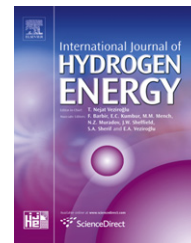


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# Kinetics of hydrogen sorption by palladium nanoparticles

C. Lebouin<sup>a</sup>, Y. Soldo<sup>a</sup>, S.A. Grigoriev<sup>b</sup>, M. Guymont<sup>c</sup>, P. Millet<sup>c,\*</sup>

<sup>a</sup>Laboratoire d'Électrochimie et de Physicochimie des Matériaux et des Interfaces, CNRS-Grenoble INP – UJF, 1130 rue de la Piscine, 38402 Saint Martin d'Hères, France

<sup>b</sup>National Research Center “Kurchatov Institute”, Kurchatov sq. 1, Moscow 123182, Russia

<sup>c</sup>Institut de Chimie Moléculaire et des Matériaux, UMR CNRS n° 8182, Université Paris Sud 11, Bât 410, 91405 Orsay Cedex, France

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## ABSTRACT

The purpose of this communication is to compare the hydriding kinetics of bulk (250  $\mu\text{m}$ ) and nano-sized (3.6 nm) palladium particles. Sorption/desorption isotherms have been measured at 25 °C from volumetric experiments. It is shown that nano-particles retain only some of the characteristics of bulk systems. Several major differences such as different hydrogen solubility, different magnitude of hysteresis and different plateau pressure slopes have been observed. Hydrogen sorption/desorption kinetics has been analyzed in the frequency domain. A model has been used to fit experimental impedance diagrams and determine microscopic rate-parameters in the solid solution, two-phase domain and hydride phase. It is shown that microscopic rate parameters of micro- and nano-particles do not significantly differ.

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## 1. Introduction

Hydrogen storage technologies using hydride forming metals, compounds or alloys remain the subject of extensive research in view of the so-called “hydrogen economy” [1,2]. To date, the development of hydrogen reservoirs with high gravimetric and volumetric energy densities remains a highly challenging issue [3–5]. In addition, application of such reservoirs in the automotive industry requires fully reversible systems with fast loading/unloading characteristics. Whereas hydrogen hydrates [6] or hydrogen cryosorption processes [7] offer interesting alternative perspectives and are currently under investigation, the development of hydride forming metallic nano-particles is expected to improve the situation of metal hydrides on several aspects, in particular yielding faster kinetics. However, thermodynamic properties may be

negatively impacted, the pressure plateau in such nano-powders being largely sloppier than on conventional bulk materials. Some recent studies (e.g [8]) have already disclosed some features of these nano Pd–H -systems. However, the nanoparticles were formed in a high temperature spark that may affect their structure and sorption properties. In addition, the hydriding kinetics was analyzed assuming surface step rate limitations. In order to provide a further insight on these systems, we report in this communication on the analysis of the hydriding kinetics of calibrated palladium nano-particles obtained by chemical reduction of precursor salts at ambient temperature. Both thermodynamic (isotherms) and kinetic properties have been measured. Microscopic rate-parameters have been determined using gas-phase impedance spectroscopy. Results are compared to those measured on bulk particles.

\* Corresponding author. Tel.: +33 1 69 15 48 12.

E-mail address: [pierre.millet@u-psud.fr](mailto:pierre.millet@u-psud.fr) (P. Millet).

## 2. Experimental section

### 2.1. Palladium micro-particles

Reference measurements have been made using a palladium powder made of bulky (250  $\mu\text{m}$ ) particles (Alfa Aesar, 99.95%). In the following, this powder is referred to as ‘bulk powder’. This bulk powder was used as received. Several hydriding/dehydriding cycles have been applied in order to fully activate the reactive bed and obtain reproducible kinetic results. The reference isotherm shown in this report was obtained after 10 activation cycles.

### 2.2. Palladium nanoparticles

There are several techniques that can be used to synthesize Pd nanoparticles [9]. The powder of calibrated palladium nanoparticles used in this research work has been obtained from NanoMEPS Co. (Toulouse, France). Nanoparticles have been synthesized by the chemical reduction of precursor salts in a liquid organic solvent. To avoid the formation of thick particles and to obtain a homogeneous powder, amine surfactants have been added to the reactor during the synthesis. A TEM micrograph of the powder is shown in Fig. 1a. The associated histogram of size distribution (measured on several hundred nanoparticles) is shown in Fig. 1b. The mean particle size was found to be 3.6 nm. These particles tend to agglomerate but analysis of larger populations has confirmed the absence of particles thicker than 10 nm. Risks associated with potential pyrophoric effects have been managed by preventing direct contact with air. The particles have been synthesized under inert atmosphere, transported in a sealed glassware and introduced to the reaction chamber for hydriding measurements using a glove box (oxygen and water vapor residual content less than 2 ppm). After connection of the reactor to the experimental setup, the setup has been purged down to secondary vacuum ( $10^{-6}$  mbar) and hydriding experiments have been carried out using Alphagas grade 2 hydrogen (Air Liquid Co.).

### 2.3. Gas-phase measurements

A schematic diagram of the experimental setup used for the measurement of the isotherms and the collection of raw kinetic data is pictured in Fig. 2. Basically, this is a Sieverts gas distribution apparatus [10]. A more detailed description of the experimental setup can be found in Ref. [11]. Briefly, pneumatic valves (PV) are used to transfer hydrogen between the different chambers. In a typical sorption experiment, hydrogen gas is first transferred from the reservoir ( $Ch_0$ ) to the calibrated reference chamber ( $Ch_1$ ). The initial pressure gradient ( $P_1^0 - P_2^0$ ) set between the reference and reaction ( $Ch_2$ ) chambers acts as a driving force for the transfer of hydrogen to the sample. Isotherms are measured by adding/withdrawing sequential amounts of hydrogen at constant temperature. The hydrogen concentration in the palladium samples is expressed by the dimensionless ratio  $H/Pd$  where  $H$  = number of moles of atomic hydrogen and  $Pd$  = number of moles of palladium. Usually, the composition change  $\Delta(H/Pd)$  is such that  $0.05 < \Delta(H/Pd) < 0.2$ .

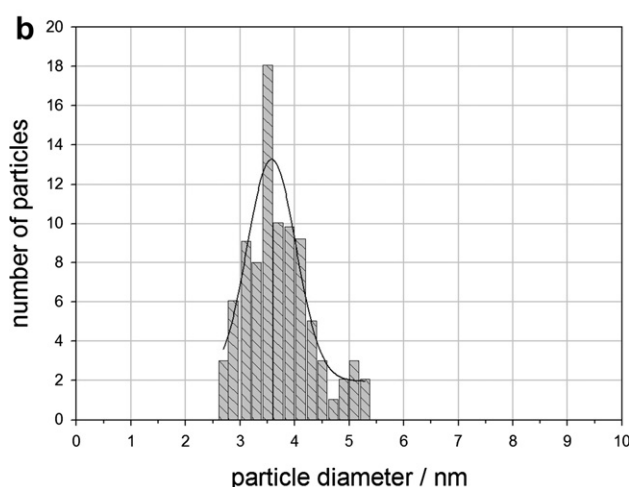
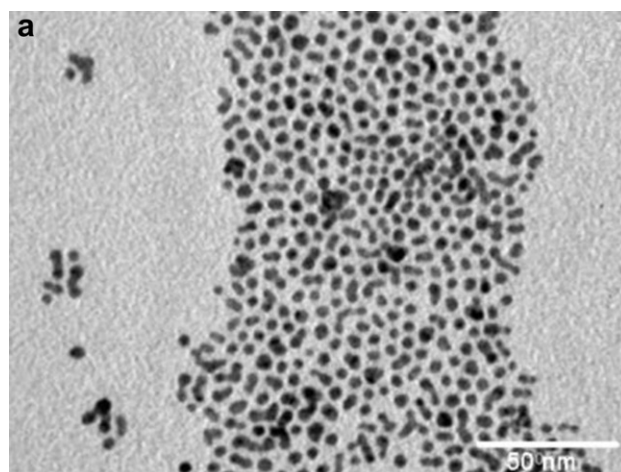


Fig. 1 – (a) TEM micrograph of the Pd nanoparticles; (b) Pd nanoparticles size distribution.

## 3. Gas-phase impedance spectroscopy

### 3.1. Experimental gas-phase impedance diagrams

Experimental gas-phase impedance diagrams have been determined using a technique described in details elsewhere

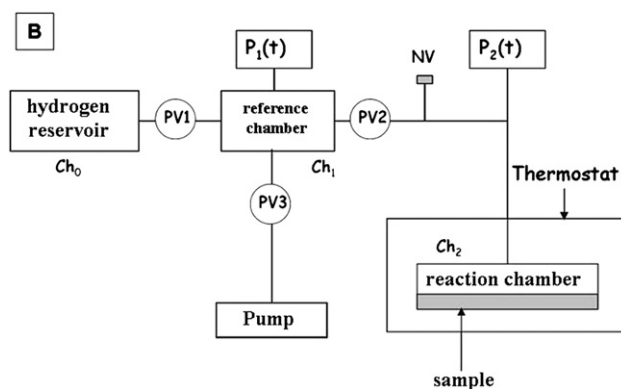


Fig. 2 – Schematic diagram of the experimental setup used to measure isotherms and gas-phase impedance diagrams.

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