SAND2011-3558C

Thermal Stability of Nanoporous Palladium Alloys and their Hydrides

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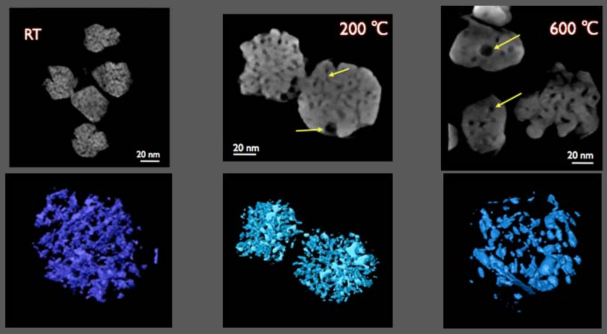
Introduction:

Nanoporous palladium and palladium alloy powders are of potential value for hydrogen isotope storage applications. These materials can improve charging and discharging kinetics for hydrogen due to their high surface area, and can help the helium decay product to escape when tritium is stored. The nanoporous palladium and palladium alloy powders, with diameters on the micrometer-scale and perforated by 3 nm pores, are synthesized in a scalable fashion by reduction of palladium salts in a concentrated aqueous surfactant. Performing *in situ* heating with a Protochips Aduro™ heating system in a TEM, we show that the pores of pure nanoporous palladium are not stable above 150 °C. To improve the pore thermal stability, we alloy the Pd particles with Rh. When Pd is alloyed with Rh, two effects are observed: 1) the pore thermal stability dramatically increases to temperatures as high as 400 °C and 2) the hydrogen storage properties are enhanced compared to pure nanoporous Pd.

Pure Nanoporous Pd Characterization:

Pore structure evolution as a function of temperature in pure Pd was carried out using electron tomography, bright field TEM, electron diffraction and porosimetry. Hydrogen storage properties were also measured. Electron tomography proved to be an especially powerful tool in determining pore structure evolution.

Tomography

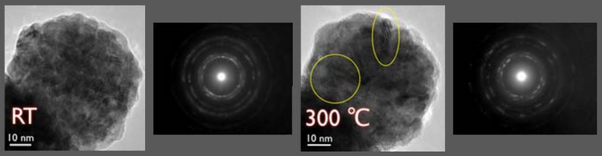


Pores evenly distributed at RT

Pores start to collapse (bottom arrow) and connect (top arrow) at 200 °C

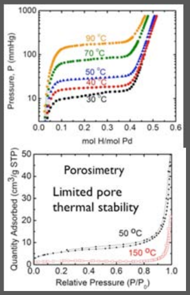
Pores collapse and form bubbles (arrows) at 600 °C

BF TEM/ Diffraction



BF TEM and diffraction at room temperature and after heating to 300 °C. The size of crystal grains increased as evidenced by the moiré patterns (yellow circles). The relative increase in spots (and decrease of rings) in the SAED patterns, which sample a larger number of particles, is evidence of grain growth that can restructure pores. This grain growth is not observed at 200 °C. Based on XRD, heating to 200 °C increased average grain size from 17 nm to 20 nm. After heating to 600 °C the average grain size increased to 32 nm.

Porosimetry and PCT Curves



PCT curves, top graph, which measures the H storage capacity, were taken for nanoporous Pd at various temperatures. The storage capacity is less than that of bulk Pd (~0.5 mol H/mol Pd vs. 0.8 for bulk).

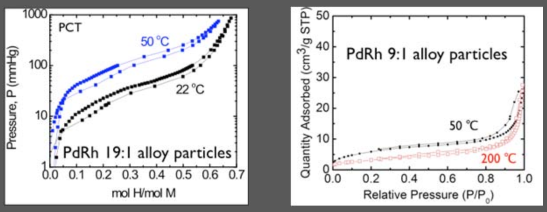
Porosimetry, done before and and after heating shows that much of the porosity is lost after heating to just 150 °C.

We seek to improve these properties through alloying Pd with other metals.

Improve on Pure Nanoporous Pd through Alloying:

Alloying with elements with higher melting points can improve pore thermal stability while maintaining hydrogen storage performance. The literature shows that adding rhodium to palladium maintains the hydrogen storage capacity in bulk. Since Rh has a higher melting point than Pd it can serve to thermally stabilize the nanopores in our materials, while not compromising the hydrogen storage capacity.

Porosimetry and PCT Curves

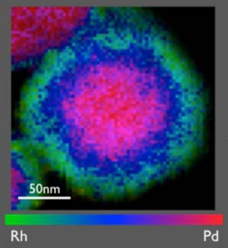


Porosimetry and PCT curves show that alloying with Rh even in small quantities dramatically increases the thermal stability of the nanopores while increasing the hydrogen storage capacity.

Nanoporous PdRh Characterization:

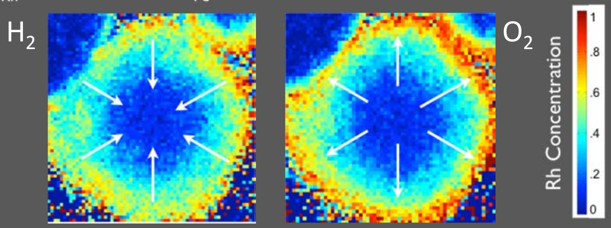
Particle and pore structure evolution as a function of temperature and environment in PdRh particles was carried out using EDS spectrum imaging, ambient pressure x-ray photoelectron spectroscopy (APXPS), Auger spectroscopy and porosimetry.

EDS Spectrum Imaging



EDS spectrum imaging revealed that the particles are not pure alloys. They separate into a core-shell structure. Pd makes up a significant portion of the core and Rh makes up a significant portion of the shell.

Analytical EDS Spectrum Imaging



We analyzed the PdRh particles using analytical EDS spectrum imaging after exposing them to real world working environments, i.e. to reducing (hydrogen) and oxidizing (air) environments at elevated temperatures (50 to 300 °C). A particle level rearrangement of the Rh and Pd was observed. The above images show that after reduction at 300 °C, left image, Rh segregates to the core of the particle (Pd segregates to the surface). After oxidation the opposite occurs, right image. Rh segregates to the surface (Pd to the core). This has significant implications for the performance of these particles in real world environments. APXPS at Lawrence Berkeley National Laboratory confirmed this surface segregation under reducing and oxidizing environments.

Conclusion:

Alloying Pd with small amounts of Rh improved the properties of the nanoporous particles. First it increased the pore thermal stability. Small pores were more stable as indicated by porosimetry and in situ TEM heating expierments (not shown). It also increased the hydrogen storage capacity over pure nanoporous Pd. We are using these results and continue to seek methods to increase thermal stability and hydrogen storage capacity.

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