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High throughput optimisation of PdCu alloy electrocatalysts for the reduction of nitrate ions

Alexandros Anastasopoulos, Louise Hannah, Brian E. Hayden *

Chemistry, Faculty of Natural and Environmental Sciences, University of Southampton, Southampton SO17 1BJ, United Kingdom

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ABSTRACT

A high-throughput methodology was used to synthesise compositional gradient thin films of PdCu alloys. The expected equilibrium phases of the PdCu alloys as a function of composition were identified using XRD. The electrochemical behaviour of the alloys in NaOH base electrolyte was measured simultaneously on a micro-fabricated array of 100 electrodes. Small concentration of Pd addition to the Cu resulted in a reversible Cu derived surface redox, and higher concentrations decreased its equilibrium potential (a destabilisation of the surface oxide). The former is due to the mediation of the redox reaction by Pd and the latter due to electronic interaction between Pd and Cu. The most active reduction catalyst (rate at constant overpotential or minimum overpotential for a fixed rate) is in a narrow compositional region around 84$\%_{at.}$ Cu. The trend in reactivity can be understood by the promotion of nitrate reduction through hydrogen spillover from Pd at low concentrations in the alloy. The reduction in activity as the palladium concentration increases further is concomitant with the destabilisation of oxygen on copper, and therefore likely to be due to the inability to stabilise the nitrate ion at the surface, or extract the first oxygen atom to produce nitrite.

1. Introduction

Nitrate pollution is an important problem affecting many countries around the world. This pollution is a result of intensive use of agricultural fertilizers, livestock faeces and industrial waste effluents. Nitrate is very soluble and it is easily transported by surface run-off during precipitation and irrigation events into rivers, lakes and groundwater supplies. The World Health Organization has imposed a maximum limit of 50 mg L^{-1} of nitrate in potable water, since elevated nitrate levels can pose a serious risk to human health. Blue baby syndrome [1] and cancer [2,3] have been linked to elevated nitrate levels in drinking water. With tightening legislation and increasing disposal costs, it is important to establish a cost-effective method for nitrate disposal or destruction. Methods are also required to reduce the large quantities of nitrate present in alkaline nuclear waste solutions [4,5].

The electrocatalytic reduction of nitrate is a promising option as it does not require an external reducing agent; it is cost effective, selective and environmentally friendly as well as being tolerant to high nitrate concentrations [6,7]. The electroreduction of nitrate is a complex reaction due to the range of stable nitrogen oxidation states. The possible products of nitrate reduction are N_2O_4, NO_2^-, NO, N_2O, N_2, NH_2OH, N_2H_4 and NH_3. An ideal electrocatalyst would be one to selectively produce N_2. The mechanism and product distribution for the electrocatalytic reduction of nitrate is known to vary with electrode composition, electrode structure, pH and the supporting electrolyte [8–10]. Nitrite is a key intermediate in nitrate reduction, and so, initial steps in the reaction mechanism in alkali supporting electrolyte are likely to proceed through nitrite as described by the equations below:

$$NO_3^- \rightarrow NO_{3ads}^-$$

$$NO_{3ads}^- + H_2O + 2e^- \rightarrow NO_{2ads}^- + 2OH^-$$

$$NO_{2ads}^- + H_2O + e^- \rightarrow NO_{ads} + 2OH^-$$

$$NO_{ads} \rightarrow N_2O, N_2, NH_2OH, N_2H_4, NH_3$$

The electrocatalytic reduction of nitrate has been studied on a range of metal electrodes which include Pt [8,10–13], Pd [10,14], Ir [10], Ru [10], Rh [10,15–17], Cu [10,18–21], Ag [10], Au [10], Sn [22–24] and Bi [25]. A comparative study by Dima et al. examined the activity of nitrate reduction on a range of transition and coinage metals [10]. Rh was found to be the most active transition metal, whilst Cu was found to be the most active coinage metal. In spite of its cost, Rh is being trialled commercially in water

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* Corresponding author.
E-mail address: beh@soton.ac.uk (B.E. Hayden).

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treatment [26] since when activated on a support selectively produces N_2 and OH^- [16]. Nevertheless, the high cost and limited supply of Rh is a major disadvantage, and considerable effort is focussed on the use of bimetallic catalysts to induce selectivity and reduce the incorporation of precious metals.

Bimetallic systems studied for nitrate electroreduction include alloys (CuSn [27,28], PdCu [29,30], CuZn [31], PtRh [15,32], PtIr [33], CuNi [34]), overlayers (PdCu [9], PtCu [35], PtSn [36], PdSn [36–38], SnRh [39], SnIr [39], SnRu [39]) and ad-atoms on the electrode surfaces (Ge on Pt, Pd and Pt on Pd [40,41], (Ni^{2+}, Cd^{2+}, Co^{2+}, Ge^{4+}) on Pt [42]). One of the most active bimetallic systems reported is PdCu. There are studies of various active PdCu surfaces in the literature [9,43,44]; however, de Vooys et al. [9] reported that the selectivity to N_2 was at its highest when the reduction current was at its lowest. In comparison, a biphasic Cu–Pd alloy electrode (77% $Pd_{80}Cu_{20}$ + 23% Cu) was reported to successfully reduce nitrate to N_2 with a current efficiency of 76% [29]. PdCu alloys prepared by electrodeposition were found to be significantly superior catalysts than either Cu or Pd [30]. PdCu alloys are also effective heterogeneous catalysts for the reduction of nitrate in aqueous media [7,45,46]. We have therefore synthesised compositional gradients of PdCu alloys over a wide composition range in order to examine the effect of alloying on the electroreduction of nitrate. We have applied a high-throughput electrochemical screening methodology employing a silicon micro-fabricated screening array incorporating 100 individually accessible electrodes allowing simultaneous electrochemical measurements to be carried out under identical environments [47]. Nitrite reduction was also studied on the same catalysts as nitrite is a key intermediate in the electroreduction of nitrate.

2. Materials and methods

2.1. Electrocatalyst preparation and characterisation

The PdCu alloy thin films were prepared using a high-throughput physical vapour deposition (HT-PVD) method. The cryopumped ultra-high vacuum (UHV) chamber (base pressure 1×10^{-10} Torr) allows deposition from up to six off-axis sources to form multi-component materials. The growth of a controlled compositional gradient across the substrate was achieved by the co-evaporation of the component elements. The HT-PVD system and methodology have been described in detail elsewhere [47]. Pd (99.95%, Umicore) was deposited using an electron beam evaporation source (e-gun) source using a Fabmate crucible. Cu (99.999%, Testbourne Ltd.) was deposited using a Knudsen cell evaporation source. The range of the compositional gradient (31–89 at.% Cu) was adjusted using the shadow "wedge" shutter position and the source evaporation rates and the deposition time used to control film thickness (70–100 nm). The film thickness was measured using atomic force microscopy (AFM). The electrode composition was measured using energy dispersive X-ray spectroscopy (EDX) using a JEOL JSM5910 and Oxford Instruments INCA 300. Initially, the PdCu alloy thin films were deposited on 32 mm^2 Si substrates (Nova Electronic Materials) to determine the deposition conditions required in order to obtain the desired composition range/thickness, before depositing onto the electrochemical array substrate used in the high-throughput electrochemical measurements. Structural information was obtained by X-ray diffraction (XRD) using a Bruker D8 powder diffractometer with a C2 area detector using a SiN substrate (Nova Electronic Materials). The electrochemical silicon micro-fabricated screening array (Ilika Technologies) comprises of 100 individually addressable gold electrodes (1 mm × 1 mm) onto which the PdCu alloy catalysts were deposited. Masks were used to constrain deposition on the screening electrodes, and a combination of two masks was used to achieve 10 randomly distributed pure Cu electrodes amongst the CuPd alloy electrodes.

2.2. Electrochemical measurements

The electrochemical measurements were made using a potentiostat combined with a 100 channel current follower (Ilika Technologies) described in detail elsewhere [48]. Experiments were carried out at room temperature in a three compartment glass electrochemical cell which can accommodate the electrochemical screening array [49]. The counter electrode (Pt mesh Alfa Aesar, 99.99%) was separated from the main body of the cell by a glass frit. The reference electrode was a homemade saturated calomel electrode (SCE sat. KCL) placed in a Luggin capillary, 2–3 mm from the face of the working electrodes. The working electrodes are the 100 individually addressable electrodes present on the screening array. Electrochemistry experiments were carried out at room temperature using 0.5 M NaOH, 0.5 M NaOH with 0.05 M $NaNO_3$ and 0.5 M NaOH with 0.05 M $NaNO_2$ (all chemicals analytical grade, Fisher scientific) prepared using ultrapure water (18.2 MΩ cm, ELGA). The electrolyte solutions were purged with Ar (Air Products, N5 grade) for 20 min before experiments were carried out to remove dissolved oxygen.

3. Results and discussion

3.1. Characterisation of the PdCu alloys

Fig. 1a and b are a representative selection of XRD diffractograms for the PdCu alloy thin films in two 2θ regions around (111) and (200) Bragg peaks of the PdCu fcc crystal structure. Bragg peaks corresponding to the reflections of known structures are indicated. At high Pd concentrations, increasing the Cu concentration results in a continuous shift of the (111) Bragg peak from around $2\theta = 40.15°$ (pure Pd [29,50]) to higher 2θ and a concomitant reduction in intensity, indicative of the formation of a solid solution [29] PdCu (SS)/*Fm3m*. The (111) peak intensity subsequently increases to a maximum around $2\theta = 41.4$ at $50\%_{at.}$ Cu corresponding to the PdCu β/*Pm3m* phase [51]. The (111) derived Bragg peak continues to move to higher 2θ with decreasing peak height with a further increase in Cu concentration, and at $69\%_{at.}$ Cu, a Bragg peak at $2\theta = 42.2°$ corresponding to the Cu_3Pd α/*Pm3m* phase [52]. The latter phase appears to coexist with the solid solution phase CuPd (ss)/*Fm3m* until at $95\%_{at.}$ Cu, a single (111) peak corresponding to the solid solution phase CuPd (ss)/*Fm3m* is observed at $2\theta = 43.2°$: the formation of this solid solution phase at $95\%_{at.}$ Cu is accompanied by a concomitant increase in intensity and narrowing of the (200) peak. Despite the fact that the alloy film was deposited at a substrate temperature of 300 K and was not annealed and hence may not represent a thermodynamic equilibrium, the observed phases, summarised in Fig. 1c, are close to those expected from the bulk phase diagram [53].

3.2. Electrochemistry of PdCu alloys in alkaline electrolyte

The composition for a typical electrochemical library on a screening chip is presented schematically in Fig. 2a, showing a composition range of $31–89\%_{at.}$Cu, with a further 10 electrodes masked to produce electrodes randomly distributed with $100\%_{at.}$-Cu. Film thickness was in the range of 70–100 nm and was measured using atomic force microscopy (AFM). Cyclic voltammograms (CV) recorded in 0.5 M NaOH electrolyte at room temperature for a representative number of PdCu alloys and a Cu electrode are shown in Fig. 2b. On pure Cu, the surface redox couple (Cu^0/Cu^I) observed at $-0.45\ V_{SCE}$ (anodic) and $-0.67\ V_{SCE}$