

Unique Behaviour of Shaped Palladium Nanoparticles in Electrochemical Hydrogen Adsorption and Absorption

A. Zalineva¹, S. Baranton¹, G. Jerkiewicz², C. Coutanceau¹

¹IC2MP, UMR CNRS 7285, Université de Poitiers, 4 rue MichelBrunet, 86073 Poitiers cedex 9, France. ²Department of Chemistry, Queen's University, 90 Bader Lane, Kingston, Ontario K7L 3N6, Canada.

christophe.coutanceau@univ-poitiers.fr

Keywords: Palladium, Nanoparticles, Hydrogen, Adsorption, Absorption, Hydrogen Evolution

Palladium (Pd) is an excellent hydrogen (H) host and find application inhydrogen storage systems and anodes in rechargeable nickel–metal hydride [Ni-M(H)] batteries. The charge and discharge kinetics of Ni-M(H) batteries are limited by the slow H diffusion in solids and pulverization of host materials. This kinetic limitation can be overcome through the use of nanoparticles (NPs) that can be quickly charged and discharged, due to their dimensions leading to high surface-to-volume ratio. Pd is capable of both adsorbing and absorbing H, and in the case of bulk materials, the amount of adsorbed H (H_{ads}) is tiny as compared to the amount of H_{abs}. H adsorption and absorption can be accomplished under gas-phase and electrochemical conditions, but the respective mechanisms are different owing to the nature of the H precursor.

In the present communication, Pd-NPs with controlled size and shape distributions (nano-spheres, nanocubes and nano-octahedrons) are synthesized using a method based on chemicalreduction of K_2PdCl_4 in ultrapure water with polyvinylpyrrolidoneas surfactant and with ascorbic / citric acid as reducing and surface agents.The Pd-H interactions examined using electrochemical techniques.The potential range in which H electro-adsorption, electro-absorption, and evolution reaction occur is examined in an acidicmedium using cyclic-voltammetry (CV). The three processes give rise to unique features CV profiles and are observed in distinct potential ranges (Figure 1). This behavior isnot observed for bulk Pd materials and arises due to the nanoscopic nature of the Pd materials.In the case of octahedral Pd-NPs the H loading is as high as 0.9^1 .On the basis of thermodynamic analysis of H adsorption and absorption as well as through the application of the surface stressmodel in the analysis of H absorption mechanism, it is proposed that the octahedral Pd-NPs develop a core-shell-skin structure².



Figure 1: CV profile for octahedral Pd-NPs acquired in 0.5Maqueous H_2SO_4 solution at T=296 K and s=1.0 mVs⁻¹ in the range of -0.05 to 0.40 V. The purple and red transients refer to UPD H (shown in detail in the inset), the green and blue transients refer to H absorption and H_{abs} desorption, and the black transient refers to HER.

Acknowledgements

A.Z. acknowledges financial support toward her postdoctoral studies from the County Council of Poitou-Charentes, France. G.J.acknowledges support from the Natural Sciences and Engineering Research Council ofCanada.

REFERENCES

1. A. Zalineeva, S. Baranton, C. Coutanceau, G. Jerkiewicz, Electrochemical Behavior of Unsupported Shaped Palladium Nanoparticles, *Langmuir*, **31**, 1605-1609 (2015)



2. A. Zalineeva, S. Baranton, C. Coutanceau, G. Jerkiewicz, Octahedral palladium nanoparticles as excellent hostsfor electrochemically adsorbed and absorbed hydrogen, *Science Advances*, in press (2017).