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The effect of electrode material on the electrochemical formation of porous copper surfaces using hydrogen bubble templating

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ABSTRACT

The electrodeposition of copper onto copper, gold, palladium and glassy carbon (GC) electrodes via a hydrogen bubble templating method is reported. It is found that the composition of the underlying electrode material significantly influences the morphology of the copper electrodeposit. Highly ordered porous structures are achieved with Cu and Au electrodes, however on Pd this order is disrupted and a rough randomly oriented surface is formed whereas on GC a bubble templating effect is not observed. Chronopotentiograms recorded during the electrodeposition process allows bubble formation and detachment from the surface to be monitored where distinctly different potential versus time profiles are observed at the different electrodes. The porous Cu surfaces are characterised with scanning electron microscopy, X-ray diffraction and cyclic voltammetric measurements recorded under alkaline conditions. The latter demonstrates that there are active sites present on electrodeposited copper whose coverage and reactivity depend on the underlying electrode material. The most active Cu surface is achieved at a Pd substrate for both the hydrogen evolution reaction and the catalytic reduction of ferricyanide ions with thiosulphate ions. This demonstrates that the highly ordered porous structure on the micron scale which typifies the morphology that can be achieved with the hydrogen bubbling template method is not required in producing the most effective material.

1. Introduction

The fabrication of materials via electrochemical methods for various applications; such as electrocatalysis [1–4], hydrogen storage [5,6], photocatalysis [7–9] and sensing [10–14] is an increasingly attractive field of research due to the relatively simple, clean, cheap and efficient processing methods involved. There are many factors which influence the electrodeposition process such as the choice of potentiostatic or galvanostatic conditions, background electrolyte, precursor concentration, presence/absence of additives and temperature [15]. It is this plethora of experimental conditions which makes electrodeposition such an attractive method for controlling the properties of an electrodeposited material whether it be metallic, inorganic or organic in nature. However, an important but often overlooked parameter is the choice of substrate upon which the material is deposited and can often influence the morphology of the final structure and therefore its functionality and applicability [16–18]. For example, even on the same electrode material, it has been shown that the deposition of Ni using a constant current of 25 mA/cm^2 formed fine grain, high strength structures on an annealed Cu substrate as opposed to large, weakly adhered crystals on cold-rolled Cu [19]. This variation was attributed to the different exposed crystalline surfaces of the annealed and cold-rolled Cu substrates ([100] and [110] respectively) which facilitate the formation of different nucleation sites for the growing nickel structures.

A relatively new approach for the electrodeposition of high surface area metal deposits is using hydrogen bubble templating. This offers a quick and easy route to the formation of porous metallic surfaces where hydrogen evolution is initiated at the working electrode during the course of metal deposition. The first reports were on the deposition of copper foam [20,21] and has since been extended to various other metals and bimetallic combinations including Ag [22], Pt [23], Au [24], Pd [25], Pb [26], Cu/Sn [27], Cu/Pd [10], Cu/Au [28], Au/Pt [29], Au/Pd [30]. In the majority of these examples little emphasis has been placed on the role of the working electrode material in influencing the morphology of the deposit. However, in one study on the deposition of porous copper

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onto copper it was concluded that the roughness of the electrode influenced the final porosity of the structure where a nodular surface promoted the formation of smaller pores with thinner wall structures compared to that of a smooth surface [31]. It is envisaged that the use of different electrode materials would also have significant implications on the morphology of the final material electrodeposited under these conditions.

Therefore, in this work, we investigate the effect that various different substrates have on the electrodeposition of copper under high overpotential conditions and evaluate them for their suitability as electrode materials for the hydrogen bubble templating approach. Substrate electrode materials were chosen to provide a large range for their effectiveness in electrocatalysing the hydrogen evolution reaction, namely glassy carbon (GC), Au, Cu and Pd. The influence of copper morphology on electrocatalytic and catalytic activity is then investigated for the hydrogen evolution reaction and reduction of ferricyanide to ferrocyanide using thiosulphate ions respectively.

2. Experimental

Solutions containing $CuSO_4$, H_2SO_4, sodium thiosulphate ($Na_2S_2O_3$) and potassium ferricyanide ($K_3[Fe(CN)_6]$) (Ajax Finechem) were used as received and made up with deionized water (resistivity of 18.2 MΩ cm) purified by use of a Milli-Q reagent deioniser (Millipore). Electrochemical experiments were conducted at (20 ± 2) °C with a CH Instruments (CHI 760C) electrochemical analyser. Copper foil (0.158 cm^2 area; 99.999% purity purchased from Goodfellow) when used as the working electrode, was first immersed in diluted HNO_3 (10% v/v) to remove any surface oxides and then washed with acetone (Chem-Supply) and methanol (Merck) followed by drying in a stream of nitrogen gas prior to use. For gold and palladium electrodes they were prepared by e-beam evaporation (Balzers™ electron beam evaporator) of a 10 nm Ti adhesion layer on a silicon (100) substrate (Montco Silicon Technologies) followed by 150 nm of Au or Pd. Prior to use the films were cleaned by successive immersions in acetone, methanol and Milli-Q water for five minutes each, and then dried under a stream of nitrogen. The reference electrode in all cases was Ag/AgCl (aqueous 3 M KCl). For the electrodeposition of Cu, an inert graphite rod (3 mm diameter, Johnson Matthey Ultra "F" purity grade) was used as the counter electrode to avoid any possible contaminants from electrodissolution [32]. All electrochemical measurements commenced after degassing the electrolyte solutions with nitrogen for at least 10 min prior to any measurement. SEM measurements were performed on an FEI Nova SEM instrument. Prior to imaging, samples were thoroughly rinsed with Milli-Q water and dried under a flow of nitrogen. To measure film thickness the samples were tilted at a 40° angle and then imaged. XRD measurements were carried out on a Bruker AXS X-ray diffraction system operating at a voltage of 40 kV and current of 40 mA with Cu Ka radiation. The reaction of 1 mM $K_3[Fe(CN)_6]$ with 0.1 M $Na_2S_2O_3$ was carried out in a beaker (100 ml vessel) containing a total volume of 24 ml of solution under stirring conditions using a stirrer bar at the bottom of the beaker rotated at 800 rpm with the sample fixed in the solution. The geometric area of the sample was 0.158 cm^2 in all cases. The progress of the reaction was monitored by taking aliquots from the reaction mixture and performing UV–vis spectroscopy using a Varian (Cary 50) in a cuvette of 1 cm path length.

3. Results and discussion

The electrochemical deposition of copper was conducted galvanostatically using GC, Cu, Au and Pd electrodes by applying a constant cathodic current of 3 A cm^{-2} in an electrolyte containing 0.4 M $CuSO_4$ in 1.5 M H_2SO_4. The use of this current density value and electrolyte composition has been shown previously to produce a well adhered and highly porous copper foam on a copper substrate [21,33,34]. Under these conditions it appears that there is a balance between the evolution of hydrogen from the surface and the rate of metal electrodeposition. It is expected that the metal deposition rate is not likely to be the dominant factor in influencing the morphology of the deposit as potentials well below that of the $Cu^{2+/0}$ process (0.34 V vs SHE) are attained as discussed below but rather the nature of hydrogen evolution from the surface given that the exchange current density for this reaction at these materials have been measured to be 1.3×10^{-4}, 1.6×10^{-6}, 6.3×10^{-7} A cm^{-2} for Pd, Cu, Au respectively [35] and 1.6×10^{-6} A cm^{-2} for GC [36]. These values can only be treated as an indicator of potential activity as the surface area during the course of the reaction will continually be changing. Also given that this is an inner sphere electron transfer process the presence of defect or active sites on the surface may play a significant role in enhancing the electrocatalytic activity for a particular metal for the HER which would influence how hydrogen is evolved from the surface and therefore bubble size and residence time.

This is reflected in the linear sweep voltammograms recorded at Cu, Au and Pd electrodes in 1.5 M H_2SO_4 where the order of activity is Pd > Au > Cu in terms of both earlier onset potentials and current density (Fig. 1). For the case of Pd, a noisy response is observed which is attributed to vigorous gas evolution perturbing the current response. Therefore at the materials used in this study the evaporated Au film is a more effective electrocatalyst than Cu foil for the HER. The active site behaviour of gold in acidic electrolytes has been well documented by Burke et al. [32,37,38] who have shown that gold is a very effective electrocatalyst for a variety of reactions. This is also consistent with previous work from this laboratory which investigated the active site behaviour of evaporated thin films of gold [2,39]. Given the difference in activity of these materials for the HER it is therefore expected that the morphology of the resultant copper layers will be influenced.

Changing the substrate material had a profound influence on the morphology of the electrodeposit (Fig. 2). The most well defined and layered structures were seen on the Cu substrate (Fig. 2A); which had a fairly even pore size distribution of 63 µm (Table 1). The diameter of only the outermost layer of pores was measured via inspection of SEM images. The pores grow in size from the bottom to the top of the deposit due to the coalescence of hydrogen bubbles which occurs with time and has been discussed in detail elsewhere [33]. The internal wall structure is

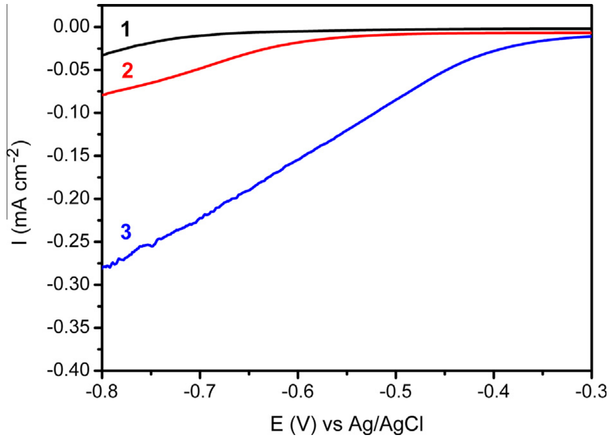

Fig. 1. Linear sweep voltammograms recorded at 10 mV s^{-1} in 1.5 M H_2SO_4 at a Cu (1), Au (2) and Pd (3) electrode.