ELECTROCHEMISTRY OF PD NANOPARTICLES SYNTHESIZED IN MICROEMULSION

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The use of nanoparticles in Electrochemistry has been focused in a great number of papers. This special attention is not only from a practical point of view (preparation of fuel cells, gas diffusion electrodes and catalyst) but also from a basic point of view.

In this work, palladium nanoparticles were synthesized by using water-in-oil microemulsions prepared from n-heptane as organic phase, Brij®30 as surfactant and $PtCl_6^{-2}$ and hydrazine aqueous solutions as a platinum precursor and reducing agent respectively. Nanoparticles were formed by mixing two microemulsions, containing the Pt precursor and the reducing agent. The final size of the nanoparticles can be controlled by changing the ratio ω=[H_2O]/[Surfactant]. A controlled decontamination procedure of particle surfaces was applied to remove residual molecules of adsorbed surfactant. This decontamination treatment was carried out without altering the particle surface structure [1]. Before electrochemical experiments nanoparticles were deposited on a gold substrate under an Ar atmosphere.

Figure 1a shows the voltammogram of clean palladium nanoparticles whereas Figure 1b shows a CO stripping profile. Both voltammograms are characteristics of palladium nanoparticles with a clean surface.

Palladium nanoparticles were further characterized by analyzing the FTIRS spectra of adsorbed CO. The spectra reported in Figure 2 were obtained in a spectroelectrochemical cell, containing 0.1 M H_2SO_4 solution. All spectra were recorded at 0,1 V vs RHE and referred to the spectrum collected at 1.0V. Two samples of palladium nanoparticles prepared with two different sizes (different ω), were studied. Figure 2a shows the spectra for the smallest nanoparticles while Figure 3b corresponds to the biggest ones. Both spectra show two absorption bands, which can be assigned to the C-O stretching vibrations of atop (2035-2025 cm^{-1}) on step sites and bridge-bonded CO (1923-1941 cm^{-1}) on terraces [2]. Increasing the particle size the dimension of the terraces increases which produces changes on the ratio between atop and bridge-bonded CO bands.

The use of EQCM offers a new way to check the stability of nanoparticles in-situ. The influence of the "classical" electrochemical activation of the surfaces was analyzed on palladium nanoparticles. These experiments were carried out by using EQCM working with a 9 MHz AT-cut quartz crystal with a gold layer upon which palladium nanoparticles were deposited. This electrochemical activation clearly produces dissolution of the sample. The final voltammogram obtained corresponds to that observed before depositing nanoparticles and is characteristic of a clean gold surface. The effect of the electrochemical activation process is reported in Figure 3, where the normalized mass losses are plotted vs the normalized electric charges for hydrogen adsorption.

References

[1] J. Solla-Gullón, V. Montiel, A. Aldaz, J. Clavilier, J. Electrochem. Soc, in press.

[2] N. Sheppard, T. T. Nguyen, Adv. Infrared Raman Spectrosc. 5 (1978) 67.

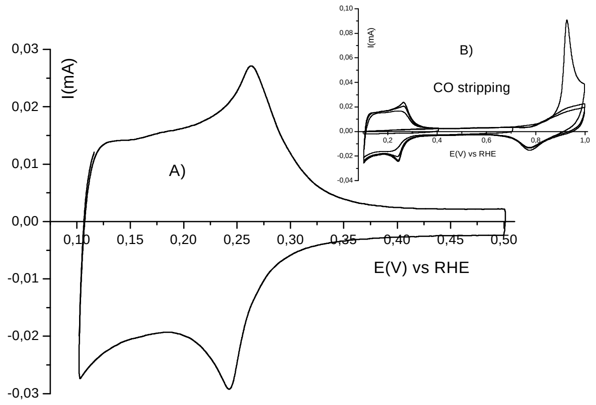

Figure 1. A) Voltammogram of Pd nanoparticles, B) CO stripping of Pd nanoparticles. Test solution: 0.5 M H_2SO_4, sweep rate 20 mVs^{-1}.

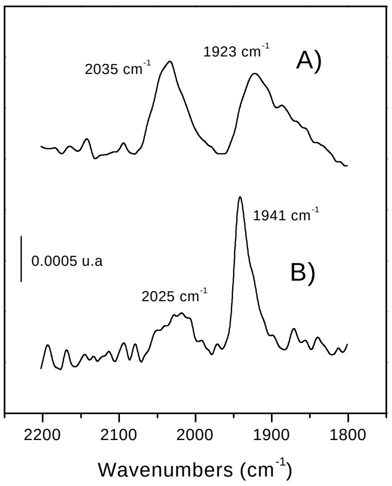

Figure 2. IR spectra of CO adsorbed on Pd nanoparticles A) small particles and B) big particles. All spectra are recorded at 0,1 V vs RHE and referred to the spectrum collected at 1.0V. Test solution: 0.1 M H_2SO_4. Resolution 8 cm^{-1}.

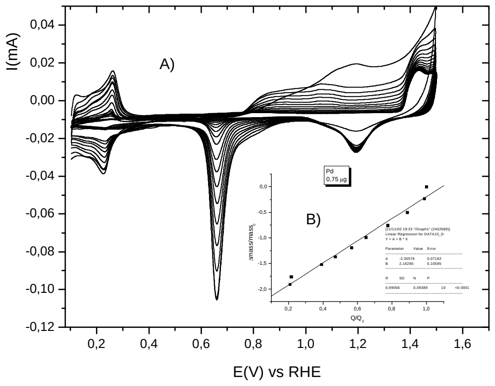

Figure 3. A) Voltammograms of Pd nanoparticles during the polarisation scans up to 1.5V. Current collector: Au-Ti plated quartz electrode. Test solution: 0.5 M H_2SO_4, sweep rate 50 mVs^{-1}. B) Normalised mass loss *vs* normalised electric charge plot