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NANOPOROUS GOLD ANODE CATALYST FOR DIRECT BOROHYDRIDE FUEL CELL

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ABSTRACT

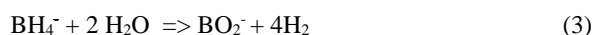
This paper reports on the direct electrochemical oxidation of borohydride ions at a nanoporous gold catalyst. The catalyst may be incorporated as an anode in a Direct Borohydride Fuel Cell (DBFC).

INTRODUCTION

DBFCs are currently under investigation in an effort to develop sustainable power sources. Their target specification of 600–1000 Wh kg⁻¹ is 5-6 times the energy density of lithiumion batteries. The DBFC system was first proposed in the 1960s: Indig and Snyder reported a practical demonstration of direct electricity generation from borohydride ions [1]. Research on DBFC technology stagnated then until the late 1990s. Amendola et al. reported on the performance of a DBFC system using Au–Pt alloy electroplated on carbon cloth as the anode [2]. Following further impressive research efforts over the next 5 years the first demonstration of a DBFC system for laptop computers was presented in 2005 by the Materials and Energy Research Institute (MERIT) who succeeded in increasing the DBFC system output from 10 to 400 W [3]. Recent vigorous research on DBFCs has greatly raised the expectation for the realization of the various benefits promised by this fuel cell system for portable applications [4]. Establishing the technology requires an understanding of the mechanism of borohydride oxidation and its associated catalytic species. The DBFC decomposes and oxidizes the fuel directly, Cathode: $2\text{O}_2 + 4\text{H}_2\text{O} + 8\text{e}^- \Rightarrow 8\text{OH}^-$ $E^0 = 0.40 \text{ V}$ (1)

Anode: $\text{NaBH}_4 + 8\text{OH}^- \Rightarrow \text{NaBO}_2 + 6\text{H}_2\text{O} + 8\text{e}^-$ $E^0 = 1.24 \text{ V}$ (2)

The theoretical equilibrium cell voltage, 1.64 V, compares favourably with DMFC and H₂/O₂ fuel cells that have equilibrium voltages of 1.21 V and 1.24 V, respectively. Borohydride is a promising fuel given its high theoretical specific energy, high specific capacity and good anode performance. Careful selection of the anode catalyst is crucial in minimising competing borohydride hydrolysis given by Eqn. (3) resulting in heterogeneous, non-faradaic hydrogen evolution which decreases fuel utilisation and lowers cell performance,



In practice the actual anodic reaction is more realistically represented by Eqn. 4



None of the more expensive platinum group metal catalysts can singularly satisfy both requirements of high catalytic activity for

borohydride oxidation and low activity for its competing hydrolysis.

Gold is an effective catalyst for borohydride oxidation and non-catalytic with regard to hydrolysis. Our focus lies in exploiting the high specific surface area of nanoporous gold (NPG) in developing an anode catalyst with high catalytic activity for oxidation of borohydride and low activity for its competing hydrolysis. NPG is as an interconnected, bicontinuous ligament network containing regions of both negative and positive curvature which topologically requires a high step density. This useful yet sparsely investigated form of gold has an intrinsically higher step density than bulk gold. This characteristic makes NPG attractive for catalysis studies; it is made even more attractive because it can be easily formed into thin, high-conductivity foils that are easily adapted to electrocatalytic measurements. Recent interest in electrolytic de-alloying has been motivated by the realization that nanoporous metals exhibit interesting properties (including large specific surface area and oriented geometry) and the prospect of applying these materials as sensors, coatings for medical, microreactors, actuators, microelectrodes, heat exchangers, filtration membranes, devices or precursor for making nanocrystalline gold and as catalysts [5, 6, 7]. Unlike platinum or palladium catalysts, NPG remains active at low temperature (room temperature or less) which is desirable for many practical applications. NPG has good thermal stability and is resistant to oxidation and thus can overcome aggregation or sintering limitations from which gold nanoparticles suffer upon elevation of temperature or in an oxidative environment. Low Temperature CO oxidation over unsupported nanoporous gold was shown by Xu et. al [8]. Zeis et. al demonstrated that NPG is an effective catalyst for reduction of hydrogen peroxide to water [9]. The reaction efficiency is sufficiently high to use it as a cathode for oxygen reduction in hydrogen PEM fuel cells.

RESULTS

Herein Ag_xAu_(1-x) films were electrodeposited from Ag(CN)₂⁻ and Au(CN)₂⁻ salts in Na₂CO₃ at pH 13 at -1.2 V. The resulting alloy composition was determined by EDX to be Ag_{0.84}Au_{0.16}. The silver component was selectively etched in 50 % nitric acid causing the remaining gold atoms to gather together in clusters that evolve into a porous material. TEM revealed a pore size of 15-20 nm and ligament size of 40 nm. The electrocatalytic activity of nanoporous gold was investigated using cyclic voltammetry. The onset potential for oxidation of 0.02 M NaBH₄ in 2 M NaOH at nanoporous gold was -1.1 V vs. SCE, 0.20 V lower than that at bulk gold. A limiting current density of 29 mA cm⁻² was recorded at a gold RDE while 60 mA cm⁻² was recorded at nanoporous gold,

as shown in the cyclic voltammetric responses in Figs. 1 and 2, respectively. Levich plot analysis revealed a diffusion-controlled reaction as shown in Fig. 3 and the attainment of near-maximum coulombic efficiency for borohydride oxidation ($n=7.85$). The specific surface area is estimated to be $4 \text{ m}^2 \text{ g}^{-1}$, which is high for a precious metal [9]. It is well established that in nanostructured form gold exhibits high activity in heterogeneous and homogeneous catalysis such as CO oxidation, oxidation of hydrocarbons and NO reduction. The oxidation of CO over supported gold nanoparticles has been most extensively investigated [10-12]. The role of catalyst support is a topic of continuous debate and different mechanisms have been proposed. The controversy arises from the fact that the supported gold catalyst is a composite system and its catalytic activity results from an interplay of pretreatment conditions, particle size, preparation method and choice of support. By eliminating the support effect in freestanding NPG a further insight into the origin of the exceptional catalytic behavior of gold in nanostructured form can be gained. As a catalyst NPG is not as cost effective as supported gold nanoparticles due to the energy consumed in its production, the amount of silver which is lost in the etch step and the significant amount of gold it constitutes; however, it has the advantage of establishing more intimate contact with an electrical substrate which is attractive from a catalytic viewpoint.

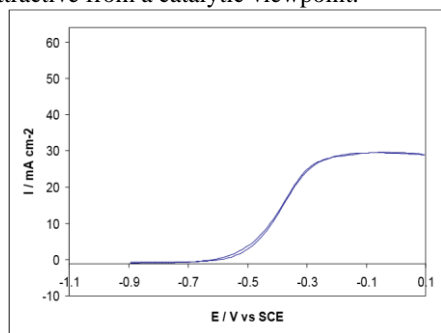


Figure 1 Cyclic voltammetric response (-0.9 to 0.1 V at 10 mV s^{-1} at 25°C) for 0.02 M NaBH_4 in 2 M NaOH at planar gold

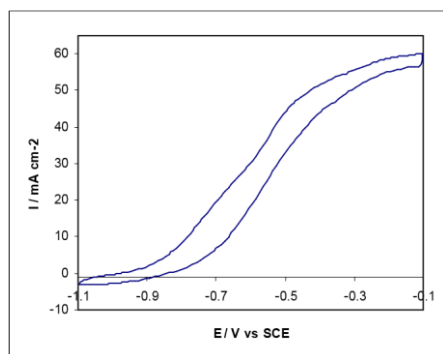


Figure 2 Cyclic voltammetric response (-0.9 to 0.1 V at 10 mV s^{-1} at 25°C) for 0.02 M NaBH_4 in 2 M NaOH at NPG.

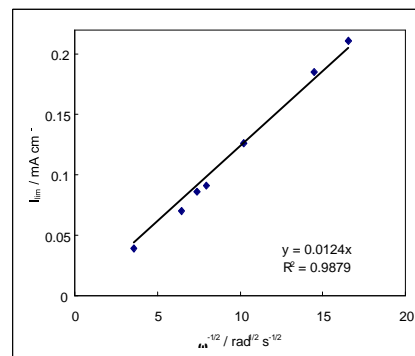


Figure 3 Levich plot for NPG on gold RDE in 2 M NaOH and 0.02 M NaBH_4 .

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