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Balkis, Ali & O'Mullane, Anthony P.
(2015)

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Australian Journal of Chemistry, 68(8), pp. 1213-1220.

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<http://doi.org/10.1071/CH15191>

Electrochemical restructuring of copper surfaces using organic additives and its effect on the electrocatalytic reduction of nitrate ions

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Abstract

This work describes the fabrication of nanostructured copper electrodes using a simple potential cycling protocol that involves oxidation and reduction of the surface in an alkaline solution. It was found that the inclusion of additives such as benzyl alcohol and phenylacetic acid have a profound effect on the surface oxidation process and the subsequent reduction of these oxides. This results in not only a morphology change but also affects the electrocatalytic performance of the electrode for the reduction of nitrate ions. In all cases the electrocatalytic performance of the restructured electrodes was significantly enhanced compared to the unmodified electrode. The most promising material was formed when

phenylacetic acid was used as the additive. In addition the reduction of residual oxides on the surface after the modification procedure to expose freshly active reaction sites on the surface prior to nitrate reduction was found to be a significant factor in dictating the overall electrocatalytic activity. It is envisaged that this approach offers an interesting way to fabricate other nanostructured electrode surfaces.

Introduction

The electrochemical formation, characterisation and utilisation of nanostructured materials is an area of burgeoning interest.^[1] In particular metals such as Au, Pt, Pd have been extensively studied due to their excellent (electro)-catalytic properties as well as their interesting fundamental electrochemical behaviour in the absence of an analyte over wide pH ranges. The latter offers significant insights into surface cleanliness, structure and activity in addition to determining the electrochemically active surface area of an electrode. In comparison to the metals mentioned previously, copper has received less attention but is still a remarkably active catalyst and electrocatalyst as well as being the choice of interconnect material in the microelectronics industry.^[2] The electrodeposition of copper has been widely studied for the latter application where smooth, defect free coatings are required. To achieve this, the electroplating bath consists of a variety of components in addition to the source of copper ions and background electrolyte such as accelerators, levellers and brighteners.^[2] However, for electrocatalytic applications creating highly active copper with a high surface area in a nanostructured form is highly desirable. Several approaches have been used to create such materials using electrochemical approaches including dynamic hydrogen bubble plating,^[3] electrodeposition of Cu nanoparticles onto high surface area support materials,^[4] or planar electrodes.^[5] For the hydrogen bubble templating method additives were often used to control

the pore size distribution via perturbing the hydrogen evolution and/or metal deposition rate.^[3b, 6]

A different approach that has been used to create highly active materials has been termed a surface rebuilding method. This has been reported for gold where the electrode is subjected to vigorous oxygen evolution to form an oxide which is then reduced under vigorous hydrogen evolution conditions to fabricate a porous structure. This is done quite quickly at a frequency of around 50 Hz for 6000s. The resultant porous gold electrode showed good activity for ethanol, glucose and ascorbic acid oxidation.^[7] This type of approach was later used to restructure the surface of a copper electrode.^[8] Pt has been roughened using a repetitive square wave potential cycle at 1 kHz involving the oxidation of the surface and its subsequent reduction for use as electrodes for neural stimulation.^[9] Highly active copper surfaces have also been produced via the reduction of electrochemically grown $\text{Cu}(\text{OH})_2$ films.^[10] In addition, copper nanoparticles have been produced via reduction of CuCl powder in an ionic liquid to produce particles of around 10 nm in diameter.^[11] Another way to create active sites on metal surfaces that has been reported is to restructure nanoparticles such as Pt via the application of a square wave potential cycle in the presence of ascorbic acid to generate high-index facets at the surface,^[12] or Pt nanorods if exposed to air prior to the electrochemical modification.^[13] Therefore in principle electrochemically restructuring an electrode via an oxide formation/reduction process in the presence of additives may offer an interesting route for creating a nanostructured surface. In this work copper was chosen given the recent attention it has received as an electrocatalyst for a wide variety of reactions including CO_2 reduction,^[14] non-enzymatic glucose detection^[15] and nitrate detection/removal,^[10, 16] to name just a few. The latter in particular is an important topic as the imbalance in the nitrogen cycle caused by human activities has led to high levels

of nitrate in ground water^[16b] which can have serious environmental effects such as eutrophication of lakes, seas and rivers^[16d] and health effects for humans such as liver damage or possibly cancer.^[16c, 16d] In addition, several processes that involve the removal of nitrate are based on biological and physicochemical methods (e.g. catalytic reduction by hydrogen, reverse osmosis, ion exchange resins, electrodialysis).^[16c] However, these approaches can be costly, time consuming and generate harmful by-products. On the contrary, electrochemical methods have shown promise for the efficient conversion of nitrate to harmless nitrogen (N_2) gas, as well as offering a method to monitor nitrate levels.

Here we explore the effect of electrochemically restructuring a copper electrode in alkaline electrolyte via application of a simple potential cycling protocol involving oxide formation and reduction in the absence and presence of additives such as benzyl alcohol and phenylacetic acid which are known to influence the electrodeposition^[17] and corrosion^[18] of metals respectively. The activated electrode is then investigated for its electrocatalytic properties for nitrate reduction.

Results and discussion

The electrochemical behaviour of copper electrodes in alkaline solution has been well documented.^[10, 19] Figure 1 illustrates a typical cyclic voltammogram recorded for a Cu electrode in 1 M NaOH. On the anodic sweep two distinct peaks can be distinguished. Peak A_1 is attributed to the oxidation of Cu to Cu_2O and peak A_2 is a mixture of two processes as evidenced by the appearance of a shoulder on the main peak, namely the oxidation of both Cu and Cu_2O to a mixture of $Cu(OH)_2$ and CuO . On the cathodic sweep, peak C_2 is the counterpart of process A_2 . The magnitude of this process is significantly lower than A_2 as a passivating layer of Cu_2O is formed when CuO or $Cu(OH)_2$ are being reduced which is quite

insulating and hence inhibits reduction of CuO and $\text{Cu}(\text{OH})_2$ at this potential. At ca. -0.98 V the Cu_2O is reduced (peak C_1) which then allows the bulk of CuO to be reduced at ca. -1.21 V which is represented as a broad peak C_0 . However the reduction of hydrated oxides formed on the positive sweep has also been considered to be included in this C_0 response. Previous work by Burke et al.,^[19b, 19c] demonstrated that Cu can be activated electrochemically and thermally to produce significantly different voltammetric responses, in particular for the reduction of oxides formed on the surface of Cu. Generally this was observed after thermally treating a Cu electrode via resistive heating in an inert atmosphere or polarisation in the hydrogen evolution region for several hours.

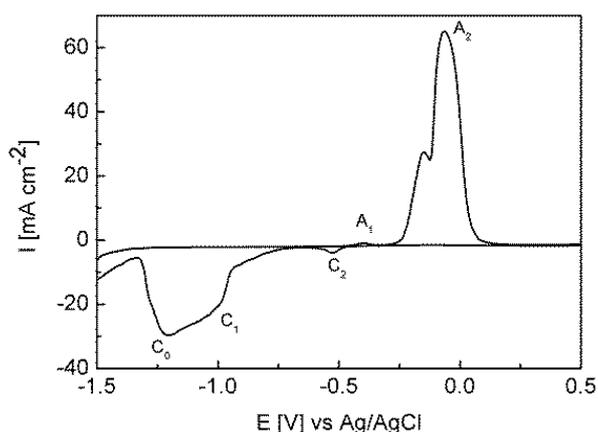


Figure 1: Cyclic voltammogram recorded at a Cu electrode at a sweep rate of 10 mV s^{-1} in 1M NaOH .

Illustrated in Figure 2 is the cyclic voltammetric response for the same Cu electrode cycled in the oxide formation/reduction region (-1.5 to 0.5 V at 10 mV s^{-1}) at room temperature for 20 cycles. It can be clearly seen that peaks A_1 and A_2 grow in magnitude upon repetitive cycling as does process C_1 and C_0 . Interestingly peaks A_1 and C_2 grow at a much slower rate, which is not too surprising given that it involves growing a passivating Cu_2O layer. However the major difference upon repetitive cycling of the potential is the

appearance and growth of new processes at ca. -1.35 V (C₋₁) and -1.47 V (C₋₂). Burke has attributed these to the reduction of hydrous oxides formed on active Cu sites created during thermal or electrochemical activation procedures.^[19b, 19c, 20] This type of behaviour has also been observed by our group on highly porous Cu electrodes where it was confirmed that these processes are not due to the re-deposition of ionic Cu²⁺ ions that may have been liberated during the process of Cu oxidation at more positive potentials.^[21] Bond et al. have added further evidence that these processes involve an active Cu/hydrous oxide transition by large amplitude Fourier Transformed ac voltammetric experiments.^[19a] Therefore it appears that upon the repetitive growth and reduction of oxides on Cu that a significantly different surface can be produced via a very simple protocol. When the oxide formed on the positive sweep is reduced, it creates highly active surface atoms which in principle will have a significant influence on electrocatalytic activity. The creation of active sites via electrochemical reduction of copper oxide formed on foils by oxidation in air at 500°C for 12 hours was reported to be highly effective for the reduction of CO₂.^[14b] It is also a dynamic process where significant changes in the electrochemical behaviour of Cu is seen upon repetitive cycling which then reaches a near steady state after 20 cycles. A similar type of behaviour was also observed when Cu electrodes were treated by a two-step protocol where the electrodes were extensively cycled (3000 times) at a scan rate of 10 V s⁻¹ into the oxide formation region and subsequently reduced via the application of 20 potential cycles in a region where oxide formation did not occur.^[10]

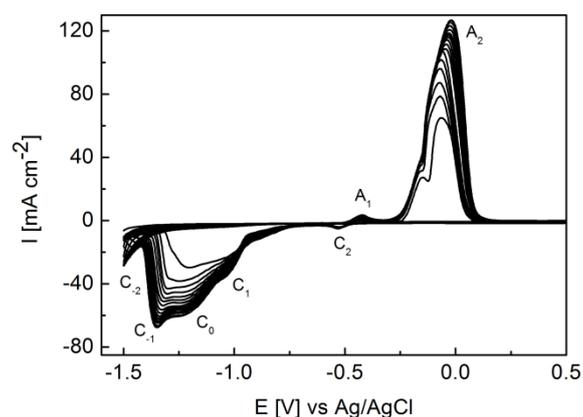


Figure 2: Multiple cyclic voltammograms recorded at a Cu electrode at a sweep rate of 10 mV s^{-1} in 1 M NaOH (20 cycles).

The surface of the Cu electrode was then investigated by SEM after the application of 1, 5, 10 and 20 potential cycles between -1.50 and 0.50 V at 10 mV s^{-1} . It can be seen that even after 1 cycle of potential that the relatively smooth Cu surface (Figure S1) has been converted into a surface containing nanosized spherical like particles of ca. 5-500 nm in diameter (Figure 3 a). Upon additional cycling these features grow in size and coalesce into a film after 5-10 cycles (Figure 3 b, c) and after 20 cycles a multilayer film can be observed where large protrusions of crystallites from the surface are evident (Figure 3d). It should be noted that lower magnification images of all surfaces are shown in Figure S2 indicating the homogeneity of the surface modification procedure. This change in morphology from relatively smooth to a rough surface is consistent with an electrode whose surface area increases as demonstrated by the cyclic voltammetric data (Figure 2) which showed an increase in magnitude of the current response upon potential cycling.

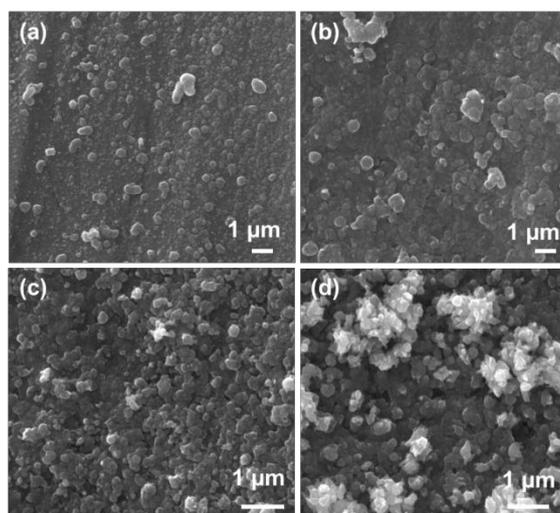


Figure 3: SEM images of a Cu electrode subjected to (a) 1, (b) 5, (c) 10 and (d) 20 potential cycles between -1.5 and 0.5 V at a sweep rate of 10 mV s^{-1} in 1 M NaOH.

XPS analysis of the surface after 20 cycles shows that both Cu_2O and CuO are formed on the surface. The Cu $2p_{3/2}$ core level spectrum shows a peak centred at 932.4 eV which is attributed to Cu and Cu_2O which are indistinguishable^[10] (Figure 4a). There is a distinct peak at 934.9 eV which is due to the formation of CuO on the surface.^[10] There is no real change in the XPS data upon repetitive cycling (Figure S3) and all peaks remain at the same binding energy. The O 1S core level spectrum for the Cu electrode cycled 20 times is shown in Figure 4b with peaks at 530.4 and 531.2 which are attributed to Cu_2O and $\text{Cu}(\text{OH})_2$ formation.^[10] Therefore the surface of the electrode consists of Cu, and residual mixed oxides consisting of Cu_2O , CuO and $\text{Cu}(\text{OH})_2$ after the application of this repetitive cycling protocol. From analysis of the electrode after 20 cycles using EDX it was found that the sample consisted of 4.5 wt % oxygen, indicating that the electrode was mostly Cu.

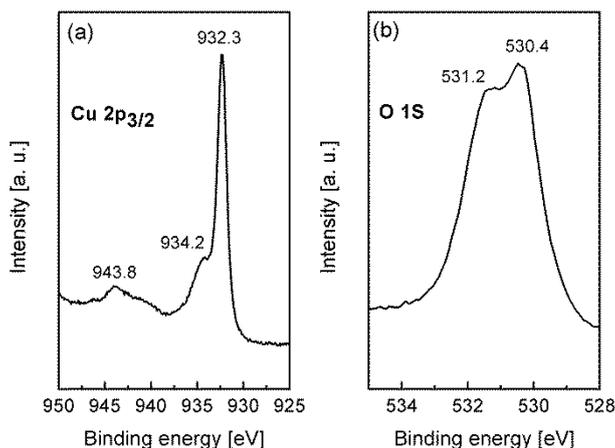


Figure 4: Cu 2p_{3/2} (a) and O 1S (b) XPS spectra for a Cu electrode subjected to 20 potential cycles between -1.5 and 0.5 V at a sweep rate of 10 mV s⁻¹ in 1 M NaOH.

The use of additives in the chemical synthesis of colloidal materials is extensive as they are used as reductants, growth directing agents and capping agents to prevent aggregation. However in comparison, this approach is under-utilised in the area of electrodeposition of nanostructured materials. As mentioned in the Introduction there was an interesting report where ascorbic acid was used in the synthesis of high energy facets of Pt to create highly active electrocatalysts.^[12] In that work electrodeposited Pt nanospheres were converted into tetrahedral nanocrystals via a square wave potential protocol, however no mention was given to the role or influence of the ascorbic acid which is a reducing agent used quite commonly in the synthesis of colloidal materials. In this work we chose to use benzylalcohol, which has been used as a mild reducing agent for the synthesis of Pd nanoparticles^[22], as well as an additive for controlling Zn and Cd deposition,^[17, 23] however with the aim that it is not electrochemically oxidised in the potential range where the Cu electrodes were cycled, as opposed to ascorbic acid which is oxidised quite readily at metallic electrodes. It has also been used as an additive in the electroplating of CuSn alloys to ensure a

lustrous finish.^[24] Figure 5 shows the cyclic voltammetric behaviour for a Cu electrode cycled in 1 M NaOH containing 0.1 M benzyl alcohol (Figure 5a) and 0.1 M phenylacetic acid (Figure 5b). The latter was chosen to see the effect of the functional group on the restructuring process as well as its ability to suppress the corrosion of metals.^[18] It is initially evident that the current being passed in the presence of these additives is lower than that in pure NaOH electrolyte (Figure 2) at all number of cycles. Significantly however, the reduction of the oxides on the negative sweep are distinctly different in all cases and in particular the cathodic peak at ca. -1.50 V emerges, indicating the formation of an additional active Cu/hydrous oxide transition state on the electrode surface. This is particularly apparent for the case of phenylacetic acid where process C₂ is very prominent. Even though the magnitude of this process is quite similar in all cases (Figure 2 and Figures 5a and b are shown on the same scale) the relative intensity of peak C₂ in comparison to all the other peaks, in particular A₂, is higher when phenylacetic acid is used. It can also be seen that the peak is more defined when phenylacetic is used.

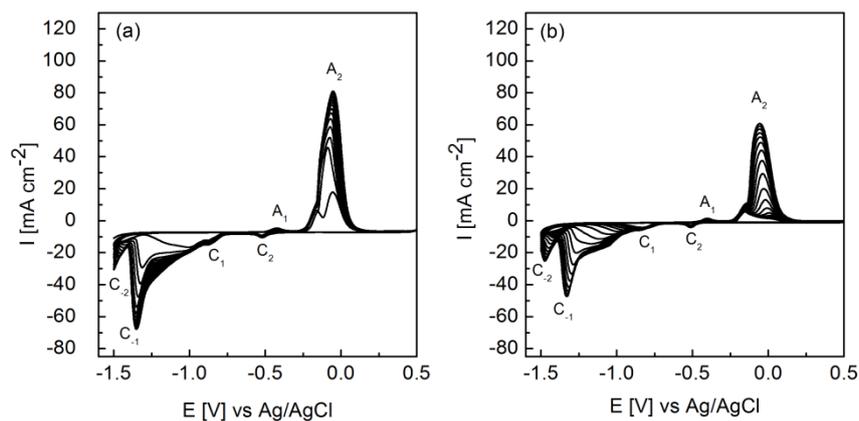


Figure 5: Multiple cyclic voltammograms recorded at a Cu electrode at a sweep rate of 10 mV s⁻¹ in 1M NaOH (20 cycles) containing (a) 0.1 M benzyl alcohol and (b) 0.1 M phenylacetic acid

Therefore restructuring Cu in the presence of these additives has a significant effect on their voltammetric behaviour which is reflected in the surface morphology shown in Figure 6. When benzyl alcohol is used as the additive there is some evidence of surface roughening after 1 cycle (Figure 6a) which becomes more apparent after 5 cycles (Figure 6b) which illustrates a film of crystallites of ca. 300 nm in diameter. After 10 cycles these have grown in size to ca. 1 μm in diameter (Figure 6c) and after 20 cycles to particles of 1-5 μm in diameter (Figure 6d). It should be noted that these structures are comprised of much smaller particles that are aggregated together. When phenylacetic acid was used, a similar trend was observed as seen for benzylalcohol in terms of growth in size of the structures, however their morphology was distinctly different. After 1 cycle (Figure 6e) surface roughening can be observed, and after 5 cycles both spherical but more elongated structures were formed (Figure 6f). Upon additional cycling (Figure 6 g and h) these structures grew larger but did not appear to be consisted of aggregates of smaller particles as seen for the other additives.

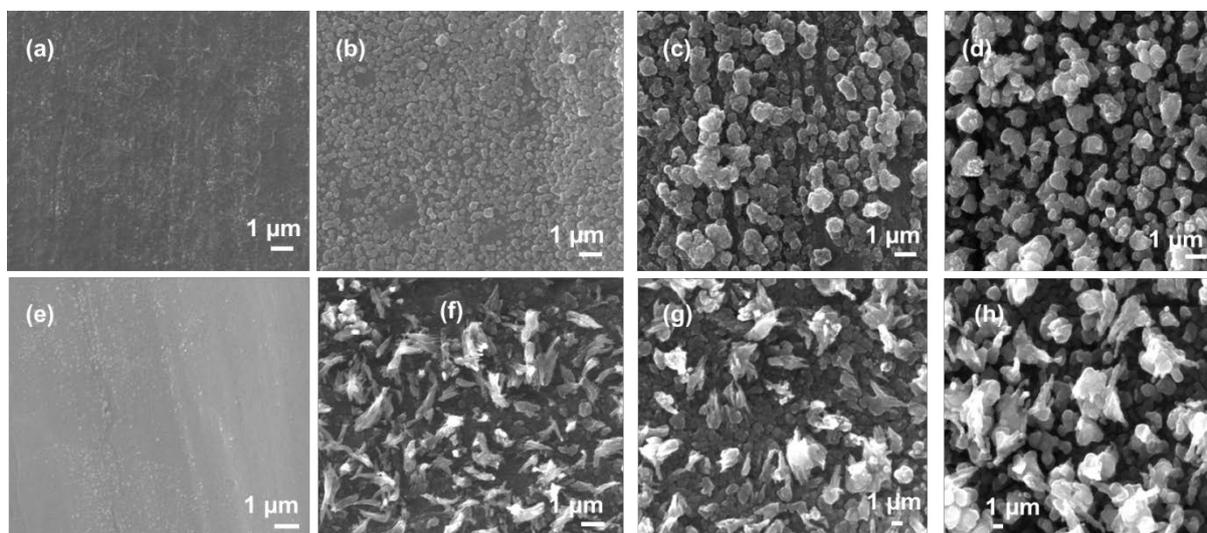


Figure 6: SEM images of a Cu electrode subjected to 1 (a, e), 5 (b, f), 10 (c, g) and 20 (d, h) potential cycles between -1.5 and 0.5 V at a sweep rate of 10 mV s^{-1} in 1 M NaOH containing (a-d) 0.1 M benzyl alcohol and (e-h) 0.1 M phenyl acetic acid.

The change in the surface of the film can be clearly seen by the digital images taken of the surface that was restructured in phenylacetic acid after various cycles. It can be seen that the shiny reddish copper surface is transformed initially to a yellow colour after 5 cycles which then after 10 cycles transforms to a darker colour indicative of the presence of some oxides on the surface^[25] as well as a nanostructured surface (Figure 7). In all cases there was no evidence of a blue film that would indicate $\text{Cu}(\text{OH})_2$ formation.



Figure 7: Optical images of a Cu electrode subjected to multiple potential cycles between - 1.5 and 0.5 V at a sweep rate of 10 mV s^{-1} in 1 M NaOH containing 0.1 M phenyl acetic acid.

XPS analysis of these surfaces shown in Figure S3 revealed that the samples comprised of Cu, Cu_2O and CuO as evidenced by the Cu $2p_{3/2}$ core level spectra showing peaks at 932.4 eV and 934.3 eV respectively as well as the satellite shake up peaks at 944 eV. Analysis of the O 1S spectra confirms the presence of Cu_2O and some $\text{Cu}(\text{OH})_2$. Therefore in all cases the presence of the additive did not significantly influence the surface composition but more so the morphology of the deposit and the surface area given the changes in the magnitude of the response recorded during the repetitive cycling process. This suppression of the overall magnitude of the response indicates that the extent of oxide formation in the presence of the additives is decreased or inhibited, however the different responses observed for the reduction of these oxides on the cathodic sweep is quite different. As discussed previously by Burke the composition of these oxides is difficult to ascertain and are generally considered as hydrous oxide type species.^[19b-d] To form oxides on Cu the electrode must have

access to OH⁻ ions and water for oxide growth to continue. Generally quite thick films can be produced on Cu via repetitive cycling at much higher potential limits (ca. 2.0 V vs RHE) or polarisation in the oxygen evolution region.^[19d] Given that the response here increases in magnitude upon cycling (Figure 2) indicates that densely packed oxide films are not produced and are readily reduced in the reverse sweep. In the presence of benzyl alcohol and phenylacetic acid the oxide formation is inhibited indicating that these additives compete with OH⁻ ions adsorbing on the surface which is the first step in copper oxide formation. This perturbs the oxide growth process which ultimately affects the coverage of oxide and its subsequent reduction. It is known in the electroplating field that benzylalcohol influences the deposition of metals and alloys such as Cd,^[17, 23] Zn,^[23] Cu, and CuSn.^[24] It's main use is for the suppression of the hydrogen evolution reaction via surface adsorption and controlling the grain size of the deposit. Therefore adsorption of benzyl alcohol on the surface of Cu during repetitive cycling is consistent with the decrease in the overall magnitude of the current passed during repetitive cycling when compared to when it is absent. A similar phenomenon is observed for phenylacetic acid which inhibits the oxide formation process to an even greater extent. This is consistent with phenylacetic acid being used as a corrosion inhibitor for Al in both alkaline and acidic media where adsorption on the surface occurs through the carbonyl group.^[18] Due to its structure the phenyl group can lie flat on the surface and maximise its efficiency for corrosion inhibition. Interestingly pharmaceutical drugs based on phenylacetic acid such as 2-(2, 6-dichloranilino) phenyl acetic acid have been shown to inhibit the corrosion of mild steel via surface adsorption but without a change in the corrosion mechanism.^[26] In essence oxide formation on Cu is a corrosion process and therefore phenylacetic acid simply acts as a corrosion inhibitor which again perturbs the oxide formed on the electrode surface and its subsequent reduction.

The restructured Cu electrodes were then tested for their electrocatalytic properties for the reduction of nitrate ions in alkaline electrolyte. Illustrated in Figure 8a are linear sweep voltammograms recorded for these electrodes in a 1M NaOH solution containing 0.1 M KNO₃. It should be noted that the current responses are normalised via the charge associated with peak A₂. The charge passed for peak A₂ on the 1st cycle of the Cu electrode in 1 M NaOH was equated to the geometric area of 0.126 cm². From this the area was then calculated for each of the restructured samples by calculating the charge passed for peak A₂ for cycle number 20 in each instance. The data in the absence of nitrate ions is also presented (Figure 8b) which was also normalised to the surface area as opposed to the geometric area in Figures 2 and 5. It can again be seen here that the magnitude and peak position of the hydrous oxide reduction peaks are significantly different for all the surfaces investigated and the response for the sample restructured in phenylacetic acid shows the highest amount of residual oxides normalised to the electrochemically active surface surface area. Therefore even though the surface area of the material formed with this additive is the lowest the relative contribution from residual surface oxides is highest in this case. The scale chosen in Figure 8b is to illustrate that the response recorded in the presence of nitrate ions is indeed an electrocatalytic process and not just associated with residual oxide reduction. For an unmodified copper foil the voltammogram in the absence of nitrate displays one prominent reduction peak associated with process C₁. There is no clear evidence of any other oxide or hydrous oxide reduction response until the end of the sweep. In the presence of nitrate ions the peak associated with process C₁ is shifted to a more negative potential and increases in magnitude due to the concomitant reduction of nitrate and oxide on the surface. Once the oxide is removed the current increases gradually which corresponds to the reduction of nitrate to nitrite.^[10] At ca. -1.3 V there is a significant increase in current due to the reduction of nitrite ions from the first step. It is interesting to note that this increase corresponds to the

point where process C₋₁ was observed in 1 M NaOH only (Figure 2). These observations are consistent with the incipient hydrous oxide adatom mediator (IHOAM) model of electrocatalysis^[27] which describes that dissolved oxidants such as NO₃⁻ ions are reduced at active metal sites (M*), in this case Cu*, which supply the electrons for this occur. Cu* is then immediately converted to an incipient oxide species which is subsequently reduced back to the active state Cu* by the current flowing in the external circuit. Thereby it is akin to a surface confined electrocatalytic process involving a Cu*/Cu incipient oxide couple that is kinetically fast enough to maintain a catalytic process. The involvement of such a redox couple was confirmed to be quasi-reversible by Bond et al. using FT-ac voltammetry where the electrocatalytic behaviour of smooth Cu electrodes and cathodically polarised electrodes were investigated.^[19a] Interestingly in that study even when a dc cyclic voltammetric response indicated only double layer charging the FT-ac technique revealed Faradaic components in the higher harmonics related to the Cu*/incipient oxide transition. Therefore, even though a clear oxide reduction response cannot be seen in the cyclic voltammogram shown in the absence of nitrate ions at ca. -1.3 V (Figure 8b) does not mean that such a process is not present. A similar study was carried out with gold electrodes where the FT-ac technique revealed Au*/hydrous oxide transitions not visible by dc voltammetric methods.^[28] The reaction products for the second step involving nitrite reduction are not the focus of the current study and will be analysed in future by batch electrolysis, however previous reports have indicated a complex process where species such as NH₃, N₂O, NO and N₂ are formed which is highly dependent on the surface conditions.^[16c]

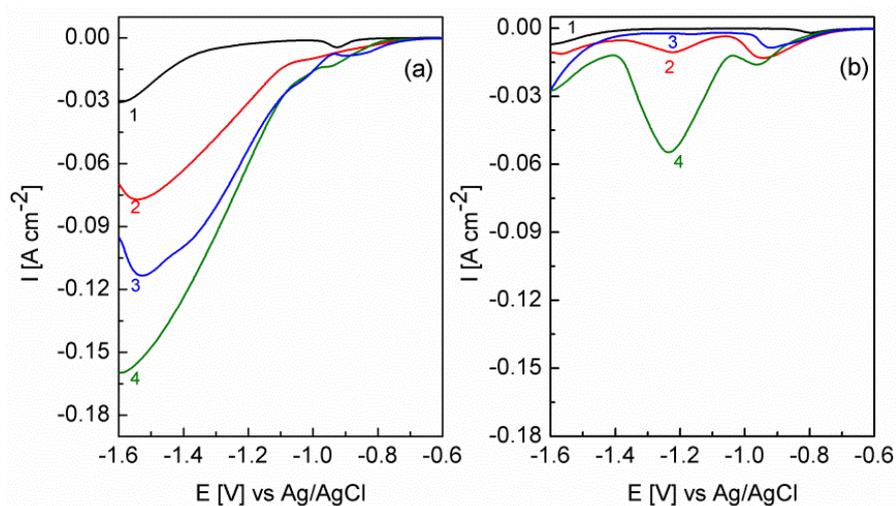


Figure 8: Linear sweep voltammograms recorded at 100 mV s^{-1} at (1) an unmodified Cu electrode, a restructured Cu electrode after the application of 20 potential cycles using (2) 1 M NaOH, (3) 1 M NaOH and 0.1 M benzyl alcohol and (4) 1 M NaOH and 0.1 M phenylacetic acid in the presence (a) and absence (b) of 0.1 M KNO_3 .

Significantly at all the restructured electrodes the current density for nitrate reduction is substantially greater than the unmodified electrode. The trend of increasing nitrate reduction current measured at -1.6 V is for Cu that was restructured in NaOH < benzyl alcohol < phenylacetic acid. Therefore once active Cu^* mediators are exposed they are highly active for nitrate reduction, in particular in the potential region after nitrate has been reduced to nitrite, i.e. below ca. -1.0 V . The higher concentration of residual oxides on the surface in the $\text{C}_{.2}$ region also appears to be linked to the sustained reduction of the nitrite species. It should be noted that in all cases the nitrate to nitrite process is also enhanced significantly at the restructured electrodes, indicating that the concentration of Cu^* active atoms at electrochemically oxidised/reduced Cu electrodes, is promoted compared to a pristine Cu electrode. However the concomitant reduction of residual oxides is also a contributing factor

to the current, in particular in the case of phenylacetic acid. Therefore it suggests that the addition of additives during the restructuring process affects the nature of the oxide formed on the electrode surface whose subsequent reduction to expose Cu* dictates the overall electrocatalytic performance, in particular at potentials from -1.2 to -1.6 V. These data also indicate that having residual oxide on the surface is not detrimental to electrocatalytic reduction reactions. This makes sense in that a freshly reduced oxide will expose highly reactive Cu* centres that then participate in the reaction. The nature of the active site will then depend on the type of oxide material it is created from as suggested by the data in Figure 8b which shows the difference in the oxide reduction profile at each of the Cu electrodes. Burke et al. have demonstrated that the formation of incipient oxides on the surface of Cu is a complicated processes and is dependent on the treatment of the electrode surface which is confirmed here. The exact composition of these incipient oxides is still open to debate and the surface is unlikely to consist of purely Cu₂O, CuO or Cu(OH)₂ but also CuO·OH, Cu(OH)·H₂O, and CuO(OH)_{0.5}^[19d] whose reduction to Cu* is expected to produce a range of metal clusters and adatoms on the surface with significantly different energies which control the electrocatalytic performance of the electrode as indicated here by the differences in the current recorded for reduction of nitrate ions. This is also consistent with previous work on CO₂ reduction on copper electrodes prepared from copper oxides where the concomitant reduction of the Cu₂O film during CO₂ reduction was the key aspect to selectively produce methanol while also maintaining high electrocatalytic activity.^[14c] This work also demonstrates that care should be taken when investigating the electrocatalytic behaviour of Cu electrodes and in particular nanostructured Cu, in that performing a cyclic voltammetric analysis such as that shown in Figures 1 and 2 can significantly influence the performance of the material given the extensive changes to the surface even after 1 cycle. This is expected to

be particularly influential in the case of Cu nanoparticles created either chemically or electrochemically which is the focus of future research.

Conclusion

The results presented here show that copper electrodes can be restructured in alkaline solution in a simple manner by applying a repetitive potential cycling protocol involving oxide formation and reduction to generate a nanostructured Cu surface with residual surface oxides. The presence of additives such as benzyl alcohol and phenyl acetic acid perturb the oxide growth process and hence the morphology of the deposit once these oxides are reduced. In all cases the cyclic voltammetric behaviour was distinctly different compared to the 1st cycle of a Cu electrode in alkaline solution and significant hydrous oxide reduction responses were observed at lower potentials indicating the formation of an active surface. These restructured electrodes showed enhanced performance for the electrocatalytic reduction of nitrate compared to an unmodified Cu electrode and the best performing material was found when phenylacetic acid was used as an additive. In all cases nitrate reduction was initiated once residual oxides were removed from the surface exposing fresh active sites that participated in the electrocatalytic reaction. This approach offers an interesting way to nanostructure an electrode surface and could be applied to many other electrode surfaces and electrocatalytic applications.

Experimental

Chemicals

All the chemicals were analytical grade reagents and used as received without further purification. Aqueous solutions of phenyl acetic acid (Ajax Finechem), benzyl alcohol

(Merk) and NaOH (Aldrich) were made up with deionised water (resistivity 18.2 M Ω) purified by use of a Milli-Q reagent deioniser (Millipore). Cu foil, thickness 0.025 mm, 99.98% trace metals basis (Aldrich) was used as the substrate.

Sample preparation

The restructured Cu electrode was achieved using a cyclic voltammetric protocol (1 to 20 cycles recorded at 10 mV s⁻¹ from -1.5 to 0.5 V vs Ag/AgCl) in a solution containing either: (a) 1 M NaOH, (b) 0.1 M benzyl alcohol in 1 M NaOH where the benzyl alcohol solution was prepared by sonicating for 15 minutes at 40°C, and left to cool to room temperature and (c) 0.1 M phenylacetic acid in 1 M NaOH where the phenylacetic acid solution was prepared by sonicating for 15 minutes at 40°C, and left to cool to room temperature. The restructured surface was washed thoroughly with Milli-Q water and dried with nitrogen gas prior to surface analysis or any further electrochemical experiments.

Electrochemical measurements

Cyclic voltammetric experiments were conducted at (22 \pm 2) °C with a CH Instruments (CHI 760C) electrochemical analyser in a electrochemical cell (BAS) that allowed reproducible positioning of the working, reference, and counter electrodes and a nitrogen inlet tube. The copper electrodes (0.126 cm² – Copper sheets (2 x 0.65 x 0.0025 cm) were masked off using Kapton tape) and were rinsed with Milli-Q water, rinsed with acetone and then in ethanol, and dried with nitrogen gas. The reference electrode was Ag/AgCl (aqueous 3 M KCl). For all of the electrochemical experiments carried out, an inert graphite rod (5 mm diameter, Johnson Matthey Ultra “F” purity grade) was used as the counter electrode to prevent any possible contamination from dissolution of the counter electrode.^[29] Electrocatalysis experiments were performed on restructured samples that were subjected to 20 cycles in

either 1 M NaOH, or 1 M NaOH containing benzyl alcohol or phenylacetic acid. These samples were removed from the electrolyte and washed with MilliQ water and dried prior to nitrate reduction experiments. The latter were carried out using linear sweep voltammetry from -0.8 to -1.6 V at 100 mV s^{-1} to avoid any further oxide formation prior to the experiment.

Surface characterisation

SEM measurements were performed on a FEI Nova SEM instrument with an AMETEK energy dispersive X-ray (EDX) system (Nova 200) operated at an accelerating voltage of 30 kV. Prior to SEM imaging, samples were thoroughly rinsed with Milli-Q water and dried under a flow of nitrogen. XPS was performed using a Thermo K-Alpha instrument at a pressure better than 10^{-9} Torr, with the data being referenced to the adventitious C 1s binding energy of 285 eV.

Supplementary material

SEM image of unmodified Cu electrode, lower magnification images of restructured electrodes and XPS spectra of restructured electrodes using benzyl alcohol and phenylacetic acid additives.

Acknowledgements

AOM gratefully acknowledges funding from the Australian Research Council (Future Fellowship - FT110100760). The authors also acknowledge the instrument and technical support of the RMIT Microscopy and Microanalysis Facility.

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