



Electrochemical hydrogen pumping using a platinum catalyst made in a fluidized bed via atomic layer deposition



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ABSTRACT

Platinum nanoparticle catalysts for electrochemical hydrogen pumping were synthesized on a functionalized powder carbon substrate (XC72R) using atomic layer deposition (ALD) in a fluidized bed reactor (FBR). Trimethyl(methylcyclopentadienyl)platinum(IV) (MeCpPtMe₃) was used as the reagent for platinum delivery. Following deposition, MeCpPtMe₃ ligands were combusted or hydrogenated to yield platinum on the XC72R surface. Reactions throughout the ALD cycle were monitored using mass spectrometry and IR spectroscopy to clarify the deposition chemistry. The resultant platinum catalysts were compared to commercial products in hydrogen pumping tests. Hydrogenation made finer, more dispersed, platinum nanoparticles that performed similarly to their commercial equivalent when pumping hydrogen. Conversely, oxygenation made a coarser catalyst that underperformed its commercial equivalent. Thus, altering chemistries shows potential for improving ALD catalyst performance.

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1. Introduction

Platinum catalysts are integral components of many chemical processes including catalytic reforming, catalytic conversion, and electrochemical power generation. As an expensive system constituent, optimal platinum use is desired, especially in emerging technologies. The use of platinum in electrochemical hydrogen pumping is one such application. Given the rising hydrogen economy [1], hydrogen separation from other gases such as CO and CO₂ will become increasingly important [2]. Electrochemical pumps have been utilized to purify and pressurize hydrogen for several decades [3]. The process can be tailored to reaction conditions by choice of ion conductor [4] and is readily integrated into larger chemical systems [5]. Just as with a hydrogen fuel cell, these pumps catalytically split hydrogen into protons and electrons at the anode. Protons conduct through the membrane, then catalytically combine with electrons from the circuit to yield a hydrogen permeate, free of gas impurities, at the cathode (similar to water electrolysis). Electric power is consumed, not produced (Fig. 1). Platinum is the most effective catalyst when coupled with proton exchange membranes [6,7]. In these devices, low loadings of platinum nanoparticles are needed to maximize the number of reaction sites while minimizing cost [8]. Atomic layer deposition (ALD) is suited to the production of these optimal materials.

ALD is a versatile engineering tool for precisely depositing metals, oxides, and polymers on particles [9–11]. Using volatile precursors,

materials of choice can be deposited over the entire surface of a substrate particle [12]. A second precursor removes any unwanted ligands or deposits more organics, growing an array of materials one submonolayer at a time. ALD can be implemented on powder substrates in fluidized beds [13–16]. The fluidized bed allows nearly 100% efficient precursor utilization, high throughput, and straightforward scale-up [17,18]. Practical applications include passivating photoactive particles [19], fabricating supported catalysts [20], and coatings for energy materials [21].

When platinum is deposited via ALD, nanoparticles are produced on most substrates, especially on particulate carbon [22–25] through an island growth mechanism [26]. In electrochemical contexts, the electrical conductivity of carbon is beneficial, although this material is poorly functionalized relative to alternative substrates [27]. This deficiency can be overcome through the generation of functional sites by carbon pretreatment. Functionalization renders ALD reactions more controllable [27]. Compared to incipient wetness and sputtering, ALD is a better method for precisely depositing nanosized catalysts on supports [28]. The ability to exchange precursors for inexpensive non-platinum materials is an advantage in producing future catalysts using ALD [29,30].

This report is the first demonstration of platinum ALD on a carbon powder substrate for electrochemical hydrogen pumping. In brief, XC72R carbon was functionalized and used as a substrate for platinum ALD. Platinum nanoparticles were deposited using trimethyl(methylcyclopentadienyl)platinum(IV) (MeCpPtMe₃) as the first precursor and either oxygen or hydrogen as a second precursor. The resulting catalyst was integrated into electrodes, evaluated via hydrogen pumping, and compared to a commercial Pt/C catalyst of

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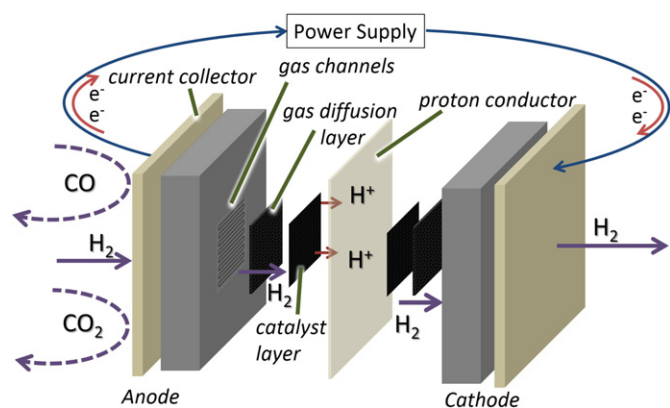


Fig. 1. Schematic of a hydrogen pump using a proton conducting membrane.

equivalent weight loading. The process from carbon support selection to hydrogen pumping is summarized in Fig. 2. Although the commercial catalyst initially outperformed the ALD catalyst using oxidation chemistry, a switch to a hydrogenation chemistry synthesis produced a competitive ALD catalyst.

2. Materials & methods

2.1. Functionalizing carbon

Ten grams of Vulcan XC72R carbon from Cabot Corporation were modified by refluxing in 150 mL of 15 M concentrated nitric acid at 120 °C for 9 h. The carbon was filtered, and then rinsed four times with DI water. The filtered modified carbon was dried in a cake overnight at room temperature to release absorbed water, and then was ground to a fine powder with a mortar and pestle. The surface groups on the functionalized carbon were characterized using diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS), obtained using a Thermo Scientific Nicolet 6700 FT-IR with a closed cell attachment (Harrick). DRIFTS spectra were taken against a background of unmodified XC72R. The change in surface area owing to nitric acid treatment and platinum deposition was monitored using Brunauer, Emmett and Teller (BET) analysis measured by a Micrometrics Gemini V surface area and pore size analyzer. Analyzed samples were prepared by evacuating at 100 °C for over 8 h using a Micrometrics VacPrep 061 sample degas system. Change in monatomic nitrogen and oxygen content was monitored using a TC600 from LECO Corporation.

2.2. Pt ALD in a fluidized bed

To deposit platinum [31], we placed 2 g of the functionalized XC72R in the fluidized bed reactor. See Fig. 3 for a schematic of an ALD FBR system. The ALD reactor was evacuated to 300 mTorr and the substrate dried overnight. The reactor sustained a temperature of 300 °C for ALD

reactions with supporting line temperatures set at 115 °C to facilitate efficient precursor flow through the ALD reactor system, under vacuum conditions between 300 and 3000 mTorr. A bubbler containing trimethyl(methylcyclopentadienyl)platinum(IV) (MeCpPtMe_3) was heated to 40 °C to maintain a constant vapor pressure. MeCpPtMe_3 was dosed by flowing 5 sccm of nitrogen through the bubbler to entrain the organometallic precursor, for a dose time of 40 min. Pure nitrogen was used as a purge gas for 70 min at 5 sccm. Pure oxygen or 20% hydrogen balance argon as a second precursor was dosed at 5 sccm for 90 min. To finish the cycle, pure nitrogen was purged through the system for 180 min at 5 sccm. One cycle was 380 min total. Five total cycles of platinum ALD were performed for each ALD catalyst material. An in-line Stanford Research Systems high pressure gas analyzer series QMS200 mass spectrometer was used to monitor by-products of the ALD reactions. Periodic spectra measuring partial pressure of species between 1 and 200 atomic mass units (AMU) were recorded. Spectra from each time point of relevant tracked species were compiled into pressure vs time graphs. The deposited platinum particles were analyzed for weight loading using inductively coupled plasma optical emission spectroscopy after digestion in an HF/aqua regia solution for 24 h. Images of the platinum particles were produced using transmission electron microscopy (TEM) on a Philips CM-100 microscope. Platinum particle characteristics, including size, dispersion, and metal surface area, were measured by hydrogen uptake at 40 °C using a Quantachrome AS-1 Autosorb.

2.3. Pt ALD in a vacuum chamber

Separately, to inspect the surface groups during the ALD process using oxygen as a second precursor, platinum was deposited on the functionalized carbon while monitored by IR spectroscopy in a vacuum chamber. Since this experimental technique was only for analysis, no actual catalyst was produced. Functionalized XC72R was prepared for analysis by diluting 50% with KBr. The diluted powder was pressed into a tungsten grid and fixed in a sample holder. The holder was placed in a vacuum chamber with windows for transmittance IR spectroscopy, performed by a Nicolet 6700 FTIR spectrometer. A nitrogen jacket around the chamber helped minimize noise generated from atmospheric gases. The powder in the holder was resistively heated to 300 °C. Dosing MeCpPtMe_3 consisted of isolating the chamber from vacuum and exposing it to a section containing precursor heated to 37 °C for 15 min. The precursor section was then isolated and the chamber was evacuated to simulate a purge for 10 min. Pure oxygen was dosed into the chamber as the second precursor step for 10 min followed by 20 min of vacuum evacuation for a subsequent purge. At various time points, IR spectra were recorded to inspect the species on the surface of the carbon powder throughout the ALD cycle. A total of two ALD cycles were performed using this analysis technique.

2.4. Electrochemical hydrogen pumping

Details of each type of membrane electrode assembly (MEA) evaluated for hydrogen pumping are summarized in Table 1. Due to the difference in cathode material, each ALD catalyst was compared to a commercial catalyst with similar weight loading on the anode. In order to reduce the platinum weight loading but maintain carbon loading for the catalyst layer, Pt/C catalysts were mixed with excess XC72R before ink synthesis. The resulting mixture was fabricated into an ink of the following composition: 3% Pt/C mixture, 10% water, 22% Nafion dispersion (LQ-1105–1100 EW at 5% weight), and 65% methanol. The ink was shaken, then sonicated for 4 h, and sprayed onto a Sigracet GDL 25 BC gas diffusion layer using a Harder & Steenbeck Evolution airbrush to form the gas diffusion electrode (GDE). GDEs were left to dry overnight at room temperature. GDEs for the anode and cathode were bonded to wet proton conduction membranes (Nafion 212) for 5 min at 130 °C and 750 psi to produce membrane electrode assemblies

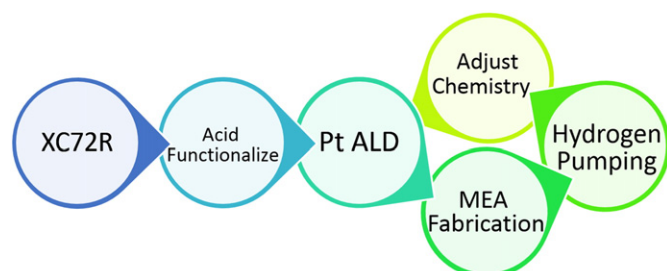


Fig. 2. Process flow: from carbon to hydrogen pumping.

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