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When cubic nanoparticles get spherical: An Identical Location Transmission Electron Microscopy case study with Pd in alkaline media

Anicet Zadick [a,b,*], Laetitia Dubau [a,b], Anna Zalineeva [c], Christophe Coutanceau [c], Marian Chatenet [a,b,d,1]

[a] Univ. Grenoble Alpes, LEPMI, F-38000 Grenoble, France
[b] CNRS, LEPMI, F-38000 Grenoble, France
[c] Université de Poitiers, IC2MP, Laboratoire de Catalyse et Milieux Non-Conventionnels, UMR CNRS 7285, 4 Rue Michel Brunet, 86022 Poitiers, France
[d] French University Institute (IUF), France

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ABSTRACT

Shape-controlled nanoparticles (NPs) are viewed as electrocatalysts of choice for fuel cell applications. However, to date very few studies focus on the persistence of the controlled shape upon operation. Herein, the degradation of cubic palladium NPs is studied in alkaline media using Identical Location Transmission Electron Microscopy (ILTEM) and electrochemical measurements; this work brings evidence that the cubic shape is rapidly destroyed in certain conditions.

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1. Introduction

Palladium exhibits great catalytic performances and has gained a special interest for dehydrogenation process and for the electrooxidation of fuels such as ethanol or hydrazine [1,2]. Scientists try to increase these intrinsic performances by synthesizing shape-controlled Pd nanoparticles (NPs), which generally show significant (electro)catalytic enhancements following the predominance of more active facets [3,4]. Nevertheless, very few studies have been focused on the degradation of the NP shape as a consequence of their intensive use. To date, only the group of Strasser [5] demonstrated that PtNi bimetallic octahedra was unstable in PEMFC environment, due to the preferential dissolution of Ni in superacidic electrolyte. Alkaline environment are supposedly less aggressive and noble metals such as Pt or Pd, even as shape-controlled NPs, are expected to exhibit larger durability upon their use in this media; herein, this statement is experimentally investigated with cubic Pd NPs degradation in NaOH alkaline solution using Identical Location Transmission Electron Microscopy (ILTEM), a characterization technique largely employed for nanoscale investigation [6]. The Pd nanocube stability is further bridged to its electrochemical response.

2. Experimental

By dissolving sodium hydroxide monohydrate (Merck, Suprapur), 0.1 M NaOH electrolyte solutions were prepared in ultra-pure water 18.2 M Ω cm and <3 ppb Total Organic Carbon (TOC, Elix + Milli-Q Gradient system, Millipore).

All experiments were performed at room temperature and pressure (ca. 20 °C, 1 atm) under argon atmosphere using a VSP (Bio-Logic) potentiostat in a PTFE-made three-electrode cell. The counter-electrode was a gold plate and the reference electrode was a freshly prepared reversible hydrogen electrode (RHE); all potential values are given versus the RHE scale. In any case, a new RHE was prepared every 2 h of experiments, to avoid any bias in the reference potential value.

The cubic palladium NPs were synthesized by Poitiers University (France) using a colloidal method described largely in [3]. ILTEM observations were performed on Gold + Lacey carbon grids from TED PELLA. For "standard" electrochemical measurements, cubic palladium NPs have been directly deposited on glassy carbon electrodes polished until 1 μm using diamond paste.

* Corresponding author. Tel.: +33 476826588; fax: +33 476826777.
E-mail addresses: anicet.zadick@lepmi.grenoble-inp.org (A. Zadick), Marian.Chatenet@grenoble-inp.fr (M. Chatenet).
[1] Tel.: +33 476826588; fax: +33 476826777.

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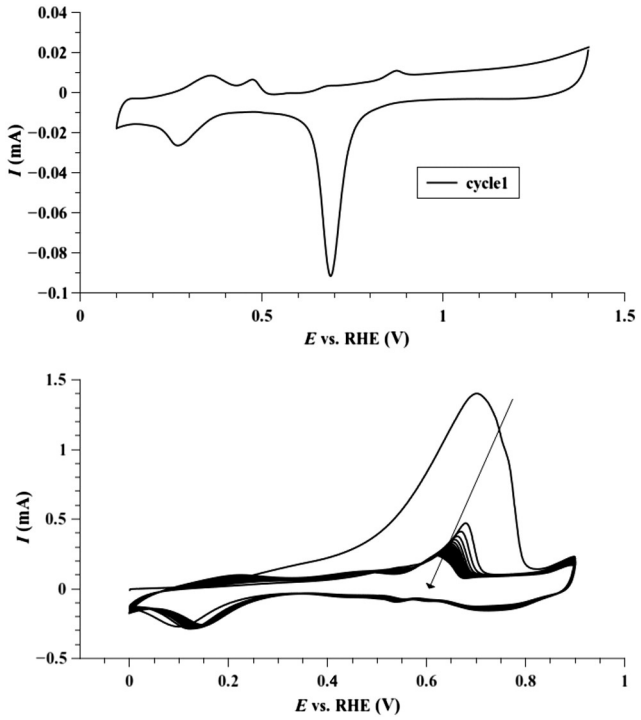

Fig. 1. a) CV (5 mVs^{-1}) between 0 and 1.4 $V_{vs.RHE}$ b) Third CV sequence (100 mVs^{-1}) of the degradation test for {0–0.9 $V_{vs.RHE}$} potential range, both performed in 0.1 M NaOH with Pd nanocubes deposited on glassy carbon electrodes.

The electrochemical degradation protocol consists of successive chronoamperometries (CA) and cyclic voltammetries (CV), as detailed below:

1. CA at E_{low} for 15 min;
2. CV from E_{low} to E_{high}, at 100 mVs^{-1}, for 25 cycles;
3. CA at E_{low} for 15 min;
4. CV from E_{low} to E_{high}, at 100 mVs^{-1}, for 100 cycles;
5. CA at E_{low} for 15 min;
6. CV from E_{low} to E_{high}, at 100 mVs^{-1}, for 25 cycles

with E_{low} and E_{high} the lowest and the highest potential values of the chosen potential range of study, respectively.

3. Results and discussion

Fig. 1a shows the voltammogram (5 mVs^{-1}) obtained in 0.1 M NaOH for cubic palladium NPs. In addition to the typical oxide formation/reduction and hydrogen adsorption/desorption features of Pd surfaces, it exhibits two irreversible peaks corresponding to the specific {100}-orientation of the cubes. For example, Hoshi et al. studied the stability with Pd single crystals in alkaline medium and the peak ascribed to the presence of {100} sites can be observed [7].

Hereafter, ILTEM was performed for the same material to unveil a possible degradation of the cubic shape upon extensive CV cycling. The widest potential window for the degradation tests was {0–0.9 $V_{vs.RHE}$} which is a region of interest for fuel cell accelerated stress tests [8,9] and also a region where the oxidation reactions of non-carbonaceous fuels (such as $NaBH_4$, NH_3BH_3 and N_2H_4) are usually characterized [10–12]. In addition, this potential range enables to investigate the impact of hydrogen insertion/desinsertion which cannot be

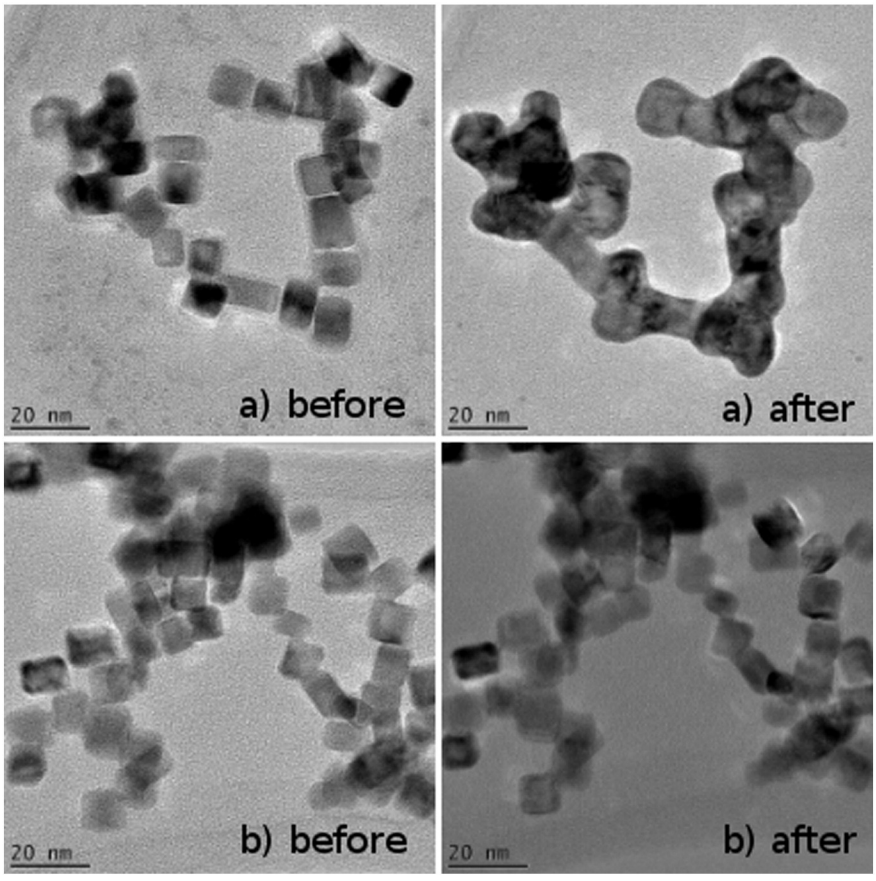

Fig. 2. Representative ILTEM micrographs of palladium cubic NPs before/after for a) a degradation test for a {0–0.9 $V_{vs.RHE}$} potential range b) an OCP technique with an identical duration (benchmark sample) than for a), both performed in 0.1 M NaOH.

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