

Ethanol electrooxidation over Pd nanoparticles deposited by Atomic Layer Deposition on TiO₂ nanotubes

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Continuous depletion of fossil fuel reserves and increase in the pollution due to growing energy demands make fuel cell an attractive alternative energy source. Among various types of fuel cells the direct alcohol fuel cells (DAFCs) are particularly attractive because ethanol, glycerol and ethylene glycol can be generated from sustainable biomass derived feed stocks. These biomass derived fuels offer significant advantages due to their non-toxicity, renewability and high power density content. There are two primary challenges that need to be overcome in order for DAFCs to see practical use. First, the alcohol oxidation kinetics over the state of the art electrocatalysts is relatively slow, which limits the power levels that can be achieved with the fuel cells. Second, the existing electrocatalysts are only able to partially oxidize alcohols, which effectively negates the high energy density of the fuels.

In the present work the atomic layer deposition (ALD) technique is used to prepare Pd nanoparticles onto TiO₂ nanotubes for ethanol electrooxidation in alkaline media. ALD is a powerful technique for catalyst preparation [1], because it allows a precise control of the thickness, composition and structure of the deposit, and can be used for preparation of well-defined multi-metallic nanoparticles on highly porous materials such as TiO₂ nanotubes (TiO₂-nt). Pd nanoparticles of various size, morphology and loading were deposited by ALD on TiO₂-nt and tested for ethanol electrooxidation in 1M KOH.

TiO₂ nanotubes have been grown by anodic oxidation at 20 V in an aqueous fluoride containing electrolyte. The diameter and length of the nanotubes is about 80 nm and 1 μm, respectively (Fig. 1a) [2]. Pd nanocatalysts have been synthesized by ALD onto TiO₂-nt using Pd(hfac)₂ and formalin (formaldehyde/methanol) as precursors [3]. The influence of parameters such as temperature, pulse duration, number of ALD cycles and the use of an Ar booster in order to increase the vapor pressure of Pd(hfac)₂ have been investigated to vary the particle morphology and size (Fig. 1).

Physicochemical properties of the resulting catalysts have been studied by scanning electron microscopy, transmission electron microscopy, x-ray diffraction and surface chemical analysis such as x-ray photoelectron spectroscopy (XPS).

Electrochemical measurements were carried out in the standard three-electrode electrochemical cell made of Teflon. The electrolyte solution (1 M KOH + 1 M C₂H₅OH) was purged before and during the measurements with high purity N₂ (99.998 Linde). High surface area Pt gauze electrode served as a counter electrode and all measurements were done using Hg/HgO

(Koslow Scientific) reference electrode. CO stripping was carried out in 1 M KOH in order to determine the electrochemical surface area (ECSA). Ethanol electrooxidation current densities are normalized per ECSA and mass of Pd.

Pd nanoparticles grown at 200°C exhibit a fcc polycrystalline structure with a main orientation of the grains in the [220] direction. The particle size, ranging from 5 to 20 nm depending on the growth parameters, is homogeneous and the deposit coats uniformly the whole surface of the TiO₂-nt walls (Fig. 1b,c). Due to the favorable surface energy of TiO₂, the growth of Pd nanoparticles by ALD is optimized. XPS showed few F and C contaminations, however the splitting of the Pd 3d peak reveals a non-negligible contribution of oxidized Pd in addition to the metallic Pd.

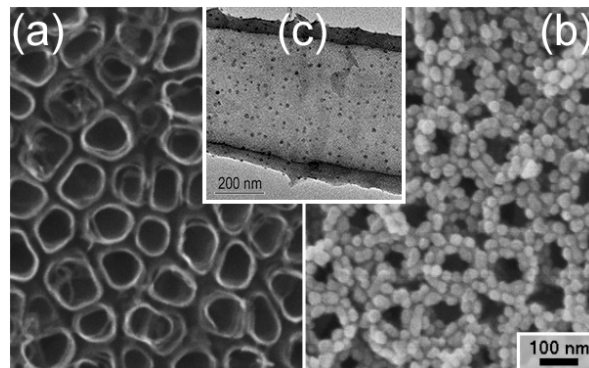


Figure 1: SEM top views of TiO₂-nt as grown (a), covered by Pd nanoparticles after 500 ALD cycles (b). TEM cross-section in the middle of a TiO₂-nt after 200 ALD cycles (c).

Figure 2 shows cyclic voltammograms (CV) of Pd electrocatalysts deposited after 900 ALD cycles on TiO₂-nt, as well as a CV of the bare TiO₂-nt. Correlation between the preparation conditions, physicochemical properties and the catalytic activity of Pd/TiO₂ nanostructures towards ethanol electrooxidation in alkaline solutions will be discussed and the interest of such well-defined catalysts preparation method will be emphasized.

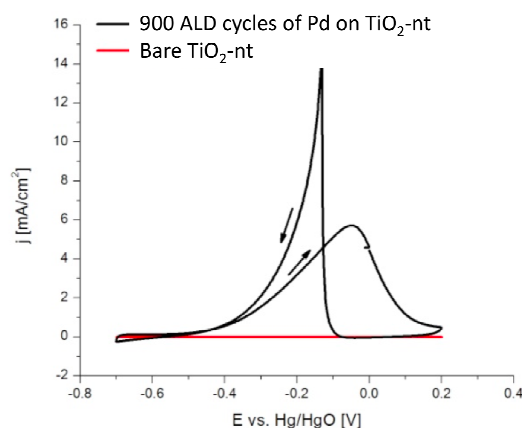


Figure 2: Cyclic voltammograms of Pd/TiO₂-nt and bare TiO₂-nt in 0.5 M EtOH + 1 M KOH, 25 mV/s, 10th cycle is shown.

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3. D.N. Goldstein, S.M. George, *Thin Solid Film*, **519** (2011) 5339.