Unexpected Activity Of Palladium Nanoparticle Catalysts For Formic Acid Electrooxidation

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Direct formic acid fuel cells have been demonstrated as a viable power source particularly for portable power applications. This paper demonstrates that palladium nanoparticles with a particle size below 10 nm have special reactivity for formic acid electrooxidation even though palladium foils show no special activity.

Figure 1 shows chronoamperometric data for Pd nanoparticles at 0.3 V with respect to RHE. We see initial currents in the order of 50 mA/mg of catalyst, which corresponds to 100 μA/cm^2 based on the total surface area of the palladium. By comparison, we previously found that platinum black produces 0.011 μA/cm^2 under similar conditions[4], while Pt/Ru produces no measurable current.

Figure 2 shows the chrononamperometric measurements at 0.3 V for a series of catalysts made by depositing palladium on a number of foils. In each case the catalysts show initially high activity. In most cases the activity slowly decays. Pd-V, Pd-Au, and Pd-Mo show the highest activity producing current densities of 15.3, 0.66, and 0.27 A/mg Pd. This corresponds to a current of 2400, 100 and 40 μA per cm^2 based on the physical surface area of the foil, and 3000, 130 and 54 μA per cm^2 based on the palladium surface area assuming every palladium atom is exposed.

A comparison to our previous results shows that Pd-V outperforms conventional Pt/Ru catalyst at 0.3 V vs. RHE by 3 orders of magnitude on a per mass precious metals basis, and by 2 orders of magnitude on a per exposed surface area basis. A fuel cell has been constructed using the new catalysts. The fuel cell with 40 m^2/g Pd nanoparticles shows near PEM performance, producing 500 mA/cm^2 at a cell potential of 0.5 V at 21° C with dry air. The current is 8 times that seen with commercial Pt/Ru, and 10 times that seen with 23 m^2/g palladium nanoparticles. Evidently, palladium nanoparticles have unusual properties for formic acid electro-oxidation.

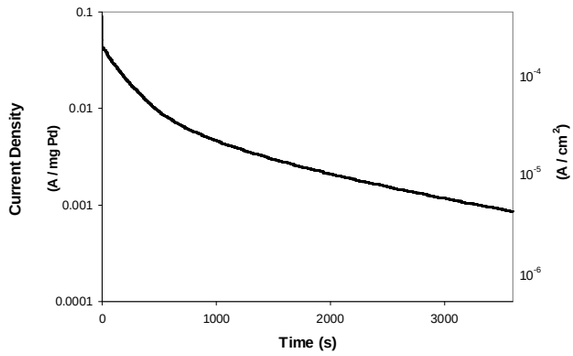

Figure 1 Chronoamperometric activity of Pd nanoparticles. The measurements were done by immersing the catalysts in a solution containing 5 M HCOOH and 0.1 M H_2SO_4 at open cell potential, stepping the potential to 0.3 V vs RHE and measuring the current as a function of time.

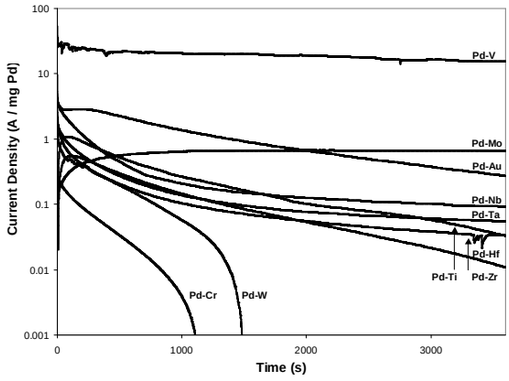

Figure 2 Chronoamperometric activity (per mass Pd) of Pd-M catalysts (M = Ti, Zr, Hf, V, Nb, Ta, Cr, Mo, W, Au) with θ_{Pd} = 0.6. The measurements were done by immersing the catalysts in a solution containing 5 M HCOOH and 0.1 M H2SO4 at open cell potential, stepping the potential to 0.3 V vs RHE and measuring the current as a function of time.

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