetic activity is often the limiting factor in hydrogen testing. For example, the time required to reach equilibrium in performing PCT measurements is directly dependent on the kinetics of the sample material. Any technique that reduces sample characterization time will help in improving the pace of material discovery and development.

An excellent example of efficient testing used by Gary Sandrock drastically reduces the time required to determine the activation energy of a sample with slow kinetics. To develop an Arrhenius diagram necessary to determine the activation energy of a chemical reaction, several experiments must be performed at different temperatures to determine the relationship between the rate constant K and temperature. Instead of performing a series of isothermal experiments, Sandrock's method changes the temperature of the sample in steps, as shown in Figure 22.

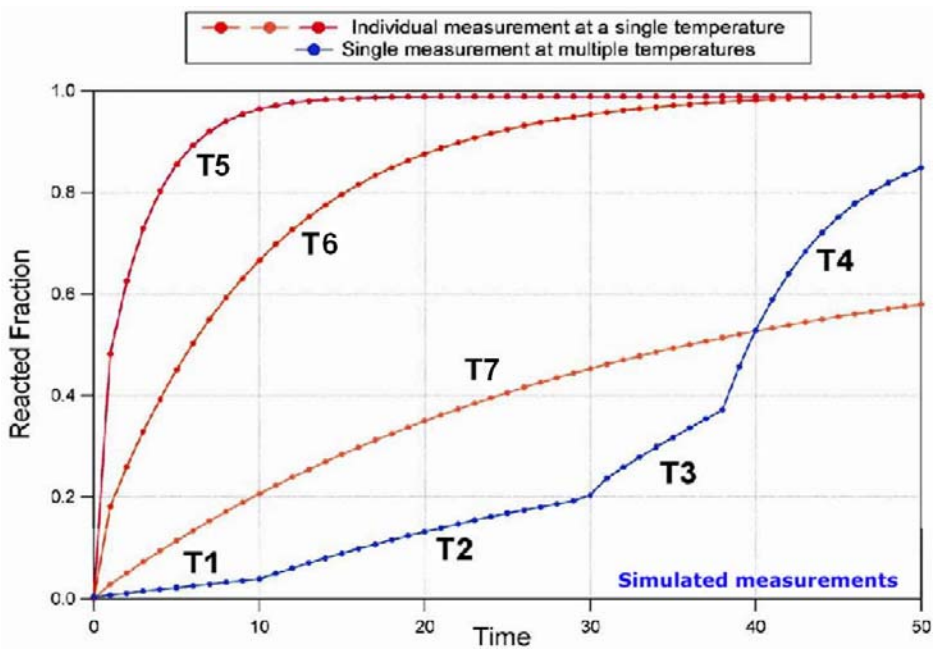

Figure 22. Example of efficient testing in determining the activation energy of a sample with slow intrinsic kinetics. The figure itself is a kinetics measurement used to relate the rate constant to temperature.[43]

Several rate measurements can be performed using this method in the same amount of time as a single isothermal measurement. It is important to remember that the temperature is stepped instead of ramped because isothermal conditions are still required to perform kinetics tests. For such type of measurements to be valid the sample holder and heater design should allow temperatures to be changed and establish a steady on a time scale that is short compared to the kinetic rates. This technique can only be used with samples that have slow enough intrinsic kinetics that the sample temperature can be increased in several steps before the sample completely desorbs. In addition, rates should be measured when the sample is below about 60% conversion to avoid the impact of changes in reactant concentration on the rate measurements.

3.5.4.1 Kinetics and Capacity

Today, hydrogen storage capacities are typically presented in units of weight percent (wt.%), where wt% is defined as:

$$wt.\% = \frac{mass_{H_2}}{mass_{sample} + mass_{H_2}} * 100\% \qquad \textbf{Equation 23}$$

This makes sense from a practical perspective, because it is a measure of how much hydrogen can actually be delivered from a storage material. And, in this vein, it is important to recognize that ultimately the practical hydrogen storage capacity must be on a systems level that includes the material, containment vessel, heat transfer system,

controls and balance of plant. However, from the perspective of a materials development level, it is equally important to be able to quantify capacity in terms of the active material only. In particular, where this becomes important is in the evaluation of improvements of kinetic performance. Since rates are typically being measured in units of wt.% per time, to make a comparative analysis of the effect on kinetics of different catalysts or additives, rates should be compared on an active wt.% capacity basis and not on total capacity. Thus, for this purpose, we may define

$$Total\ wt.\% = \frac{mass_{H_2}}{mass_{sample} + mass_{H_2}} * 100\% \qquad \textbf{Equation 24}$$

$$Active\ wt.\% = \frac{mass_{H_2}}{mass_{active\ sample} + mass_{H_2}} * 100\% \qquad \textbf{Equation 25}$$

The mass of the active sample only includes the mass of material that participates in hydrogen storage and the mass of the sample is the total weight of the sample including both the active and inactive material in the sample. Another possible way to perform such a comparative analysis is to use rates based on reacted fraction per time rather than absolute capacity values. As will be seen in the next section, for comparative kinetics it can be very important to present capacity in terms of reacted fraction or active wt.% rather than true wt.%.

3.5.4.2Active Capacity

For example, $NaAlH_4$ doped with $TiCl_3$ will react during the milling preparation process to form NaCl according to:[45]

$$NaAlH_4 + xTiCl_3 \rightarrow xTi + 3xNaCl + 3xAl + (1-3x)NaAlH_4 + 3xAl + 6xH_2 \qquad \textbf{Equation 26}$$

This means that only

$$\frac{54(1-3x)}{54+154.5x} \qquad \textbf{Equation 27}$$

of the sample, representing the fraction of active sodium alanate to the total sample, is active for hydrogen uptake and release. Without taking this into account, improvements in alanates by doping with 6 mol% vs. 2 mol% $TiCl_3$ would be underestimated by up to 30% (Figure 23). In this case, this has little impact on the conclusions with respect to the level of dopant since the correction actually improves the rates with increasing levels of doping. However, another example may serve to demonstrate how this effect could impact such an evaluation.

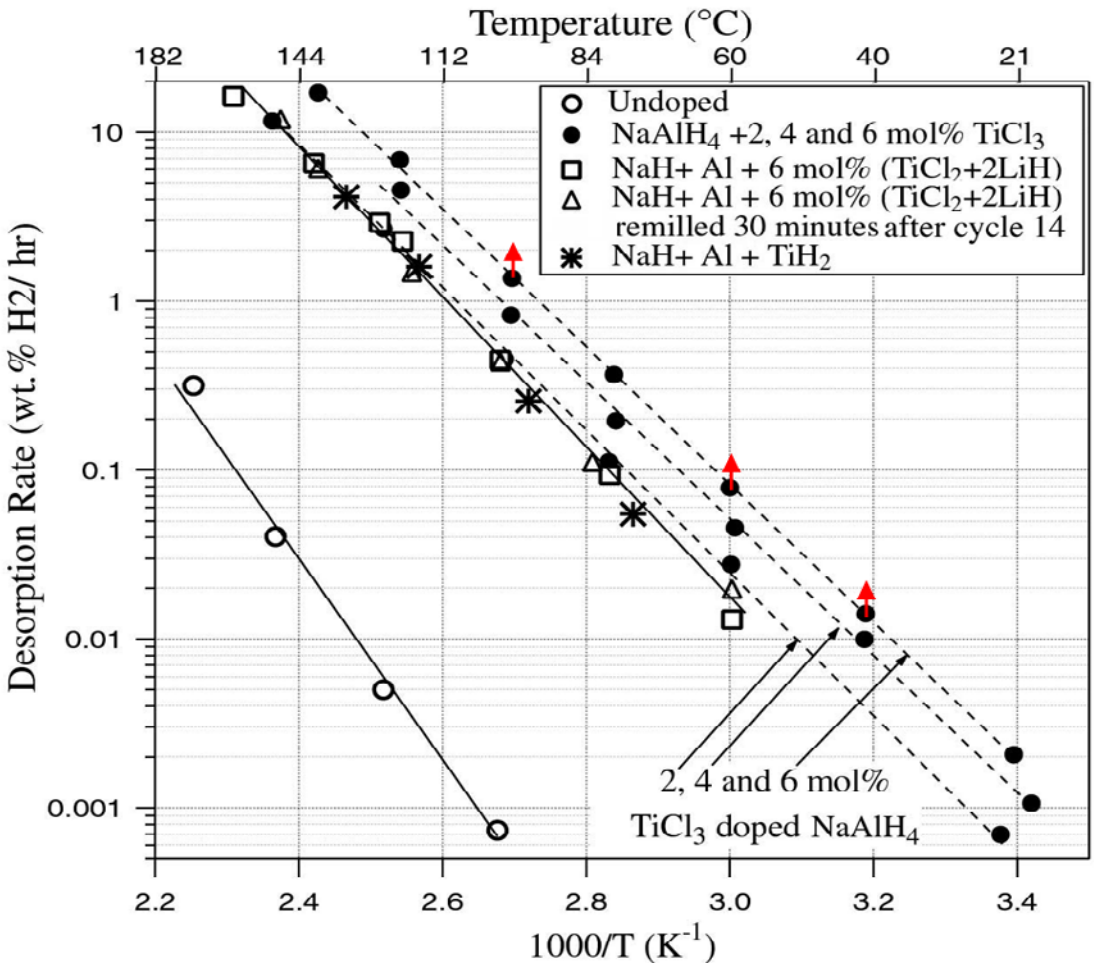

Figure 23. Arrhenius plot comparing desorption rates of $NaAlH_4$ Generation II, III-D, and III-E alanates (rates: II on a total weight basis, III-D and III-E on a NaH + Al weight basis). Red arrows indicate change in data points on converting from a total to an active weight basis.[47]

To investigate the effects of active capacity versus total capacity on kinetics measurements, a sample was tested using only TiH_2 instead of $TiCl_3$.[47] In this case, a mixture of NaH, Al, and TiH_2 in a 1:1:1 composition was mechanically milled and tested for hydrogen absorption and desorption. From an applications perspective, TiH_2 as a precursor should overcome the problem of capacity loss associated with the formation to Na-halides when using Ti-halide precursors. This composition did absorb hydrogen (130˚C and 82 bar H_2) to form $NaAlH_4$. In this case, the inactive component (TiH_2) makes up almost half of the samples mass. Thus rates would be off by a factor of 2 if capacity were measured on wt.% basis using the sample's total weight. However, by plotting rates on an active material mass basis (NaH + Al), the desorption rates are nearly identical to those of the indirectly doped material and the 2 mol% $TiCl_3$ doped alanates (Figure 23). Had the total weight of the sample been used, an incorrect conclusion may have been drawn about Ti-hydride vs. Ti-halide additives. With optimization, kinetics may be achieved without a severe degradation in hydrogen storage capacity. This example of kinetic analysis based on active versus total weight

capacity serves to demonstrate that even small details in how the analysis is performed can have a big impact on the conclusions and ultimately on decisions concerning the direction of materials research and development.

Note that it may be better to report results for this type of analysis in terms of reacted fraction. Capacities reported as wt% of the active material can be misleading if not fully and carefully explained, because the capacity reduction that accompanies additives and catalysts is suppressed.

3.5.5Consideration: Activation Effects

Activation effects are important in kinetics measurements because the kinetic character of a reversible storage material can change drastically during the first five to ten cycles. The change in kinetic character is most significant early in cycling and gradually approaches the intrinsic kinetic character of the material. In application, a hydrogen storage material will typically cycle hundreds, if not thousands, of times so it is important to characterize the intrinsic kinetics in order to evaluate a material's suitability for end-use. It is also important to run samples of new materials through several absorption/desorption cycles to determine their true intrinsic kinetic character. While the activation process is time-consuming, it is better than missing a viable storage material because its kinetic properties appear uninteresting after the first few cycles.

Pre-reacted sodium alanate is an excellent example of kinetic activation effects. Figure 24 is kinetic data taken from a cycling experiment on sodium alanate and clearly shows the drastic impact activation effects can have on kinetic character.

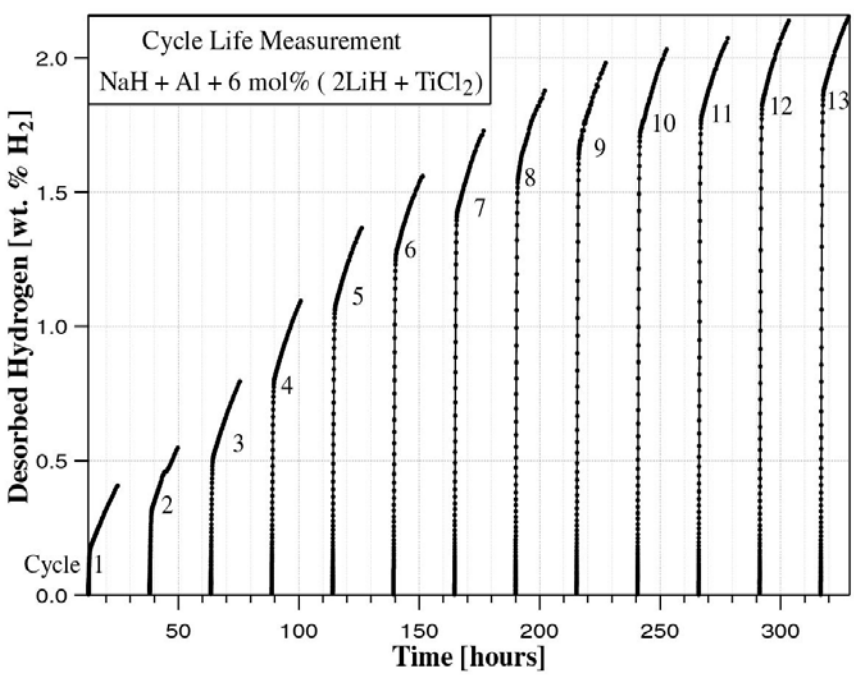

Figure 24. The kinetic activation effects of pre-reacted sodium alanate. The marked increase in desorbed hydrogen indicates increasing kinetic rates.[47]

Each desorption measurement is taken in a fixed time interval so the increasing hydrogen desorption indicates that the kinetics of the sample are improving. The rate of hydrogen evolution increases markedly the first five cycles and gradually approaches the intrinsic kinetic rate from cycle 5-13. The class of pre-reacted sodium alanates would have been completely disregarded if judgment were passed based only on the kinetic character and capacity of the first few cycles.

Digging a little deeper into the kinetic character of sodium alanate, it is interesting to note that there are two distinct rates in each desorption cycle in Figure 24. Each represents a separate step in the two-step equilibrium desorption reaction.

$$NaAlH_4 \rightarrow \frac{1}{3} \quad {}_3 \quad {}_6 + \frac{2}{3} \quad + \quad {}_2 \rightarrow \quad + \quad + \frac{3}{2} \quad {}_2 \qquad \textbf{Equation 28}$$

The difference in the kinetic rates of the two reactions is probably due to the difference in the thermodynamic stability of $NaAlH_4$ and Na_3AlH_6. $NaAlH_4$ is less stable than Na_3AlH_6 and forms at a higher equilibrium pressure (Figure 25). In these desorption measurements, the under-pressure is below both equilibrium plateau pressures, allowing the decomposition of both alanate phases. However, the pressure difference driving the desorption reaction from $NaAlH_4$ to Na_3AlH_6 (DPd (1)) is greater than for Na_3AlH_6 than for NaH (DPd (2)), leading to higher kinetic rates for $NaAlH_4$ than Na_3AlH_6. It is important to note that the situation is exactly the opposite during absorption measurements. The lower plateau pressure of the NaH to Na_3AlH_6 transition would provide a greater driving pressure differential (DPa (2)) compared to the Na_3AlH_6 to $NaAlH_4$ transition (DPa (1)). Thus, in absorption, higher kinetic rates would be observed for the reverse NaH + Al to Na_3AlH_6 step in the reaction of Equation 28.

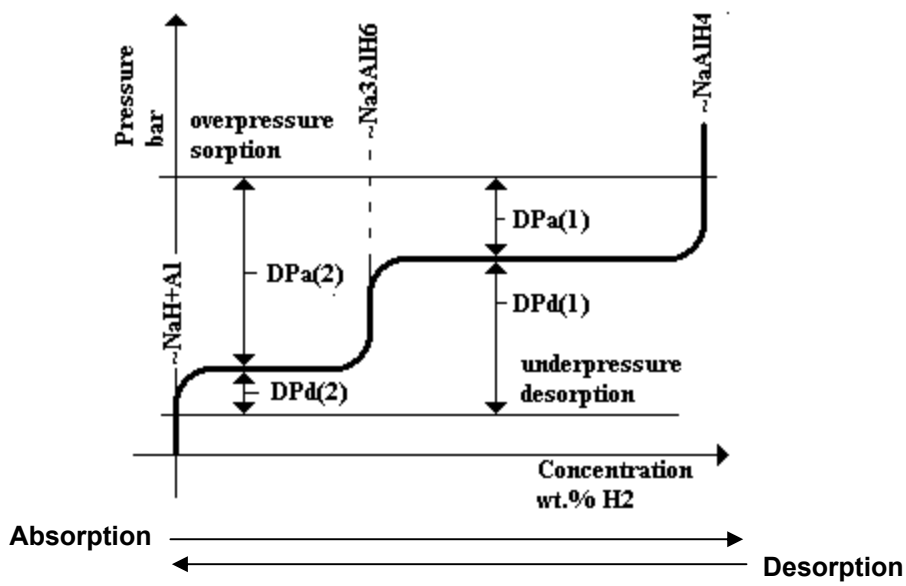

Figure 25. The reaction follows the equilibrium pressure (darkest line) from bottom left to top right for absorption and top right to bottom left for desorption. The horizontal section of the equilibrium pressure line represent phase transitions (reactions), the vertical lines represent the alanate compounds as indicated.

At first glance it appears that only the first reaction in Equation 28 is affected by activation because nearly all of the increased desorption capacity occurs during the first section of each desorption profile. As the material is cycled, the $NaAlH_4$ to Na_3AlH_6 reaction becomes more active while the Na_3AlH_6 to NaH reaction remains constant. This is easily rationalized with the aid of Figure 25. Before the first hydriding of the material, the sample is in its as prepared NaH + Al state. After the first charging which is incomplete (a1), the sample is dehydrided (d1) but can not completely desorb all of the hydrogen taken up in the first absorption due to the poor desorption kinetics of the second Na_3AlH_6 to NaH step and the fixed absorption/desorption times used for each cycle. This creates a permanent offset in total hydrogen concentration. During subsequent cycles (a2-d2 and a3-d3), only the $NaAlH_4$ to Na_3AlH_6 reaction improves (activates) because the NaH to Na_3AlH_6 to has *already* been taken to completion in the first cycle. It is important to remember that Figure 24 presents desorption rates only and not both sorption and desorption rates.

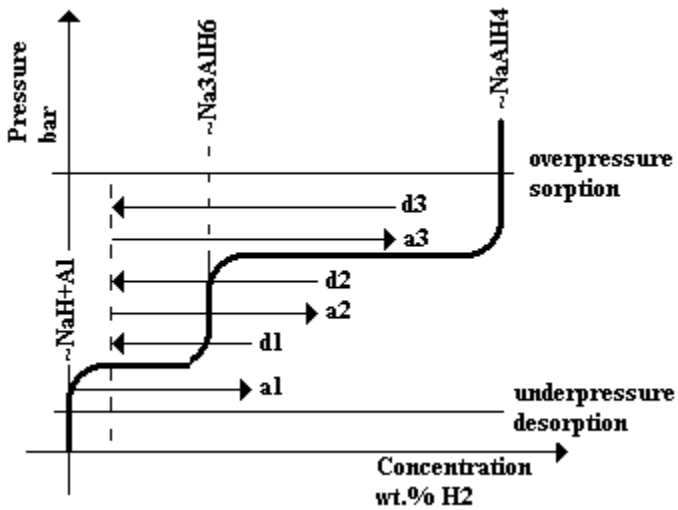

Figure 26. Concentration offset caused by incomplete desorption. Due to thermodynamic limitations, the sample cannot be fully desorbed during the experiment, which causes the concentration to offset.

3.5.6Consideration: Gas Impurities

3.5.6.1Retardation

Retardation in kinetics occurs when impurities such as CO_2, H_2O and NH_3 in the H_2 gas stream react with storage material surfaces, leading to decreased kinetic activity. The gas stream impurities occlude catalytic sites and diffusion pathways and can be difficult to desorb from the storage material because of their high thermodynamic activity. These

effects influence the mechanisms discussed in the theory section. The primary retardation considerations for physisorbing materials like porous media are decreased surface area due to physisorbed impurities and the occlusion of internal pore networks; blocked catalytic sites and diffusion pathways affect chemisorbing materials like metal hydrides. Unlike poisoning (see considerations section in the concentration and capacity chapter), retardation does not significantly affect ultimate hydrogen storage capacity: the sorption curve of a material experiencing retardation asymptotically approaches the original hydrogen storage capacity of the material, albeit at a slower rate.

Sandrock et al. presents an excellent example of the retardation effects of NH_3 on $LaNi_5$ during cycling.[48] Although Figure 27 only shows the beginning of the sorption curve, each arc eventually approaches the ultimate hydrogen sorption capacity dictated by cycle 0. The effects of retardation are often reversed by flushing and subsequent use of high-purity H_2.

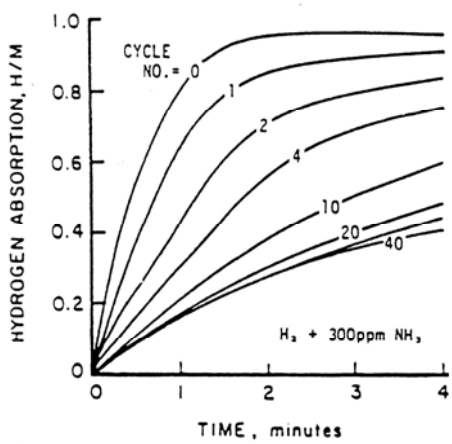

Figure 27. Effects of retardation of NH_3 on isobaric sorption curve of $LaNi_5$ during repeated cycling.[48]

3.5.6.2Gas Impurity Effects on Kinetic Performance

An important consideration is whether fresh or recycled gas is used during cycling kinetics measurements. For recycled gas measurements, the temperature of the sample is increased and decreased with each cycle with the sample exposed to the same gas in a fixed gas volume. Thus, the total amount of impurities in the hydrogen gas/system remains the same. When fresh gas is used for every cycle, gas impurities may have a much larger impact on the retardation of the material's kinetics. This is because the gas impurities are strongly bound to the surface of the material and are not released upon desorption. With cycling, the concentration of impurities on the sample increases, degrading the material's storage performance. In this sense the storage material is simply acting as an impurity getter. The advantage with gettering storage materials is that the hydrogen delivered to the application (e.g. fuel cell) will be much higher purity than that provided by the gas supplier. The disadvantage, of course, is that the performance of the storage system may be significantly affected.

As a side note, kinetics measurements performed on gravimetric systems in flowing gas mode, impurities in the gas stream that react with the sample will be observed as a slow linear increase in weight rather that the curved behavior expected for a true kinetics curve (much like leaks in a volumetric system discussed below). Such behavior should be taken as an indicator that impurities are present in the hydrogen gas stream.

3.5.7Consideration: Leaks

Leaks cause kinetic sorption/desorption profiles to appear linear in time, as opposed to true sorption profiles that exhibit curvature. An example of a leak is demonstrated in Figure 28, where the expected capacity of the sample is 1.39 wt.%. Sorption steadily increased with a linear behavior until a fitting was tightened about an hour in to the experiment. With respect to new materials, one should weigh on the side of skepticism and review the setup and measurements if the results appear too good to be true.

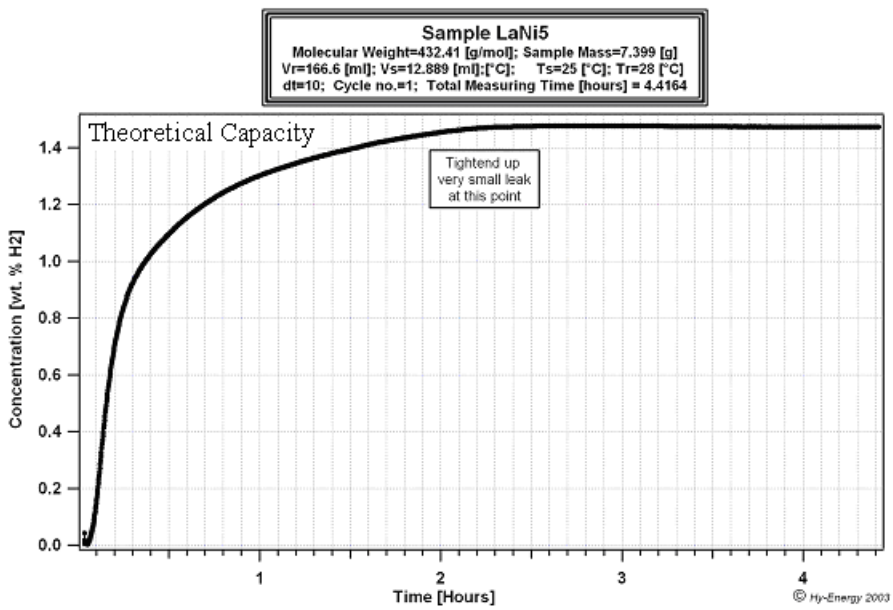

Figure 28. Example of a leak on kinetics measurement. A little after an hour in to the experiment, the leak was eliminated.[42]

3.5.8Consideration: Pressure Effects

Observed kinetic rates are highly dependent on the pressure differential between the gas reservoir and the sample reactor that drives the sorption/desorption reaction. In order to investigate the intrinsic kinetic properties of a material, it is important to reduce the degree of variation in pressure differential during testing. If the system pressure changes significantly during a sorption/desorption reaction, the changing pressure differential will affect the observed kinetic rates and mask the intrinsic kinetic properties of a material. It is, however, important to balance loss in sensitivity in the measurement due to the smaller total pressure change with the ultimate impact that a changing

pressure may have on the kinetic behavior. In the volumetric method, this is done by appropriate selection of the volume reservoir so that the system pressure change is relatively sufficient for accurate measurements but not large compared to the driving pressure differential during reaction.

3.5.8.1 Reservoir Selection

The effect of pressure on kinetics is illustrated in Figure 29 for a 1 g sample of $LaNi_5$. When using a volume reservoir that is too small (10 mL, dashed line), there is not enough hydrogen to hydride the entire sample to $LaNi_5H_6$. Therefore the pressure in the system must be the plateau pressure of $LaNi_5$. The amount of hydrogen in the reservoir is

$$n = \frac{PV}{RT} = \frac{5bar * .01L}{.083 \frac{*}{mol \quad K} \quad 298} = .002 molH_2 \qquad \textbf{Equation 29}$$

A small portion of the hydrogen remains as a gas in the system to satisfy the thermodynamic plateau pressure.

$$n = \frac{PV}{RT} = \frac{1bar * .01L}{.083 \frac{*}{mol \quad K} \quad 298} = .0004 molH_2 \qquad \textbf{Equation 30}$$

The remaining hydrogen, .0016 mol H_2, enters the $LaNi_5$ sample to create .234 g of $LaNi_5H_6$. Because there is not enough hydrogen in the 10 mL reservoir, the system pressure drop is from 5 bar to 1 bar and is equal to the driving pressure differential; such a situation would greatly affect the observed kinetics.

In contrast, a 400 mL reservoir (solid line) under the same conditions has enough hydrogen to hydride the entire sample. The amount of hydrogen in the 400 mL reservoir is

$$n = \frac{PV}{RT} = \frac{5bar * .4L}{.083 \frac{*}{mol \quad K} \quad 298} = .08 molH_2 \qquad \textbf{Equation 31}$$

After complete hydriding, there is .073 mol H_2 that remains in gas phase. The pressure associated with .073 mol H_2 is

$$P = \frac{nRT}{V} = \frac{.073mol * .083 \frac{bar \quad L}{mol \quad K} \quad 298}{.4} = 4.5 \qquad \textbf{Equation 32.}$$

In contrast, a large reservoir under the same conditions has enough hydrogen to hydride the entire sample. After complete hydriding, there is enough H_2 remaining in the gas phase to maintain a pressure of 4.5 bar. The change in system pressure during hydriding is about .5 bar (solid line), much less than the 4 bar pressure differential driving the sorption reaction. Data from the large reservoir experiment would have measured sorption to full capacity. The larger reservoir also provides the quasi-isobaric

sorption kinetics of the $LaNi_5$ sample as the rates are not impacted by a significant change in the driving which is logarithmic with pressure differential.

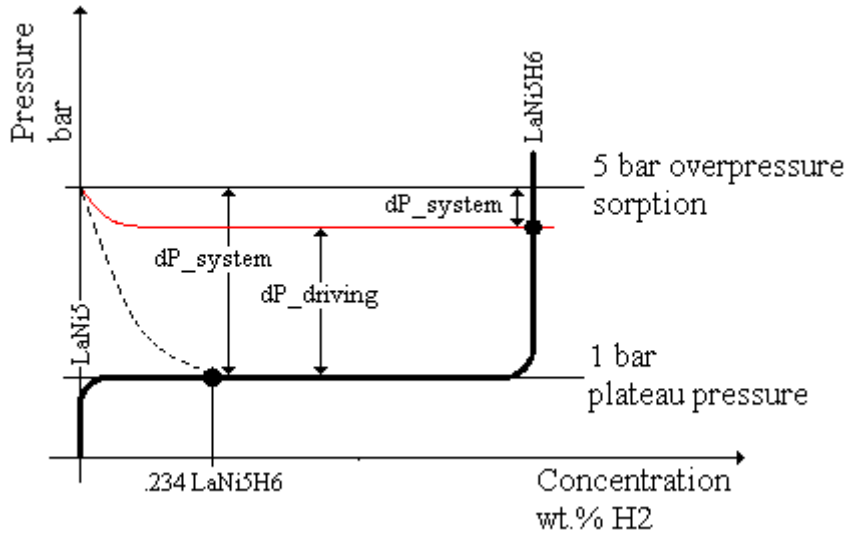

Figure 29. Diagram of the pressure in sorption/desorption system during hydriding reaction. The dashed line represents a test using a reservoir that is too small and the solid red line represents a test using a sufficiently large reservoir.

Another example is presented below to show the important effect of the driving pressure on kinetics. A series of absorption and desorption measurements were performed on $NaAlH_4$ by Weifang Luo who then fit the data with an empirical rate model.[49] In this model, the absorption and desorption rates were dependent not only on temperature but also on the driving pressure (ΔP is the difference between the equilibrium pressure at a given temperature and the applied pressure). The model was validated by comparing predicted desorption curves with measured curves for changing pressures and temperatures. Once validated, the model was then used to predict absorption and desorption rates over a wide range of pressure and temperatures. Absorption rates for the formation of $NaAlH_4$ from Na_3AlH_6, Al and H_2 are presented in Figure 30. These results have important consequences for how such materials would be used in a hydrogen storage application and a first look may be counter intuitive. That is because the plateau pressures increase with temperature for a given applied pressure and the driving pressure differential decreases. Therefore, it is possible that even though mobility increases with temperature, there are practical conditions where it is better to operate at a lower temperature to have faster hydrogen charging of the storage material. This can be seen if one compares the absorption rate at 120°C versus 140°C at a charging pressure of 50 bar in Figure 30.

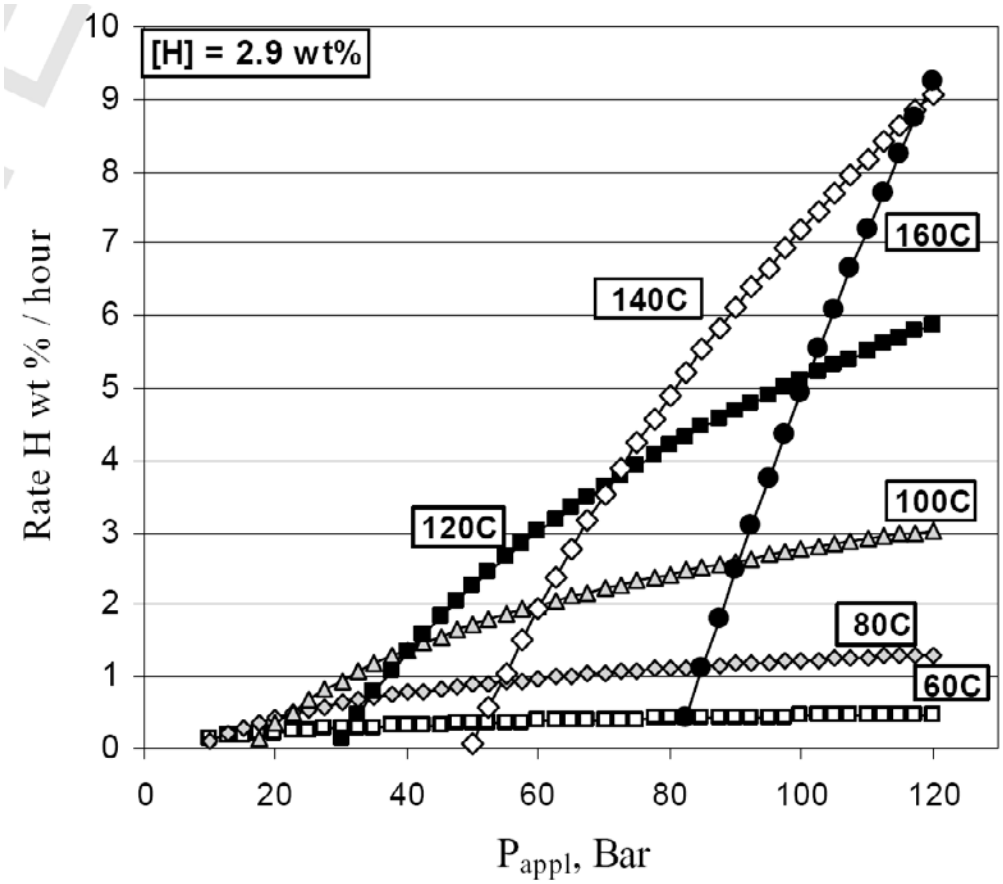

Figure 30. Calculated formation rates of NaAlH4 at several temperatures and applied pressures[49].

3.5.9Consideration: Thermal Effects

Arguably the most significant factor in accurate kinetics measurements is the interplay of thermal effects in the hydrogen storage material, material holder and measurement system. The importance of thermal effects has been discussed on several occasions in this best practices manuscript and will be reiterated. Isothermal or controlled scanning temperature conditions are required to take meaningful fundamental kinetics measurements, in particular when attempting to identify rate-limiting mechanisms. Unfortunately, large temperature variations can occur locally due to the exo- and endothermic reactions and inadequate material thermal conductivity.

3.5.9.1Thermal Ballast

Several techniques have been developed to ensure isothermal conditions and minimize thermal effects. Goodell and Rudman were two of the first to obtain approximately isothermal conditions in the kinetics testing of hydrogen storage materials.[17] Their method is simple: 'thermal ballast' is added to the hydride to increase the heat capacity of the sample and dampen the thermal gradients in the system. Ballast material is carefully paired with the hydride being tested to ensure porosity, non-reactivity and

minimal contamination. The effect of ballast on the temperature excursions upon hydriding is defined by

$$\Delta T = \left(-\frac{\Delta H}{6.2R}\right)\ln\{1+(1-b)x_P\} \qquad \textbf{Equation 33}$$

with ΔH the heat of reaction, b the atomic fraction of ballast and x_P the fractional hydride composition of the sample. Equation 33 is presented graphically in Figure 31.[13] To give an example of the significant thermal effects at work in kinetics studies, 98% of a $LaNi_5$–ballast sample must be thermal ballast in order to limit the temperature change during reaction to within 10K of ambient temperature.

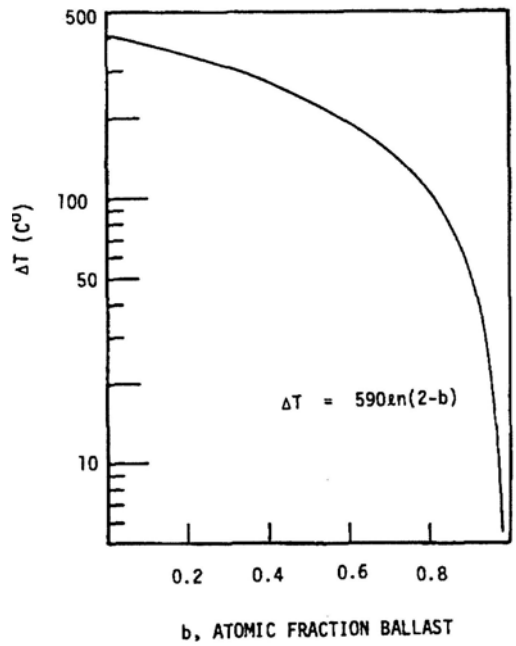

Figure 31. Dependence of the change in the adiabatic temperature during hydriding on the fraction of thermal ballast for the $LaNi_5$-H system.[13]

3.5.9.2Heat Transfer-Maximizing Cell

The second method used to eliminate heat transfer effects is to employ a specially designed testing cell to maximize heat transfer to the sample. Maximum heat transfer is accomplished by using a reaction bed that is as thin as possible along with a thermocouple in the bed itself. Supper et al. designed a specialty cell to eliminate heat transfer effects and study the influence of other parameters on kinetics.[50] In the Supper cell, a thin disk of sample material is sandwiched between a porous metal disk that allows for gas transfer and an integrated water-copper heat pipe that acts as an isothermal heat source or sink. The heat pipe is regulated using an external water loop.

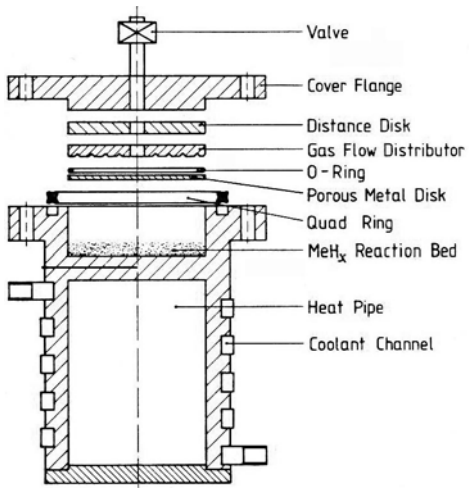

Figure 32. Schematic diagram of the Supper heat-pipe-cooled fast reactor specially designed cell to eliminate heat transfer effects during kinetics testing.[50]

The Supper cell in Figure 32 was used to investigate the effects of temperature and sample thickness on kinetics in $LaNi_{4.7}Al_{.3}$. For the sample with 1 mm bed thickness, increasing the temperature of the sample enhanced the kinetics of the material in agreement with Arrhenius' law.

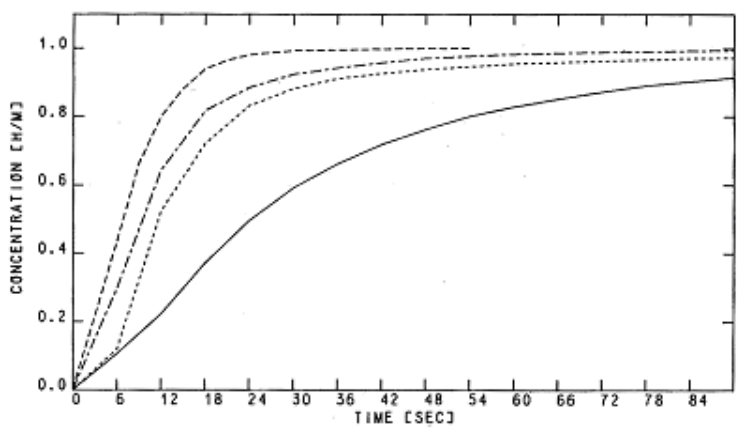

Fig. 3. Absorption reaction rates for $LaNi_{4.7}Al_{0.3}$ (bed thickness, 1 mm; distance from equilibrium, 2 bar): ——, 293 K; - - - -, 303 K; — - —, 313 K; — — —, 323 K.

Figure 33. Measurements taken with the Supper Cell on $LaNi_{4.7}Al_{.3}$ to investigate the effects of temperature and sample thickness on kinetics. Sample bed thickness of 1 mm.[50]

3.5.9.3Effect of Sample Thickness

The effect of increasing sample thickness on the kinetics at various temperatures in the example above is worth noting. As the thickness of the sample bed is increased, the relation between temperature and kinetics is inversed; reaction rate decreases with elevating temperature, as seen in Figure 34. Supper et al. provide an excellent explanation: the increased thickness of the bed increases the temperature in the bed as the reaction proceeds because the heat of reaction cannot be removed effectively. The

van't Hoff thermodynamic relation dictates that the increase in temperature of the sample requires a commensurate increase in the equilibrium pressure in the system. The increased equilibrium pressure reduces the driving pressure differential at higher temperatures because the experiments were all performed at the same distance from equilibrium at the initial sample temperature. This decrease in the true pressure differential because of non-isothermal conditions in turn decreased the rate of reaction. This example of the effect of sample thickness on kinetics shows the complexity of heat transfer effects in drawing conclusions from experimental observation.

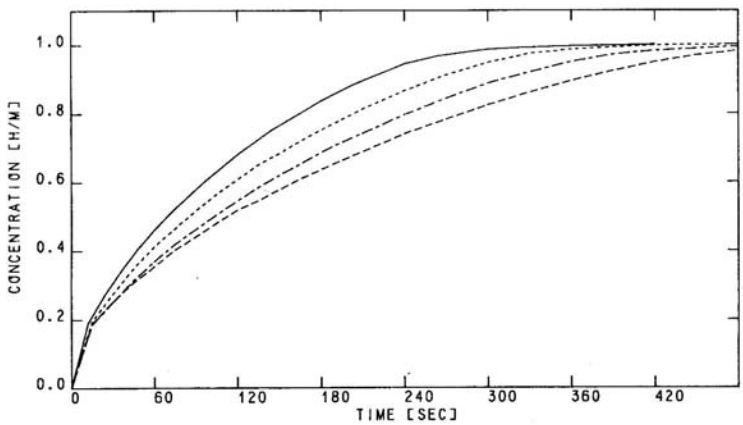

Fig. 6. Absorption reaction rates for $LaNi_{4.7}Al_{0.3}$ (bed thickness, 6 mm; distance from equilibrium, 2 bar): ——, 293 K; - - - -, 303 K; — · —, 313 K; — — —, 323 K.

Figure 34. Measurements taken with the Supper Cell on $LaNi_{4.7}Al_{.3}$ to investigate the effects of temperature and sample thickness on kinetics. Sample bed thickness of 6 mm.[50]

3.6 Approaches to Improve Kinetics

The kinetic behavior of a material is controlled by mechanisms that are determined by specific material properties. Consequently, it should be possible to improve kinetics by altering these material properties.

3.6.1 Alloying

By alloying hydrogen storage materials with catalysts and/or other foreign substances, it is possible to improve kinetics in a variety of ways. In chemisorbing materials, catalysts aid in the dissociation of hydrogen at the gas/material interface and allow for more rapid diffusion of atomic hydrogen into the bulk. A stylized view of how this may affect the rate-controlling mechanisms is presented in Figure 35. Although oxygen (white) may passivate one metal (dark gray), the introduction of a second element (light gray) may provide active sites for dissociation, and may also create diffusion paths into the bulk. Metal hydrides can also be blended together to manipulate the thermodynamic and kinetic properties of the base material. The addition of catalysts in physisorbing media may enable the material to utilize the spillover effect (see associated paragraph in the index). This effect is most pronounced in carbon-based physisorbing media including graphitic sheets and carbon nano-tubes.

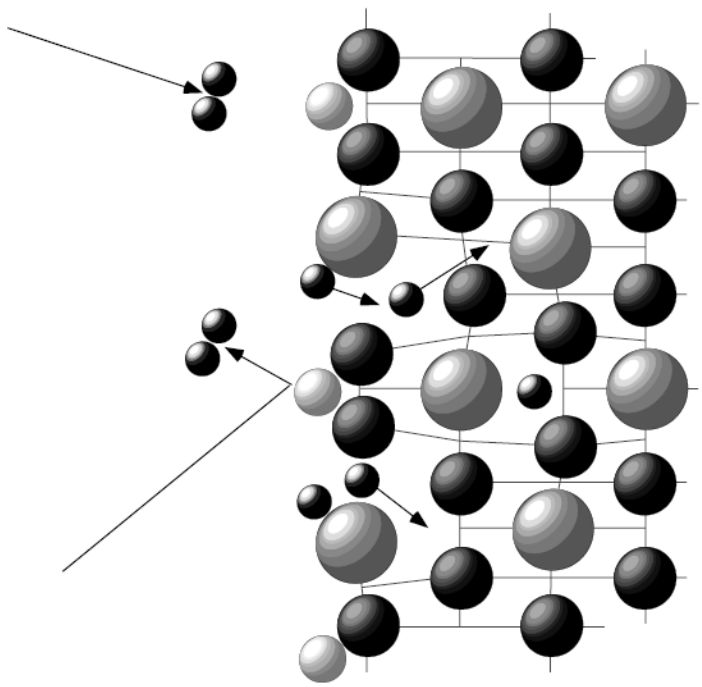

Figure 35. The presence of a second element, either in solution or as a compound, can improve kinetics by providing active sites for dissociation and creating a diffusion path through the lattice.[20]

3.6.2Grain Boundaries

Intimate contact between two different phases may improve kinetics by enhanced diffusion through inter-phase grain boundaries (Figure 36). Intimate contact between separated phases can be produced by mechanically milling a mixture of phases together, by vapor deposition of one phase onto the others, or by the solid-state disproportionation reaction of a compound upon hydriding.

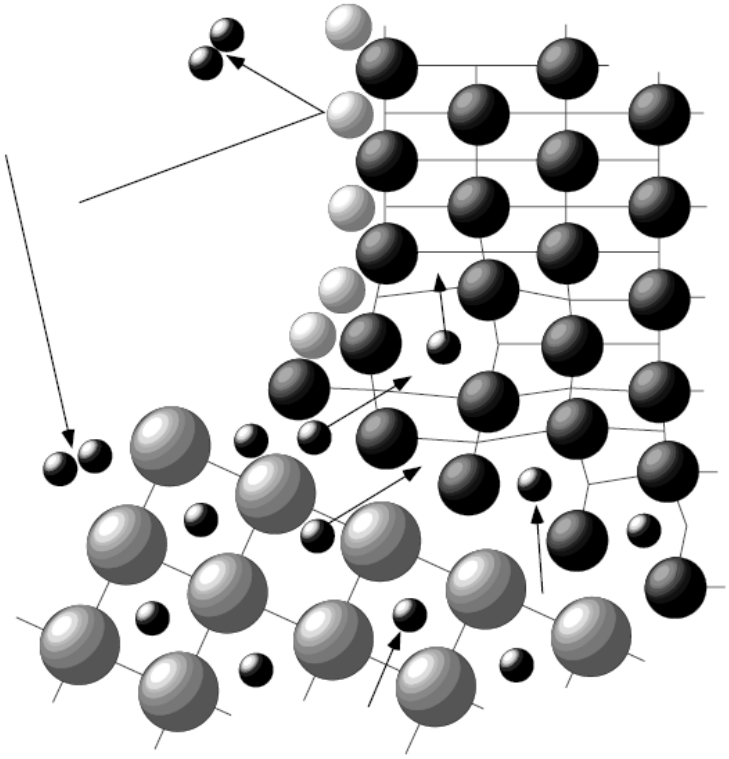

Figure 36. Intimate contact between two different phases may allow atomic hydrogen to diffuse through an active phase and cross the phase boundary into the passivated phase.

3.6.3Decrepitation

Kinetics may be enhanced by crack formation due to lattice expansion during hydrogen sorption. In metal hydrides, these cracks bring clean metal surfaces into contact with hydrogen. The oxygen-free surface may promote the hydrogen dissociation reaction and diffusion into the bulk. This process may also be enhanced in multi-phase systems by cracks that form along inter-phase boundaries because of the different amount of lattice expansion in separate hydride-forming as well as non-hydride phases. Such a situation is pictured in Figure 37.

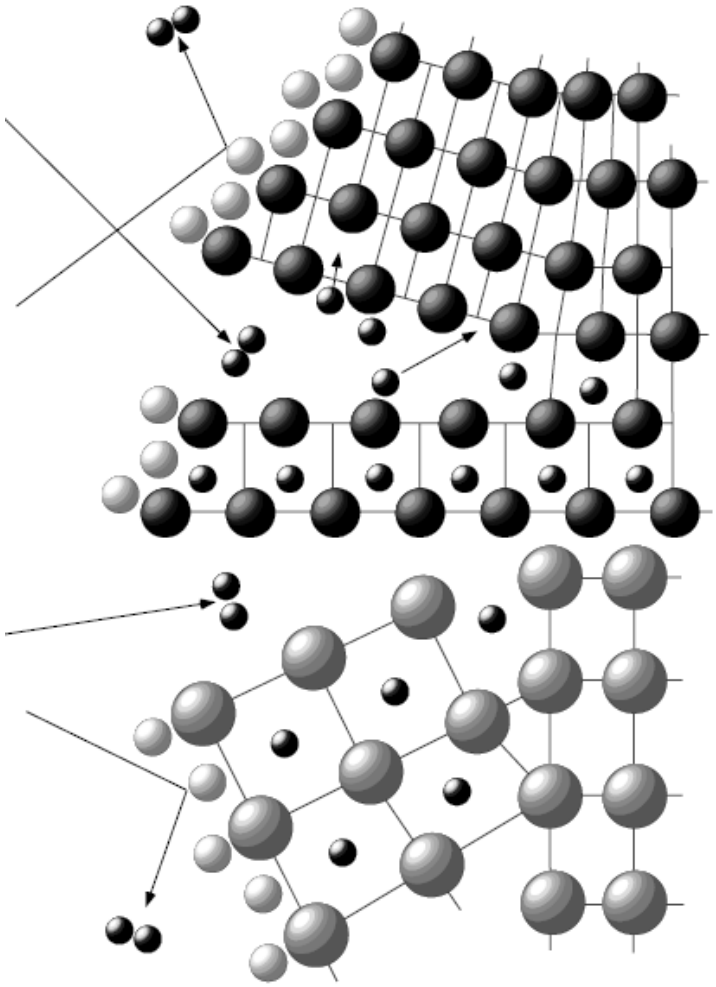

Figure 37. Lattice expansion and crack formation along phase boundaries create clean metal surfaces for dissociation and diffusion.

3.6.4Nano-Structuring

Kinetics may be inhibited by diffusion through the lattice of chemisorbing media or through the internal pore network of high-surface area physisorbing materials. In both cases, nano-structuring can increase the diffusivity of hydrogen. In chemisorbing media, nano-structuring increases the surface area-to-volume ratio, which allows for greater access to the bulk and shorter diffusion paths (Figure 38). Diffusion pathways through the internal pore network of physisorbing media are often tortuous and can become occluded. Nano-structuring can offer more direct diffusion pathways and greater access to internal surfaces.

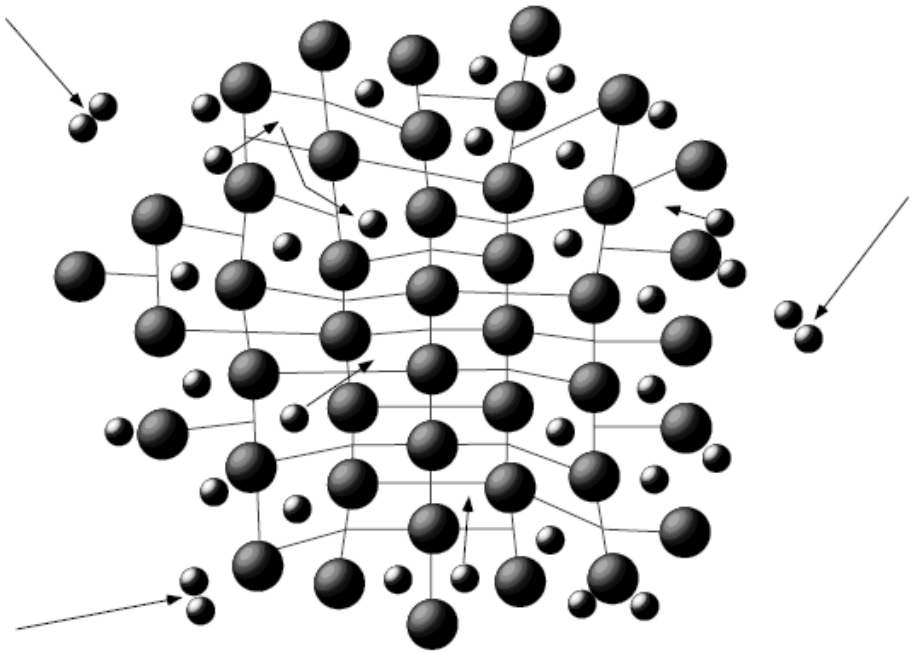

Figure 38. Poor kinetics due to a surface hydride diffusion barrier can be overcome by increasing the material's surface area to bulk ratio (i.e. decreasing the particle size).[20]

3.6.5Example of Improvements

An example of enhanced sorption kinetics by altering material properties is the observed rapid absorption and desorption kinetics of Mg-hydride formation in multi-phase composite materials based on Mg, Mg_2Ni and La. A combination of the above concepts was ascribed to improved kinetics measured in these composite materials.[20] The composites were produced by mechanically milling La_2Mg_{17} together with $LaNi_5$. In the process, fine particles of $LaNi_5$ were encompassed by the softer La_2Mg_{17} to create an intimate contact between the two phases (Figure 39). In a second step the composites underwent a phase and morphology transformation during the rapid absorption and desorption of hydrogen at 300°C. This resulted in the disproportionation of the La_2Mg_{17} and $LaNi_5$ phases. Morphological changes occurred as the La coalesced into fine particles and the Ni combined with Mg in a solid-state reaction to form larger grains of Mg_2Ni. During desorption cycles the remaining Mg likely diffused and sublimated to form a matrix around the other phases. The final product was a composite of fine particles (<1 micron) composed of Mg_2Ni covered with small grains of La-hydride all held together and coated with Mg (Figure 40).

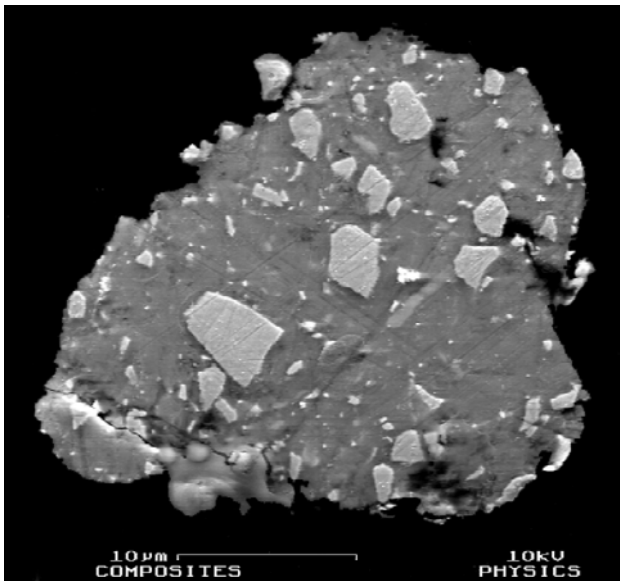

Figure 39. SEM-BSE image of the cross-section of a composite particle formed by mechanically milling La2Mg17 together with $LaNi_5$. The lighter phase is the $LaNi_5$.[20]

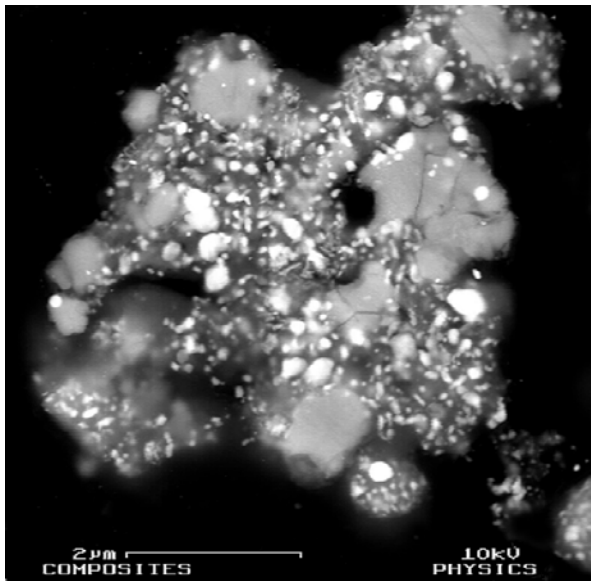

Figure 40. SEM-BSE image of the cross-section of a composite particle after treatment by cycling under hydrogen at 300°C. The lightest phase is La, the medium-grey phase is Mg_2Ni, and the dark matrix is the Mg phase.[20]

The kinetics of these composite materials proved to be far superior to those of the individual Mg and Mg_2Ni phases. A study of the relative kinetics of each phase in the composite revealed that the probable mechanisms for the enhanced kinetics were enhanced catalytic dissociation of hydrogen on the Mg_2Ni and La phases, rapid diffusion along inter-phase boundaries and a reduction of the MgH_2 diffusion barrier due to the extremely large surface area of the Mg phase.

3.7 Distinguishing Between Kinetics and Thermodynamics

In pursuit of the ultimate hydrogen storage material it is important to separate kinetic effects from the thermodynamic properties of a material. This is because a material may be kinetically hindered, requiring high temperatures and pressures to achieve reasonable hydrogen sorption/desorption rates, and these high operating conditions are regularly mistaken as inherent thermodynamic properties of the sample. All too often, a material is hastily excluded from hydrogen storage consideration on the basis of its initially observed inability to sorb/desob hydrogen at moderate temperatures and pressures. In reality the equilibrium thermodynamics may be perfectly adequate for a useful hydrogen storage system but poor kinetics require testing outside a practical range of temperatures and pressures. Figure 41 shows what is considered the range of standard operating conditions for a Proton Exchange Membrane (PEM) fuel cell (shown in grey). As an extreme example, consider a hypothetical material that can thermodynamically operate at room temperature, but which is kinetically hindered such that much higher temperatures would be required to overcome the kinetic barriers. Because the equilibrium pressure increases with increasing temperature Figure 41, it is possible that the kinetic barrier could suppress hydrogenation over the entire range of experimentally accessible pressures, i.e., by the time a temperature is reached where the kinetics allow reaction, the required pressure is too high to be achieved.

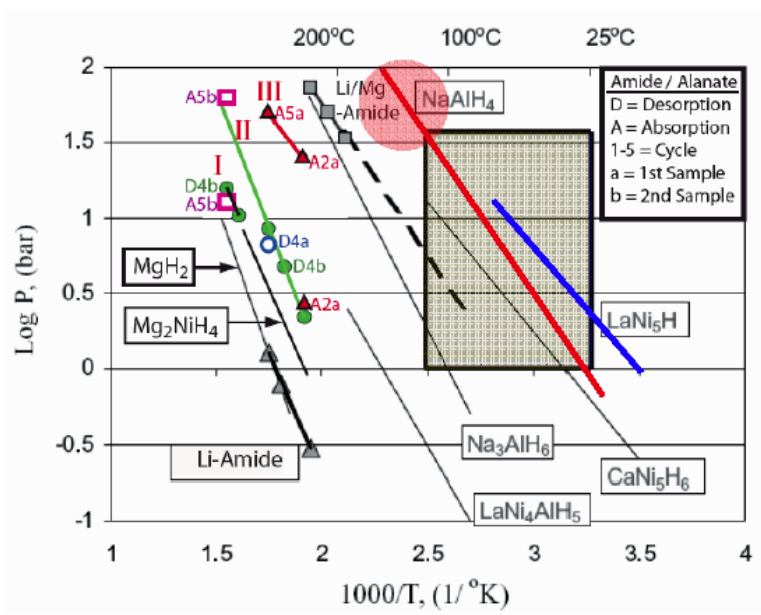

Figure 41. Equilibrium thermodynamics of some commonly researched hydrogen storage materials. The boxed area represents the range of practical operating conditions for a PEM Fuel Cell.[47]

A classic example of the relationship between kinetics and thermodynamics is investigated in the work by Bogdanovic and Schwickardi on the effect of Ti-additives on

the hydrogen sorption properties of alanates.[51] Prior to their work, alanates were not seriously considered as hydrogen storage materials because of the extreme pressures and temperatures required for hydrogen absorption. Bogdanovic et al. systematically doped sodium alanate with varying levels of titanium compounds and found that this significantly improved kinetics and by consequence reversibility. This opened the doorway to what followed as an intensive worldwide study of the alanate family as practical hydrogen storage materials. Until the Bogdanovic work, little was done to determine the thermodynamics of the sodium-alanate system because it was nearly impossible to reach thermodynamic equilibrium due to slow intrinsic kinetics of the pure alanate system. Only after the discovery of greatly enhanced kinetics in samples doped with titanium precursors was it was even feasible to make equilibrium PCT measurements, and even these achieve only partial equilibrium conditions at lower pressures and temperatures due to kinetic limitations.

3.8 Summary

It is our intent that this overview of fundamental processes and measurement considerations will aid research and development of new and better hydrogen storage materials. In particular we hope to have clarified some of the best practices and caveats in performing high-quality experiments to measure the hydrogen sorption and desorption kinetics properties of advanced materials.

3.9 Acknowledgements

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3.10 Disclaimer

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