

Mathematical Modeling of a Plasmonic Palladium-Based Hydrogen Sensor

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Abstract—The presented plasmonic palladium-based perfect absorber hydrogen sensor is used to detect hydrogen via measured reflectance spectra. The perfect absorber geometry enables a highly sensitive, cost-effective, miniaturizable, and purely optical detection system. Through fiber optics, this scheme allows for a clear separation of the detector and all electronic components rendering it inherently safe, even in explosive environments. The sensor has a complex transient behavior, which exhibits temperature-dependence, nonlinearities, and hysteresis. This transient behavior is mathematically represented by a physically motivated model. The derived model is a distributed parameter system, which considers the dispersed hydrogen diffusion in the palladium and describes the nonlinear input and linear output characteristics. Experimental measurements are conducted at 25 °C, 30 °C, and 40 °C to identify the model parameters and to show the model accuracy.

Index Terms—Sensor phenomena and characterization, nonlinear dynamical systems, distributed parameter system, hydrogen gas detector, optical sensors, localized surface plasmon resonance.

I. INTRODUCTION

RELIABLE and sensitive detection of hydrogen gas (H_2) is important for process control in chemical industry [1] and crucial to ensure safety in hydrogen systems such as fuel cells [2]. Optical sensing offers a great potential, as electronic components are unnecessary near the hydrogen gas and thus one large safety hazard can be avoided.

The optical plasmonic sensor described here is based on palladium (Pd), which is known for its high and reversible absorbability of hydrogen (H). Palladium-hydrogen (Pd-H) systems were well researched during the past decades and it was discovered that these systems are strongly temperature-dependent and exhibit properties such as nonlinearity, hysteresis and slow dynamics [3]–[6]. These properties make it very difficult to obtain an accurate estimate of hydrogen concentration from the measured optical sensor data. Thus, a model which accurately represents the sensor's transient behavior is necessary, so that in future these challenges

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can be compensated by a model-based estimation procedure. In previous work [7], we published a model that consists of literature-based pressure-composition isotherms, a partial differential equation describing the diffusion process with a concentration-dependent diffusion coefficient and a linear output map representing the shift in the optical measurement spectra. That model is significantly extended and improved within this work. The pressure-composition isotherms are exchanged by an experimentally determined pressure-concentration map, which is also able to represent the hysteresis characteristic of the sensor. Additionally a principal component analysis is performed to improve the optical output map such that the whole spectral range is represented.

Previously published research on modeling of metal-hydrogen kinetics mostly states hydrogen diffusion as rate limiting factor [4], [8]. Borgschulte *et al.* [9] however stated that describing the kinetics by only a single rate limiting factor is not sufficient and they developed a simplified model which considers both diffusion and dissociation. Those models are based on and derived from the chemical potentials of hydrogen and focus on gaining insight into hydrogen-sorption kinetics. The purpose of this publication is to develop a simplified model that describes the presented hydrogen sensor accurately, but is not too complex for a future model-based estimation procedure. The derived model considers the distributed hydrogen diffusion in the palladium by a partial differential equation with concentration-dependent diffusion coefficient and describes the nonlinear input and linear output characteristics by an experimentally determined pressure-concentration map and an optical output map. This allows us to describe the sensor behavior throughout PdH phase transition from α -PdH over the coexistence region to β -PdH.

The manuscript is structured in six sections. Section II specifies the sensor design and its working principle in order to understand the physical processes. The gained knowledge is relevant for the derivation of the mathematical model in section III, which describes the relationship between the hydrogen (H_2) partial pressure and the respective optical spectral output of the sensor. Its parameters are identified from experimental measurements as explained in section IV. In section V, the model accuracy is evaluated through the experimental measurements. Finally, a conclusion is given in section VI.

II. SENSOR DESIGN AND WORKING PRINCIPLE

The following section presents the structure and the manufacturing steps of the hydrogen sensor. Afterwards, the sensor