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Glancing angle deposited Ni nanopillars coated with conformal, thin layers of Pt by a novel electrodeposition: Application to the oxygen reduction reaction

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ABSTRACT

Glancing Angle Deposition (GLAD) was used to prepare 500 nm long Ni nanopillars directly on glassy carbon disc electrodes (Ni_{GLAD}/GC). $Ni_{GLAD}\{Pt\}$/GC core-layer nanopillars were prepared by depositing Pt on the Ni_{GLAD} substrate via a novel rotating disc electrode galvanostatic deposition, where a stationary blackened Pt counter electrode served as the Pt source. Scanning electron microscopy, cyclic voltammetry, and inductively-coupled mass spectrometry were employed to characterize the deposits. Results indicated that the Pt was deposited in a conformal manner on the Ni_{GLAD} giving a loading of 11.6 μg. The $Ni_{GLAD}\{Pt\}$/GC electrode was *ca.* three fold more active than a {Pt}/GC (made with the same deposition in the absence of Ni) towards the oxygen reduction reaction (ORR) in 1.0 M KOH. As well, long term potentiostatic ORR studies showed the $Ni_{GLAD}\{Pt\}$/GC deposit was more durable than the {Pt}/GC, with the former completely retaining its initial performance after 5000 s polarization at 0.85 V *vs.* RHE, while {Pt}/GC lost 38% of its activity. Subsequent control experiments in the absence of O_2 showed that such decay was not due to loss of Pt over the prolonged ORR.

1. Introduction

We report a novel, convenient preparation of Ni nanopillars with thin, conformal films of Pt on glassy carbon disc electrodes, as well as preliminary studies on their activity towards the oxygen reduction reaction. Tireless efforts have been directed towards improving the sluggish oxygen reduction reaction (ORR) over Pt because Pt is a common component of the most active ORR catalysts in the literature [1–3]. The objective is to develop catalysts that are more active than Pt, more economic, and easy to prepare. The most studied approach is to prepare alloys or composite structures containing Pt and various non-noble metals and then study their properties in acidic or basic electrolytes [2,4–6]. Such alloys often undergo dealloying (*i.e.* selective dissolution of the non-noble party in acid), or lose activity due to the destructive electrodissolution of the active materials in acid [7]. In most cases, then, the initial use of basic conditions to study a newly developed combinatory catalysts would minimize significant changes in structure and composition due to dissolution. The use of alkaline electrolytes thereby allows for convenient screening of the near as-prepared structure, activity, and durability of ORR electrocatalysts. Furthermore, the results of such studies are relevant to the development of alkaline fuel cells [8].

A great deal of attention has been focused on the study of ORR in alkaline media using Pt as catalyst in binary and ternary combinations with non-noble transition metals. For instance, Garcia-Contreras et al. [9] reported that PtNi and PtNiCo made by chemical vapor deposition were both more active than Pt in KOH solution, with the latter giving the best activity. A comparative theoretical and experimental survey of ORR in 0.1 M KOH by Pasti et al. showed that Pt-In alloy was 2.6 times more active than Pt [10]. More recently, Jaeger and coworkers [11] showed that a Pt-C(Mo_2C) catalyst was more active than Pt/Vulcan carbon towards ORR in base.

Vacuum sputtering/deposition methods have been used to reproducibly prepare electrocatalysts with control over structure and composition [12–27]. The use of glancing angle deposited (GLAD) materials as oxygen reduction electro-catalysts was also reported recently [18–25]. GLAD is a physical vapor deposition

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(PVD) technique performed *in vacuo*, and microstructural control is achieved by the precise motion of the substrate relative to the incoming vapor flux [26,27]. The oblique deposition angle, α, is the angle between the incident vapor flux and substrate normal, while the angle of rotation about substrate normal is denoted as ϕ. During the deposition, the obliquely incident atoms are only able to nucleate onto the highest points of the substrate surface due to a self-shadowing effect. With increasing flux deposition, this self-shadowing effect leads to columnar or pillar-shaped growth. The porosity and nanopillar spacing can be controlled by changing α. Further morphology control can be achieved by modulation of substrate rotation in ϕ and allows access to various structures (e.g. vertical columns, slanted posts, chevrons, square spirals, helices, and combinations thereof). The high level of morphology control, inherent to GLAD, would lead to well-tailored nanostructures that can be used in a variety of applications including electro-catalysis. Moreover, large area GLAD films have been prepared in a prototype roll-to-roll system that can be further extended to mass production of these materials [28].

The Gall group reported various studies of GLAD-based electrodes in PEM fuel cells [18–21]. For example, 100 to 500 nm GLAD Pt nanorods were sputtered at $\alpha = 87^\circ$ directly onto gas diffusion layers and incorporated into polymer electrolyte membrane (PEM) fuel cells as cathodes. These were compared to Pt cathodes prepared at normal incidence ($\alpha = 0^\circ$). The GLAD Pt cathode had a lower electrochemically active surface area but a higher porosity than the cathode prepared at $\alpha = 0^\circ$. The mass specific activity of the GLAD-based cell was higher than the $\alpha = 0^\circ$ system, suggesting that mass transport was more facile in the GLAD-based cathode [21]. In another report, Pt sputtered onto 500 nm GLAD carbon nanorods were incorporated into a fuel cell and etched *in situ* by applying cell voltages between 1.2 and 1.7 V. The etching improved the performance of the cell, suggesting that mass transport was also more facile in the etched cathode [19].

The Brett group has collaborated with the research groups of Wilkinson and Dahn to report Pt sputtered on GLAD annealed niobium oxide and titanium nanopillars respectively [22,23]. Both reports showed catalyst surface enhancement factors on the order of 11 to 13 due to the high surface area of the supports. Room temperature ORR studies in 0.1 M $HClO_4$ showed that Pt/GLAD Ti could achieve current densities of 0.5 mA cm^{-2}, while the annealed niobium oxide-supported Pt displayed current densities $\geq$ 1 mA cm^{-2} at 0.9 V_{RHE}. Moreover, the latter catalyst withstood aggressive electrochemical testing up to 1.4 V_{RHE} and its morphology was stable at 1000 °C.

We recently reported the first study of alcohol oxidation with GLAD-based electro catalysts [29]. Specifically, Pt was electrochemically deposited onto 500 nm long Ni_{GLAD} nanopillars supported on Si wafers (Ni_{GLAD}/Si). Two Pt deposition methods were compared. The first was a traditional potentiostatic deposition from Pt salts dissolved in acidic electrolytes. This deposition mainly placed the Pt on the *tops* of the Ni_{GLAD} nanopillars to give a layered structure with Ni below and Pt on the top (referred to herein as $Pt_{Tr}Ni_{GLAD}$/Si). The second Pt deposition was an unconventional, self-limiting, galvanostatic one (J = (–) 100 mA cm^{-2}, normalized to the geometric area of the Si support under the Ni_{GLAD}), with a Pt counter electrode (CE) as the source of Pt in a 2.0 M NH_4Cl electrolyte [30,31] to result in a conformal Pt coating on the Ni_{GLAD}/Si. This core-layer catalyst is referred to as Ni_{GLAD}{Pt}/Si. Both $Pt_{Tr}Ni_{GLAD}$/Si and the core-layer Ni_{GLAD}{Pt}/Si were more active for the electrooxidation of 2-PrOH in base than were Pt foil or Ni_{foam}{Pt} (made by a similar Pt CE deposition on a Ni foam [30]). At low potentials, (50–300 mV_{RHE}) the electrochemically active surface atom-normalized activity of Ni_{GLAD}{Pt}/Si was higher than unsupported Pt and Pt-Ru nanoparticles as well. Interestingly, the Ni_{GLAD}/Si substrate without added Pt was also active towards 2-propanol electro-oxidation at low potentials.

This study presents the first ORR study on GLAD Ni supports over which Pt was electrochemically deposited using a rotating disc electrode. Using the versatile GLAD deposition methodology we have been able to cast Ni on a bare glassy carbon electrode with control over shape, quantity, and distribution. Here a higher value of α than for our previous studies with Ni_{GLAD}/Si ($\alpha = 85^\circ$) was set to decrease the surface density of the nanopillars in an attempt to facilitate the mass transport of O_2 in the catalyst layer [32,33]. As well, in the present work we used a modified version of the Pt CE deposition with the working electrode rotating at high rates to prepare Ni_{GLAD}{Pt}/GC core-layer nanopillars with minimal mass transport effects. This technique appears to deposit controlled amounts of Pt uniformly over the Ni particles. The resulting structures survived fast WE rotation during ORR tests in the absence of binders such a Nafion®. This approach is beneficial for mechanistic studies, for benchmarking catalysts, and for testing novel catalyst materials while avoiding intrinsic complications (e.g. mass transport and stability problems) commonly encountered with binding agents.

2. Experimental

2.1. General

The following chemicals were used as received from the supplier: Nitrogen (Praxair, pre-purified), oxygen (Praxair, pre-purified), concentrated sulfuric acid (Caledon), hydrochloric acid (EMD chemicals), nitric acid (EMD chemicals), perchloric acid (Anachemia Corporation), potassium permanganate (Fisher Scientific), 30% hydrogen peroxide (Fisher Scientific), potassium hydroxide (Caledon Laboratory Chemicals), ammonium chloride (Caledon Laboratory chemicals), ethanol (Greenfield Ethanol Incorporated), and potassium hexachloroplatinate (Aithica Chemical Corporation). The following materials were used as received from the supplier: platinum gauze (Alfa Aesar, 52 mesh woven from 0.1 mm wire, 99.9% metals basis), and nickel metal chunks (Cerac, Inc. 99.9% purity). The glassy carbon discs (Pine Research Instrumentation, 5 mm outer diameter × 4 mm thick, 0.196 cm^2 geometric surface area) were polished and cleaned as described below before use.

Triply distilled H_2O was used to prepare all aqueous solutions and was itself prepared by distilling a mixture of alkaline $KMnO_4$ and doubly distilled H_2O. 2-Propanol (ACS reagent grade, Sigma–Aldrich) was distilled under N_2 from Mg. Analytical grade reagents were used to prepare all electrolyte solutions. All aqueous solutions were saturated with N_2 gas by purging for 30 min before use. All electrochemical experiments were carried out under N_2 using standard Schlenk techniques. Rinse water and electrolytes were transferred under flushing N_2 with cannulas. ORR experiments were carried out in O_2-saturated 1.0 M KOH under an atmosphere of O_2. All glassware was cleaned with Piranha solution (5:1 by volume concentrated H_2SO_4 and 30% H_2O_2), rinsed thoroughly with triply distilled H_2O, and then dried at 80 °C. The platinum blacked gauze counter electrodes were prepared as described previously [29].

The electrochemical experiments were performed with a Solartron SI 1287 Electrochemical Interface controlled by CorrWare for Windows Version 2–3 d software. During the rotating WE depositions, the potential of the Pt CE was recorded with a Radio Shack multimeter. Rotating disc electrode experiments were performed with a Pine Research Instrumentation Modulated Speed Rotator equipped with an AFE6MB RRDE shaft and E5TQ series Change-Disk tip. The shaft and tip were connected to the