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Proton Exchange Membrane Fuel Cell Flooding Caused by Residual Functional Groups after Platinum Atomic Layer Deposition

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ABSTRACT

Proton exchange membrane fuel cell (PEMFC) catalysts manufactured using atomic layer deposition (ALD) on unmodified and functionalized carbon were compared to a commercial catalyst in half- and whole-cell tests. Half-cell tests showed the ALD catalyst performed better or comparable to a commercial catalyst. Conversely, whole-cell tests revealed flooding in the ALD catalyst produced on functionalized carbon. Residual functional groups had reduced the hydrophobicity, and rendered this catalyst impractical for use in whole-cell PEMFC applications. However, the ALD catalyst produced on unmodified carbon performed better than the commercial catalyst, which illustrates the power of ALD on appropriate catalyst supports.

1. Introduction

Invented at the infancy of electricity generation during the 1830s [1], fuel cells have enabled efficient and direct chemical to electrical energy conversion [2]. Recently, stationary [3], space [4] and automotive [5] industries have adopted fuel cells for practical and sustainable electricity generation. Cost-competitive market demand requires further optimization of fuel cell systems and their manufacturing [6]. Here, atomic layer deposition (ALD) for fuel cell catalyst fabrication was explored in both half-cell and whole-cell systems.

In brief, ALD was used to grow platinum nanoparticles on a commercial carbon support, XC72R. One ALD half-cycle consisted of a vapor organometallic precursor deposition on the XC72R surface. To complete the cycle, the ligands were removed with a hydrogen dose. Since reactions are surface limited, a sub-monolayer of platinum is grown with each ALD cycle, which coalesce into nanoparticles [7]. A myriad of precursors can deposit ceramics or metals, depending on the chemistry [8]. Repeated ALD cycles deposit a film or nanoparticles concisely on a support. ALD has been used to generate many types of catalysts [9,10]. High throughput ALD on particle substrates is easily achieved in a fluidized bed reactor [7,11–14] and is adaptable for industrial-scale catalyst manufacture. Often, functional groups are placed on the substrate to facilitate deposition [15–17]. A previous study developed ALD as a large-scale method to produce PEMFC catalysts via combustion or hydrogenation chemistries, on plain or functionalized carbon [18]. In this report, catalysts grown from a hydrogen ALD chemistry were evaluated for promoting the oxygen reduction reaction (ORR). The ALD-derived catalyst on XC72R without functional groups was found to have better performance than a commercial catalyst, advocating ALD as an effective synthesis methodology for PEMFC catalysts. However, the performance results on a functionalized substrate were influenced by type of cell, and the conditions therein.

The bulk of literature presents half-cell evaluation for promising PEMFC catalysts within a liquid electrolyte environment. Naturally, the components of whole-cell tests convolute performance relative to half-cell measurements due to two electrodes

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Abbreviations: ALD, Atomic layer deposition; Pt/C, platinum on carbon; PEMFC, proton exchange membrane fuel cell; DRIFTS, diffuse reflectance infrared Fourier transform spectroscopy; ORR, oxygen reduction reaction; ECSA, electrochemical surface area.

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and a multitude of interfaces. Additionally, both triple- and two-phase boundaries dominate function within the cell [19]. Despite complex processes, based on our results we recommend only a whole-cell configuration can reveal ultimate catalyst performance for electrical generation. Furthermore, the effect of altering interfaces can be exploited more effectively within a whole-cell, such as varying Nafion® or Teflon® content in a catalyst layer [20–22]. We found comparison of half- and whole-cell tests can leverage interfacial effects in either environment to provide a more thorough investigation of PEMFCs materials. By also varying water management methodology within the whole-cell, residual hydrophilic surface groups prone to flooding on a functionalized catalyst were determined to contribute to diminished cell performance. This is the first study to compare plain and functionalized carbon support materials for ALD-prepared catalysts in both half-cell and whole-cell PEMFC configurations.

2. Experimental methods

2.1. ALD catalyst synthesis and material characterization

Platinum nanoparticles were deposited on unmodified or functionalized XC72R carbon support materials by ALD according to a previous report [18]. To summarize, XC72R was functionalized by refluxing in nitric acid for 9 hr. During ALD, trimethyl (methylcyclopentadienyl)platinum(IV) vapor was dosed by flowing 5 sccm of nitrogen through a bubbler of platinum metalorganic at 40 °C. This vapor flowed through a fluidized bed containing 2 grams of unmodified (plain) or functionalized XC72R. In a subsequent dose, 20% hydrogen balance argon at 5 sccm was used for ligand removal. Pure nitrogen at 5 sccm was used as a purge gas between precursor doses. All depositions occurred at 300 °C and an in-line high-pressure gas analyzer series QMS200 mass spectrometer (Stanford Research Systems) monitored breakthrough, where breakthrough was indicative of reaction completion for each precursor dose. One ALD cycle consisted of a 40 min platinum precursor dose, a 70 min nitrogen purge, a 90 min second precursor dose (20% hydrogen balance argon), and a 180 min nitrogen purge. Each ALD catalyst was generated from 5 total cycles. ALD catalysts were compared to a commercial catalyst, Premetek P10A200 with nominal 20 wt% platinum on XC72R.

Reported previously, TEM imaging was produced from a CM-100 microscope (Phillips). Platinum weight loading of the Pt/C catalysts was measured by inductively coupled plasma optical emission spectroscopy (ICP-OES) after digestion in an hydrofluoric acid/aqua regia solution for 24 hr. Platinum particle size, dispersion, and surface area were determined using H_2 chemisorption by an AS-1 Autosorb (Quantachrome). The XC72R surface before and after platinum deposition was inspected by diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS) using a Nicolet 6700 FT-IR (Thermo Scientific) with a closed cell attachment.

A LECO combustion oxygen analyzer (LECO Corp TC600) determined total oxygen content. Analysis was calibrated using a 20% tungsten trioxide standard (oxygen 502-141, green powder).

2.2. Electrochemical half-cell evaluation

Catalysts were evaluated for ORR efficacy using a rotating disk electrode (RDE). Catalysts inks were synthesized from 1.5 mg of Pt/C, 7.5 mL of ink solution containing 76% (v/v) deionized water with balance isopropyl alcohol, and 30 μL of Nafion® dispersion (LQ-1105 – 1100 EW at 5% weight). The mixture was sonicated for 20 min or until homogenous. The ink was drop-coated onto a 0.196 cm^2 glassy carbon electrode (Pine Research Instrumentation) in two 10 μL casts. The electrode was rotated in an inverted configuration at 700 rpm to ensure uniform dispersion of catalyst [23] by a rotator (Pine Research Instrumentation).

The Pt/C catalyst dispersions were evaluated as the working electrode in a 0.1 M $HClO_4$ electrolyte, with a Pt coil as the counter electrode, and a saturated calomel electrode (SCE, Gamry) as the reference electrode. Initially, the cell electrolyte was purged with pure nitrogen for 20 min followed by conditioning of the stationary working electrode by 100 cyclic voltammograms (CVs) between 0.00 V vs SCE and 1.20 V vs SCE at 500 mV/s by a Reference 3000 Potentiostat (Gamry). Electrochemical surface area (ECSA) of the platinum catalyst was determined by the third cycle of three CVs at 0.05 V vs SCE to 1.20 V vs SCE at 50 mV/s, assuming hydrogen adsorption of 210 $\mu C/cm^2$ of Pt [23]. Background scans were performed by CV between 1.03 V vs SCE to 0.05 V vs SCE at 20 mV/s, and subtracted from the polarization analysis to account for Pt oxidation/reduction currents. The electrolyte was then purged with pure oxygen for 20 min. At 1600 rpm, another CV was performed; the anodic scan provided polarization analysis after background subtraction. Anodic scans were analyzed at 0.2 V vs SCE (0.503 V vs RHE) for half-wave potential metrics.

2.3. Electrochemical whole-cell evaluation

Catalyst inks were fabricated from 3% Pt/C catalyst, 10% deionized water, 22% Nafion® dispersion (LQ-1105 – 1100 EW at 5% weight), and 65% methanol. The mixture was stirred for 1 hr and sonicated for 3 hr. A 25 BC gas diffusion layer (Sigracet) was sprayed with 53 $\mu L/cm^2$ of catalyst ink and left to dry on a glass plate for 24 hr, forming the gas diffusion electrode (GDE). Membrane electrode assemblies (MEAs) were fabricated from the catalyst of interest for the cathode, and 20% platinum on carbon commercial catalyst (Premetek P10A200) containing GDEs for the anode. The proton-conducting layer was prepared by boiling Nafion® 212 (DuPont) in 0.5 M sulfuric acid for 2 hr. The hot membranes were rinsed in boiling deionized water 3 times, and left to cool to room temperature in deionized water, where they remained stored. To fabricate MEAs, GDEs were bonded to the wet proton conductor using a heated hydraulic press (Carver Model C) under 500 psi at 130 °C for 5 min.

MEA performance was evaluated in a single cell setup (Fuel Cell Technologies) with 10 cm^2 active area operated by a fuel cell test stand (Ceres Technologies PEM 221). Featured wet polarization performance was evaluated at 60 °C, with 78% humidity, with pure hydrogen at 1.2 times the stoichiometric flow on the anode and pure oxygen at 2 times the stoichiometric flow on the cathode after a stabilization hold step at 0.1 A/cm^2 for 6 hr. Drier polarization conditions were evaluated at 60 °C, with 61% humidity, pure hydrogen on the anode at 200 sccm and pure oxygen on the cathode at 200 sccm after purging the cathode with nitrogen for 3 hr, and a stabilization step at 0.2 A/cm^2 for 30 min. A potentiostat (Gamry Reference 3000) determined electrochemical impedance spectroscopy at open circuit voltage (OCV) from 100,000 Hz to 0.1 Hz, where ohmic resistance was determined to be the real high frequency intercept on a Nyquist plot. All polarization curves were IR corrected.

2.4. Surface contact angle measurement

Wettability of the catalyst layers on the GDEs was evaluated by relative surface contact angle of a water droplet on the surface. Measurements were taken by pipetting a 5 μL droplet of 18.2 MΩ-cm ultrapure water onto the planar GDEs in three separate locations on each electrode. The electrodes were then placed on a backlit stage, and images of the droplets were taken using a Dantec Dynamics FlowSense EO camera equipped with a Nikon AF Micro-Nikkor 200 mm lens. Images of the droplets were analyzed using