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Review

Towards a consistent understanding of the metal hydride reaction kinetics: Measurement, modeling and data processing

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ABSTRACT

Hydriding/dehydriding reaction kinetics of metal hydrides (MH) is an important yet controversial issue. In the last few decades, numerous studies have been dedicated to elaborate the reaction phenomena for various hydride materials. Some crucial aspects sketching the physical picture of the reaction, e.g. the controlling mechanism, Avrami exponent as well as apparent activation energy, are frequently discussed using the solid-state kinetic models. It is noted, however, that the results show considerable disagreement even for the material prepared in a single batch. From the literature review, it appears that no consistent understanding on the reaction kinetics of hydride materials could ever be achieved, unless carefully selected models and appropriate statistical processing techniques are used to interpret data obtained from well-designed experiments.

Contents

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Nomenclature

C	Hydrogen concentration mol·mol^{-1}
E_a	Activation energy J·mol^{-1}K^{-1}
k	Rate constant s^{-1}
m	Avrami exponent
m_s	Sample mass kg
M_{MH}	Molecular weight of MH kg·mol^{-1}
n_a	Absorbed hydrogen mol
N_{sat}	Number of hydrogen atoms per formula unit of MH
P	Pressure Pa
R_g	Gas constant J·mol^{-1}K^{-1}
t	Time s
t_c	Characteristic time s
T	Temperature K
V	Volume m^3
X	Reacted fraction
Z	Compressibility factor
δP	Resolution of pressure transducer Pa
ρ	Sample bulk density kg·m^{-3}

Subscript

0	True or typical value
cell	Sample holder
dead	Dead volume
est	Estimate
f	Final state
i	Initial state
ref	Reference reservior

1. Introduction

Efficient and cost-competitive hydrogen storage is a crucial issue for the so-called "hydrogen economy" [1] to come true. The metal hydride (MH), which is a class of reversible materials able to be recharged with hydrogen under normally available conditions [2], has been an attractive option due to the advantages of large volumetric capacity [3] and high security. Till now, numerous MH materials [4–9] based on different compositions and preparation methods have been developed with improved properties to meet the performance targets set by US Department of Energy (DOE), e.g. volumetric density, gravimetric density, cost, refueling rate [2].

Of all the fundamental properties, hydriding/dehydriding kinetics for the concerning material, which depicts how fast the reversible reaction proceeds under various conditions, is a hot topic for both academic and industrial communities. On one hand, hydriding/dehydriding kinetics could reveal the physically rich picture of the reaction phenomena and is rather informative from the scientific point of view. On the other hand, it is closely related to the refueling rate [5] under given conditions, one of the key requirements specified by DOE, although some other issues like thermal management [10–14] should also be considered in a practical hydride-based hydrogen storage system. Therefore, the kinetic properties of MH materials have been investigated extensively in the last few decades, and the commonly-adopted procedure starts from measurement of hydriding/dehydriding rate curves by experiments, which are generally performed under isothermal and isobaric conditions. Thereafter, these data are fitted against a group of candidate models, either empirical or mechanistic, from which the one deems to best represent the intrinsic reaction characteristics is selected and the relevant unknown parameters are estimated, e.g. rate constant, activation energy, Avrami exponent [15]. Finally, the underlying physics such as the controlling mechanism, the energy barrier and the diffusion path, are inferred with the form of selected model and the values of the parameters.

Unfortunately, the results from the existing kinetic studies, including both the models and the parameter values, could hardly arrive at a general consensus for the same material prepared by the identical procedure, e.g. $LaNi_5$ [16], MgH_2 [17]. Although irreproducibility in hydrogen storage material research, the central issue in a rigorous literature review by Broom [18], is not limited to that on kinetic properties, it seems to be particularly notable from the literature reports. As pointed out by Nogita et al. [17], "*…of these models the first two contain largely opposing ideas yet both approaches have been used with some success in the modeling of experimental results…*" This inconsistence makes the understanding of the reaction phenomena difficult, not to mention applying the knowledge to guide rational R&D work on material and relevant equipment. Even if the resulting debate on reaction controlling mechanism could be partly resolved by collecting direct evidence using advanced in-situ apparatus, as done by Mooij and Dam [19], Nogita et al. [17], an improvement on the abovementioned procedure for kinetic investigations, which could diminish the inconsistence and make the inference further approach to the physical reality, is still tremendously valuable.

Many researchers attempt to address the tricky problem from either experimental or theoretical aspects, see the rigorous review by Wang and Suda [20], Broom [21], Block and Mintz [22], Pang and Li [15]. However, please note that the intermediate scenario between the two aspects, namely data processing that deals with model selection and parameter estimation, has been paid quite little attention before. In addition, some recent developments on the models and experimental techniques are not broadly known to the researchers in this field, hence a unified rigid framework for consistent kinetic studies on the MH materials is still lacked.

This review focuses on the three interacting scenarios in quantitative kinetic studies for MH materials, i.e. measurement, modeling and data processing, see the flow diagram in Fig. 1.

Since the hydriding/dehydriding reaction phenomena is extremely complex and the data will be inevitably contaminated with some "noise", i.e. errors from various sources and measurement uncertainties, considerable efforts have to be made to deal with such complexity and minimize the adverse effects of the noise. Common practice, as well as some novel tools that may benefit the consistence of kinetic studies for the MH material, especially with regard to the model formulas and parameter values, will be covered in the following sections.

2. Measurement

2.1. Classification of experimental techniques

For MH materials, the hydriding/dehydriding reaction rate is generally defined by the temporal change of hydrogen concentration in the host material after being perturbed from quasi-equilibrium. Three categories of techniques with varied working principles, i.e. volumetric, gravimetric and temperature programmed desorption (TPD, also termed thermal desorption spectroscopy), can be applied to determine the kinetics of the sorption and desorption processes.