



Structural and activity comparison of self-limiting versus traditional Pt electro-depositions on nanopillar Ni films

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HIGHLIGHTS

- ▶ This is the first report of Pt–Ni glancing angle deposited (GLAD) based electrocatalysts.
- ▶ We contrast 2 methods to electro-deposit Pt on GLAD Ni nanopillars.
- ▶ We evaluate 2-propanol oxidation activity of the Pt–Ni deposits in alkaline media.
- ▶ Activity at low potentials results from the combined activity of Ni and Pt.
- ▶ At high potentials, Ni promotes Pt activity via a bifunctional effect.

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ABSTRACT

We report the fabrication, characterisation, and electro-catalytic activity of $<0.3 \text{ mg cm}^{-2}$ platinum deposits onto $\sim 500 \text{ nm}$ long nickel nanopillar substrates (Ni_{NP}) synthesised by glancing angle deposition (GLAD). This is the first reported study of GLAD-based Pt–Ni electro-catalysts and the first alcohol oxidation study on any GLAD based electro-catalyst. The Pt was deposited onto Ni_{NP} via either 1) an unconventional, self-limiting, relatively high current density galvanostatic deposition, with a Pt counter electrode as the source of Pt, or 2) via a conventional potentiostatic deposition from Pt salts dissolved in acidic electrolytes. X-ray Diffraction (XRD) and Inductively Coupled Plasma Mass Spectrometry (ICP-MS) confirm the successful deposition of Pt onto Ni_{NP} , while Scanning Electron Microscopy (SEM) shows that the nanopillar morphology is preserved but the Pt morphology is significantly different between the two methods. The galvanostatic procedure resulted in a conformal Pt deposition over the entire surface of the Ni_{NP} . The conventional procedure appeared to be mass-transfer limited, with most of the Pt being deposited on the tops of the Ni_{NP} . Cyclic voltammetry in 1 M KOH shows an enhancement of the surface area of the catalysts upon Pt deposition and corroborates the presence of Pt on the Ni_{NP} surface. Both prepared catalysts show high electro-catalytic activity towards 2-propanol oxidation in the KOH electrolyte at 60°C . The activity enhancement below 300 mV vs. RHE (RHE = reversible hydrogen electrode) was attributed to the combined activity of the Pt and Ni components in the catalysts. At higher potentials, a bifunctional mechanism was suggested. Finally, a geometric/composition effect may be at work in the traditionally deposited catalyst, and requires further investigation.

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1. Introduction

Alkaline Direct Alcohol Fuel Cells (ADAFCs) are being investigated as power sources for portable electronic devices for several reasons. Alcohols are readily available, liquid over wide temperature ranges [1], have promising electrochemical activity at

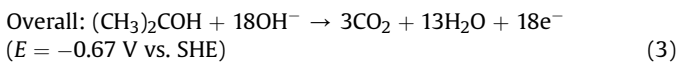
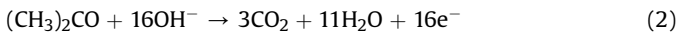
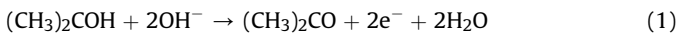
moderate temperatures [2], and have higher energy densities than hydrogen [3]. Alkaline systems are studied because the kinetics for both alcohol electro-oxidation and oxygen reduction are faster in base than they are in acid [3]. Methanol (MeOH) is the most studied alcohol fuel due to its ready availability and the absence of C–C bonds, making the complete oxidation of MeOH to CO_2 more facile than higher alcohols [4]. It is well known, however, that the electro-oxidation of MeOH self-poisons by CO or related intermediates that bind strongly to the catalyst surface. Further, the electro-oxidation of primary alcohols generates carboxylic acids or CO_2 as

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products – species that consume the alkaline electrolyte unless they can be removed from the system. 2-Propanol (2-PrOH) is investigated as an alternative to MeOH in ADAFCs in part because 2-PrOH is less toxic [5] and its electro-oxidation onset potentials are lower over Pt and Pt–Ru catalysts [6,7]. Further, the two-electron oxidation of 2-PrOH is reversible in principle, leading to a rechargeable system [7].

The mechanism for the oxidation of 2-PrOH over Pt in base is potential dependent, as represented schematically by Equations (1) and (2) [8].



In the voltage range from ~ 50 to 250 mV vs. RHE (RHE = Reversible Hydrogen Electrode), the oxidation product is believed to be predominantly acetone (Equation (1)). This oxidation is substantially more facile than that of MeOH because the build-up of strongly adsorbed intermediates does not occur to an appreciable extent over this potential range. The results are substantive currents in potentiostatic 2-PrOH electro-oxidations over Pt, Ru, and Pt–Ru catalysts in base over this low potential range [7,9,10]. These facile kinetics at low anode potentials were also demonstrated in fuel cells. For example, in a Nafion®-based cell, the 2-PrOH fuel exhibited ~ 200 mV higher cell voltage at 80 mA cm^{-2} than MeOH fuel [11]. In a liquid KOH electrolyte cell, a higher open circuit voltage (OCV) was recorded for 2-PrOH fuel and up to 16 mA cm^{-2} the performance of the 2-PrOH cell was stable with potential cycling from OCV to 0.5 V while the MeOH cell performance degraded severely after three cycles [1]. This degradation was attributed to substantial poisoning in the presence of MeOH.

At moderate electrode potentials, however, acetone and other intermediates strongly adsorb to the Pt surface, slowing the 2-PrOH oxidation until they are removed at higher potentials where oxyhydroxide species form on the Pt surface (Equation (2)). This poisoning manifests itself as low-potential current maxima in potentiostatic 2-PrOH electro-oxidations [7,9,10], and as unstable, dropping cell voltages for 2-PrOH fuel cells at $E_{\text{cell}} < \sim 0.5$ V [12,13]. In summary, over the entire potential range, the major 2-PrOH oxidation product is acetone, whereas CO_2 is a minor product at higher potentials [8].

Previous work in our group showed that incorporation of Ru [7] and Ni [9,10] increases the stabilized, potentiostatic currents for the electro-oxidation of 2-PrOH over Pt. The enhancement over Pt–Ru occurs from low to high potentials, whereas Ni promotes the electro-oxidation at potentials above 250 mV vs. RHE. At high potentials, it appears that Ni promotes the electro-oxidation mainly by a bifunctional mechanism, where Ni provides oxygen-containing species to oxidize the strongly bound intermediates and form CO_2 .

In this study, we report the use of nanopillar Ni films deposited by glancing angle deposition (GLAD) as substrates for Pt electro-deposition. Comprehensive reviews of the GLAD technique have been reported previously [14,15]. In summary, GLAD is a physical vapour deposition (PVD) technique performed *in vacuo*, and is achieved by the precise motion of the substrate relative to the incoming vapour flux. The oblique deposition angle, denoted as α , is the angle between the incident vapour flux and substrate normal, and the angle of rotation about substrate normal is denoted as ϕ . These angles are shown schematically in Fig. 1a. A schematic of a GLAD apparatus in typical PVD system can be found

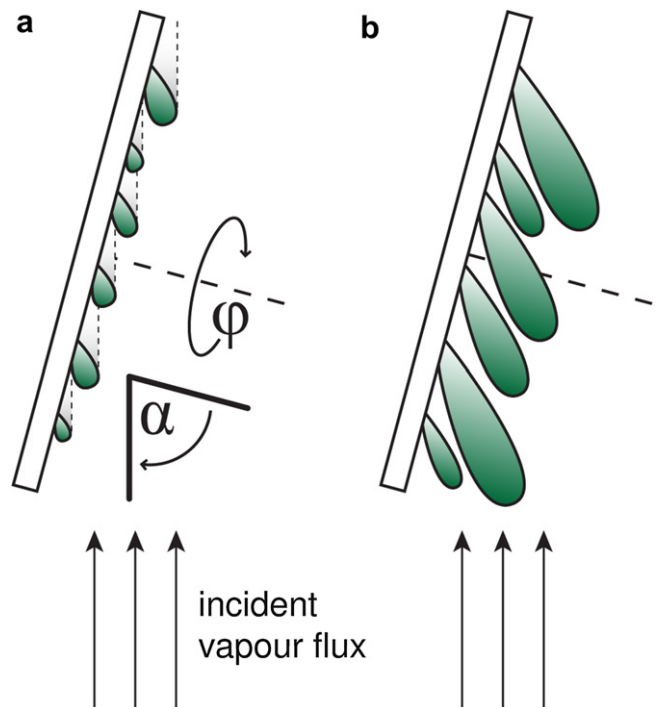


Fig. 1. (a) Schematic of the oblique deposition angle, α , and rotation angle about the substrate normal, ϕ , as defined in the GLAD process and (b) self-shadowing effect resulting in pillar-shaped growth.

in Figure 1.6 of Ref. [15]. During the deposition, the obliquely incident atoms are only able to nucleate onto the highest points of the surface due to a self-shadowing effect (Fig. 1a). With increasing flux deposition, this self-shadowing effect extends to columnar or pillar-shaped growth, as shown in Fig. 1b. Control over porosity and nanopillar spacing is achieved by changing the deposition angle α . Modulation of substrate rotation in ϕ adds further morphology control and access to various structures (e.g. vertical columns, slanted posts, chevrons, square spirals, helices, and combinations thereof).

The GLAD technique has been used for advanced nanostructuring in a variety of applications, including: nanoengineered optical thin films, such as square spiral photonic crystals [16] and antireflection coatings [17,18]; ordered small molecule organic photovoltaic bulk heterojunctions [19,20]; columnar microbattery electrodes [21]; and anisotropic ultrathin-layer chromatography plates [22]. The high level of morphology control inherent to GLAD leads to well-tailored nanostructures for each application.

GLAD-based nanostructures have been studied as electrocatalysts in fuel cells and related systems. For example, Bonakdar-pour et al. sputtered Pt onto high-surface area GLAD columnar Ti to prepare oxygen reduction electro-catalysts with a 10–15 times increase in electrochemical surface area compared to smooth Pt [23]. Khudhayer et al. also reported GLAD-fabricated nanostructures as catalysts for the oxygen reduction reaction (ORR) [24]. Their nanorod arrays of Pt on glassy carbon substrates have higher area-specific activity towards the ORR, as well as higher stability towards potential cycling in acid, than conventional Pt/C catalysts. In fact, the reported specific activity was similar to bulk polycrystalline Pt. This high area-specific activity was attributed to the large crystallite size and to the results of a crystallographic analysis that concluded that the nanorod sidewalls were dominated by Pt (110) planes. The mass-specific activity of the GLAD Pt deposits was lower than that of Pt/C. Gasda et al. incorporated GLAD Pt cathode catalyst layers onto gas diffusion layers and evaluated their

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