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Hydrogen sorption properties of Pd nanoparticles dispersed on graphitic carbon studied with a cavity microelectrode

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ABSTRACT

The hydrogen sorption properties of nanosized palladium particles dispersed in high surface area graphite powders are studied by both solid/gas and electrochemical methods. Using either classical powder electrodes or a cavity microelectrode we show that cyclic voltammetry peaks coming from the hydrogen sorption/evolution, that are usually strongly overlapped in powder electrodes, can be resolved at low scan rates. With the cavity microelectrode, we could measure voltammograms over a 3-decade range of potential scan rates and thus describe the sorption processes in this hybrid material.

1. Introduction

Palladium (Pd) arouses great interests since a long time due to its high ability to absorb hydrogen. Numerous studies have been devoted to the electrochemical sorption/desorption processes in limited volume Pd electrodes [1–12]. For the most part they relate to ultra-thin films, which present the advantage of being well controlled in thickness or number of monolayers, and allow resolving adsorption and absorption processes by comparison with bulk Pd.

More recently, Pd/C composites have drawn attention due to their numerous applications in the fields of hydrogen storage and supported catalysts in fuel cells. For electrochemical studies Pd has been deposited as ultra-thin films on reticulated vitreous carbon [2,13], in the form of nanoparticles directly supported on a flat carbon surface (either by evaporation [14,15] or electrodeposition [16]) or in a matrix (carbon black [17–22], activated carbon [23], mesoporous carbon [24,25], polymers [26–28] or carbon nanotubes [29]) to handle well-separated metallic nanoparticles. Pd is sometimes alloyed with other metal such as Pt, Mo, Bi or Fe. Voltammetric studies on Pd nanoparticles in the hydrogen region are usually limited to adsorption and to a partial absorption, in particular for Pd/C hybrid systems. Only the works of Takasu et al. [14,15] on flat glassy carbon electrodes decorated with ~2–3 nm Pd particles describe hydrogen absorption up to the β phase formation as usually reported in the case of Pd thin films.

Few authors have attempted to determine hydrogen electrosorption capacity of Pd/C hybrids [17,18,26]. These studies revealed very high H/Pd ratios (~1 H/Pd at 0.01 MPa H_2, i.e. +30 mV/RHE) by comparison to usual absorption capacities obtained under equivalent hydrogen sorption conditions in Pd thin films [2,3,5,7,9] or on dispersed particles [15]. However the relative contributions of the Pd particles and the matrix are not clearly distinguished and further investigations are needed.

Recent work in our group reported that Pd nanoparticles embedded in porous carbon [30,31] or organometallic compounds (MOFs) [32] exhibit promising solid/gas properties toward hydrogen sorption. It was shown that such materials combine physisorption at the pore surface of the host and hydrogenation of the metal-forming hydride. The aim of the present work is to compare hydrogen sorption properties of nanosized Pd embedded in a high surface area graphite measured from classical solid/gas method and from electrochemical curves. Two electrochemical tools, classical powder electrodes and cavity microelectrodes, were used in a complementary way to bring information on the sorption mechanisms.

2. Experimental

“High Surface Area Graphite 500” from TIMCAL (hereafter designated as C_G) has been used for the preparation of Pd/C_G hybrid materials synthesized via a chemical wetting procedure already described in [30,32]. This graphitic carbon in powder form was impregnated with a tetrachloropalladous acid (H_2PdCl_4) solution.

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The $PdCl_4^{2-}$ ions were reduced by heating the impregnated carbon in an Ar/H_2 flow ($0.5\,L\,min^{-1}$) at 1023 K. The Pd content in the hybrid was determined by ICP-OES and is equal to 9.12 wt.%.

Structural characterizations were performed by X-ray diffraction (XRD) using a D8 advanced Bruker diffractometer (Cu Kα radiation). The XRD pattern of the Pd/C_G hybrid has been analyzed by the TOPAS software (Bruker AXS Topas 4.2). The lattice parameter of Pd nanoparticles has been obtained from the position of the diffraction peaks and their crystallite size by line-profile fitting using the fundamental parameters approach (TOPAS). Microstructural observations were performed by transmission electron microscopy (TEM) with a 200 kV FEG TEM (FEI Tecnai F20 equipped with a Gatan Energy Imaging Filter; resolution 0.24 nm). Hydrogen excess sorption properties were determined by measuring the pressure–composition isotherm (PCI) at 300 K up to 0.1 MPa hydrogen pressure. The PCI curve was recorded using an automated volumetric device (Autosorb IQ Quantachrome).

Electrochemical measurements were carried out with a classical 3-electrode cell using an Autolab PGSTAT 30 potentiostat. The working electrodes were either classical powder electrodes (PEs) or an homemade cavity microelectrode (CME). The reference and counter electrodes were a saturated calomel electrode with KCl (SCE) and a platinum wire, respectively. The potential of the SCE reference electrode was determined experimentally to be −0.294 V with respect to a reversible hydrogen electrode (RHE) at 0.1 MPa H_2 in $0.1\,mol\,L^{-1}$ H_2SO_4. It is well established that absorption isotherms for the Pd–H system obtained from gas and solution based methods are equivalent [33]. The correspondence between the equilibrium hydrogen pressure (P_{H_2}) and the electrochemical potential E_{eq} is given by the Nernst equation:

$$E_{eq} = E^0 + \frac{RT}{F}\ln\frac{a_{H^+}}{\sqrt{P_{H_2}}}$$

H_2SO_4 solutions at $0.1\,mol\,L^{-1}$ were prepared from concentrated H_2SO_4 (95%, AnalaR Normapur, Prolabo) and ultra-pure water (18.2 MOhm cm). All the experiments were carried out under argon bubbling.

The PEs were prepared by pressing on a stainless steel grid of 1 cm^2 diameter ~20 mg of a film made of 90% Pd/C_G powders and 10% Teflon pressing under 3 tons. The grid was then fixed on a gold wire as current collector. The CME was fabricated by etching the Pt wire tip of a classical Pt microelectrode, as described in detail elsewhere [34]. In this work, the cavity was 50 μm in diameter and 90 μm in depth. It was filled up with material grains using the electrode as a pestle. We ensured that the cavity was conveniently filled up by optical microscopy observation (Olympus BX30). The cavity was washed out with an ultrasonic cleaner in ultra-pure water for 5 min.

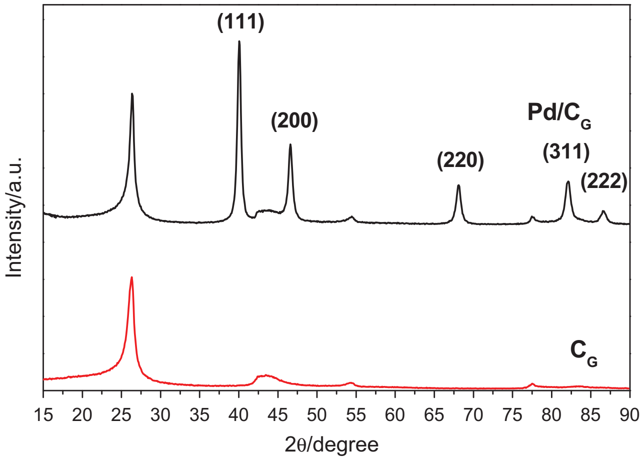


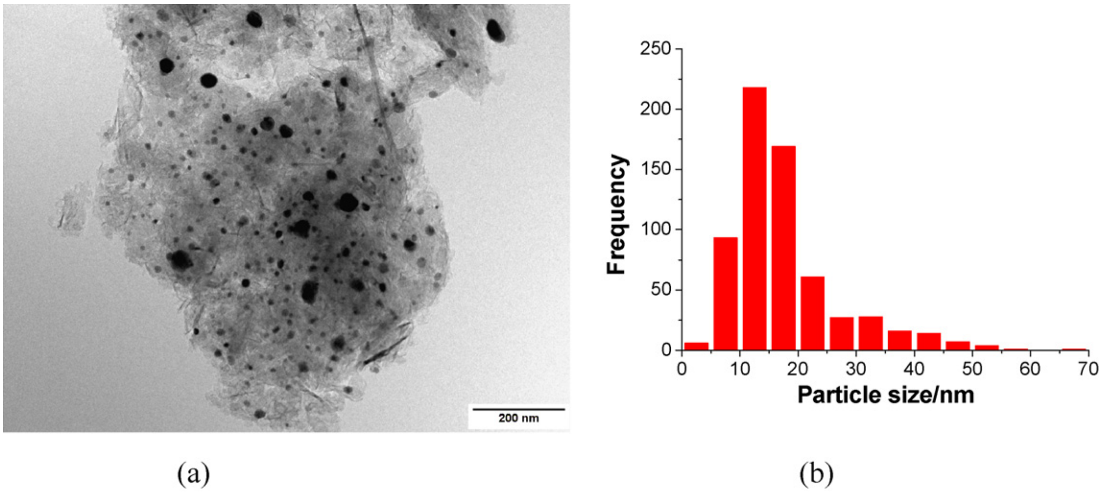
Fig. 1. XRD patterns of C_G and Pd/C_G hybrid.

3. Results and discussion

3.1. Structural and microstructural characterization

The XRD patterns of C_G and Pd/C_G hybrid are presented in Fig. 1. Pd nanoparticles crystallize in a fcc structure (PDF 01-087-0639). The C_G has a graphitic structure, which is not affected by the Pd nanoparticles insertion. The lattice parameter for Pd/C_G is equal to 3.887 (±0.003) Å, in agreement with previous values for Pd (PDF 01-087-0639 and [30]). The deduced mean size of Pd nanoparticles from XRD is 21 (±2) nm.

Fig. 2 presents the TEM bright field image of Pd/C_G and the corresponding histogram of Pd nanoparticles as determined by analysis of several TEM images. The mean particle size determined from the statistical analysis of the histogram is equal to 17 (±2) nm, this value being of the same order of magnitude than the one determined from XRD analysis.



(a) (b)

Fig. 2. TEM image of Pd/C_G (a) and the corresponding histogram of Pd nanoparticles in Pd/C_G (b).