



Control of both particle and pore size in nanoporous palladium alloy powders



Christopher G. Jones^a, Patrick J. Cappillino^a, Vitalie Stavila^b, David B. Robinson^{a,*}

^a Energy Nanomaterials Department, Sandia National Laboratories, PO Box 969 MS 9291, Livermore, CA 94551, USA

^b Hydrogen and Combustion Technologies Department

ARTICLE INFO

Article history:

Received 10 April 2014

Received in revised form 14 June 2014

Accepted 5 July 2014

Available online 15 July 2014

Keywords:

Mesoporous

Monodisperse

Uniform

Hydride

Microspheres

Copper

ABSTRACT

Energy storage materials often involve chemical reactions with bulk solids. Porosity within the solids can enhance reaction rates. The porosity can be either within or between individual particles of the material. Greater control of the size and uniformity of both types of pore should lead to enhancements of charging and discharging rates in energy storage systems. To control both particle and pore size in nanoporous palladium (Pd)-based hydrogen storage materials, we have first created uniformly sized copper particles of about 1 μm diameter by the reduction of copper sulfate with ascorbic acid. In turn, these were used as reducing agents for tetrachloropalladate in the presence of a block copolymer surfactant. The copper reductant particles are geometrically self-limiting, so the resulting Pd particles are of similar size. The surfactant induces formation of 10 nm-scale pores within the particles. Some residual copper is alloyed with the Pd, reducing hydrogen storage capacity; use of a more reactive Pd salt can mitigate this. The reaction is conveniently performed in gram-scale batches.

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1. Introduction

Hydrogen fuel cell technology is among the most promising alternative energy systems being developed to replace fossil fuels. Metal hydride batteries are frequently used in electric vehicles due to their safety and reliability [1]. The power densities of both of these technologies are limited by rates of chemical reactions at electrode surfaces, and their lifetimes are often diminished by changes in electrode geometry [2]. Efficiency and range are impacted if a battery cannot absorb braking energy rapidly enough in an electric vehicle [3]. Nanoporous palladium can provide fast charging and discharging in hydrogen gas storage systems, and accommodate swelling and shrinking of electrodes [4]. While the cost of Pd may be prohibitive for many applications, study of this material may lead to increased efficiency, reliability, and range of the more general class of hydrogen-based energy storage and conversion devices. A convenient, inexpensive and scalable method to produce nanoporous Pd with control of both nanopore size and particle size would ease further research and development of clean energy technology and help reduce our overall dependency on fossil fuel.

Pd in particular has a number of advantageous properties that make it a prime choice for the energy technologies discussed above. Pd has the ability to absorb up to 900 times its volume of hydrogen at room temperature and pressure, and then release it with only mild heating or pressure reduction [5,6]. The rate of uptake and release is inherently

fast, but is often limited by such factors as surface area, particle size, and packing density. We seek to optimize these properties in order to improve upon current energy storage and conversion technologies that rely on the chemistry of hydrogen.

Nanoporous noble metals with highly uniform, ordered pores are usually made by the reduction of metal salts in the presence of a surfactant [7]. The surfactant is at high enough concentrations that it forms arrays of cylindrical (or more complex) micelles a few nanometers in diameter, around which the metal is grown. The surfactant is then washed away. The metal can be reduced by electrodeposition on an electrode [8], use of a solution-phase reducing agent like ascorbic acid [9], a gas-phase reducing agent like hydrogen [10], or a solid-phase reductant like zinc metal [11]. The surfactant usually contains a poly (ethylene oxide) hydrophilic end. The hydrophobic end can be a long-chain alkyl group such as hexadecyl, or a hydrophobic polymer such as polystyrene. Adjusting the surfactant size allows tuning of the resulting pore size [4].

While these methods can reliably produce highly regular pores, there is much less control over larger-scale geometry. An example from previous work in our laboratory is shown in Fig. 1. In this case, uniform, regularly spaced nanopores are apparent, but the material arranges into irregularly shaped flakes on the 10 μm scale. Control of particle size is complicated by the transport rates of the metal salt and reducing agent, and the geometry of particles growing through the surfactant mixture, typically leading to highly heterogeneous products. Planar processing methods have been reported that control both particle and pore size, but they require many steps and generate only about a milligram per batch [12,13]. We have developed a scalable strategy to

* Corresponding author. Tel.: +1 925 294 6613.

E-mail address: drobins@sandia.gov (D.B. Robinson).

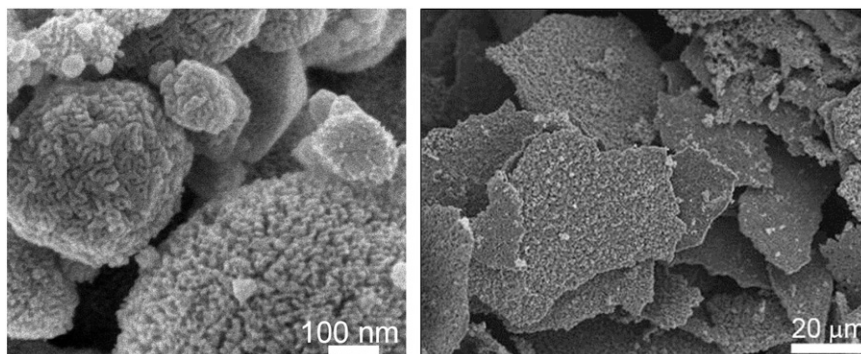


Fig. 1. Nanoporous Pd reduced by H₂ gas in a block copolymer template, produced according to Cappillino et al. [4], shows well defined pores (left) but uncontrolled particle shape and size (right).

control both the particle size and pore size in nanoporous Pd powders. We first create uniform-sized, nonporous particles of copper, a metal that is less noble than Pd. We then use these as self-limiting reducing agents for a palladium salt. The Pd should react 1:1 with the copper, resulting in a similarly sized porous Pd particle and a copper salt. This galvanic exchange reaction has been previously used in the production of nanoparticles and nanowires [14,15] and in the growth of atomic multilayer films. [16] Some of the copper remains in the form of an alloy that retains useful hydrogen storage properties [15]. By this approach, we can consistently produce micrometer-scale Pd alloy particles of uniform shape and size. Our work contrasts with the prior work on nanowires and films [15,16] because it involves larger scale particles in larger scale batches. We expect to be able to adjust the particle and pore size by changing the surfactant or the reductant particle size. By adopting a literature procedure that uses inexpensive, dilute surfactants [17], we are able to routinely synthesize batch sizes large enough for many important characterization methods, enabling further research and development of these materials.

2. Experimental

2.1. Materials

Copper(II) sulfate (CuSO₄•5H₂O) was obtained from EM Science. Acetone, sodium chloride (NaCl), sodium ascorbate (>98%) and palladium nitrate dihydrate (Pd(NO₃)₂•2H₂O) were obtained from Aldrich. Ammonium tetrachloropalladate(II) (H₈Cl₄N₂Pd, 99.998%) was obtained from Alfa Aesar. Pluronic F127 Prill is a low-cost triblock copolymer from BASF with a central block of hydrophobic poly (propylene oxide), with a degree of polymerization of about 56, and outer blocks of hydrophilic poly (ethylene oxide) each with a degree of polymerization of about 101, containing about 0.01 wt.% 2,6-Di-tert-butyl-4-methylphenol as an antioxidant. Deionized water was 18 MΩ cm and prepared in the laboratory.

2.2. Synthesis of Cu particles

A solution of copper sulfate (6 mL, 1 M) was added to a solution of sodium ascorbate (10 mL, 2 M) at room temperature. After approximately 2 min, the solution began to change from a dark brown to an orange/yellow color. Within 2–4 min when a yellow color had fully developed throughout the solution, 1 mL 10 wt.% Pluronic F127 was added to the reaction. The addition of a surfactant did not result in pores in the copper, but prevents aggregation of the particles. This process does not require any stirring or other sustained agitation during the reaction period.

To ensure adequate reaction time, the solution was left for 24 h. After this, a noticeable copper precipitate had formed on the bottom of the vial. The copper and remaining solution were placed in a centrifuge tube for washing and extraction. The copper was first centrifuged at 8000 rpm

for 2 min. The supernatant was then removed, and the copper was re-suspended in 1.0 wt.% aqueous Pluronic F127, and again placed in the centrifuge for 2 min at 8000 rpm. This process was repeated 3 times in order to thoroughly remove any remaining reactants from the suspended copper solution. After the third wash, the copper was again suspended in 100 mL 1.0 wt.% Pluronic F127 for use as a reducing agent. The particles were used in subsequent steps immediately, or within a few days, being stored in a sealed container. Before storing, nitrogen was bubbled through the solution of suspended particles to prevent oxidation.

2.3. Synthesis of Pd particles

To prepare the palladium reactant solution, 1.0 wt.% Pluronic F127 surfactant was dissolved in an aqueous sodium chloride solution (135 mL, 3.5 M). After the surfactant had been dissolved, (NH₄)₂PdCl₄ (1.34 g, 4.71 mmol) was added to the solution and lightly stirred until fully dissolved. The 100 mL of suspended Cu particles prepared above (299 g, 4.71 mmol Cu) was slowly added to the Pd solution with continuous stirring. This resulted in a gradual change of color from light brown to black over the course of approximately 10 min. Prior to this mixing step, nitrogen was bubbled through the suspension of Cu particles and the Pd salt solution to remove oxygen and reduce the rate of oxidation during the reaction period. The mixture was then left stirring while nitrogen was once again bubbled through. After another 10 min, the nitrogen line was removed and the flask was capped immediately. The flask contents were stirred for 48 h. At this point, the formation of a black precipitate was noticeable on the bottom of the flask. The reaction mixture was placed in the centrifuge at 4000 rpm for 3 min. The remaining supernatant was discarded. The powder was re-suspended in 30 mL of acetone, and was again centrifuged at 4000 rpm for 3 min to remove surfactant and other byproducts. The acetone wash cycle was repeated 3 times, followed by a water wash cycle using the same procedure. The powder was dried overnight under reduced pressure.

2.4. Treatment to reduce copper content

Samples of nanoporous Pd (50 mg, 0.47 mmol) were added to two solutions of Pd(NO₃)₂ (10 mL, 11.8 mM, and 10 mL, 23.6 mM) and placed on an orbital shaker for 24 h to remove residual copper. These treatments corresponded to a 1:2 and 2:1 molar ratio of Pd(NO₃)₂ to Cu, respectively. The powder was washed three times by suspending in 30 mL deionized water, centrifuging at 4000 rpm, and discarding the supernatant. The powder was then dried overnight under vacuum.

2.5. Characterization

Scanning Electron Microscopy (SEM) was used to analyze the copper and palladium powders. SEM analysis was performed using either a JEOL JSM 7600F field-emission electron microscope or a Hitachi S-

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