



Short communication

Galvanic and bipolar cells as probes of electroless deposition: The Cu–dimethylamine borane system

Daniela Plana¹, Robert A.W. Dryfe^{*}

School of Chemistry, University of Manchester, Oxford Road, Manchester M13 9PL, United Kingdom



ARTICLE INFO

Article history:

Received 20 August 2013

Received in revised form 20 September 2013

Accepted 23 September 2013

Available online 29 September 2013

Keywords:

Electroless deposition

Mixed potential

Bipolar cell

ABSTRACT

Galvanic and bipolar cells were used to demonstrate the complexity of electroless deposition reactions. The separation of the half-reactions, and the ability to control the potential, demonstrate the effect of the substrate and the interdependence of the anodic and cathodic processes. The effect of applied potential, substrate and temperature on Cu electroless deposition was studied, using dimethylamine borane as reducing agent.

© 2013 The Authors. Published by Elsevier B.V. Open access under [CC BY license](http://creativecommons.org/licenses/by/3.0/).

1. Introduction

Electroless deposition has attracted attention as a simple method for selective metallisation of surfaces [1–6]. Although applications are broad, the complexity of the baths and the lack of net current flow mean that mechanistic knowledge is rather scant. A particularly significant debate revolves around the driving force within an electroless bath and that measured in the corresponding physically separated half-cells; it has widely been assumed that they are identical, hence the use of the mixed potential theory (MPT) to interpret electroless processes [7–11]. This has been specifically criticised [12], however, and a few detailed mechanistic studies have noted deviations between its predictions and kinetic data, which are generally attributed to interactions between the two half-reactions [13–18]. In the current study we compare the rate of electroless copper deposition with the associated galvanic case (separate half-cells) and a bipolar cell, which allows control of the applied potential. Bipolar electrochemistry has lately reached prominence, being used to prepare Janus objects, investigate coupled reactions and generate surfaces with molecular gradients [19–21]. Recent reviews describe the bipolar concept and its applications [22]; however only one communication has reported its application to electroless deposition [23].

2. Experimental

Two experimental configurations were used, which separate the anodic (reducing agent oxidation) and cathodic (deposition) reactions: bipolar and galvanic cells. The bipolar configuration allows potential control by connecting the “reference” and “counter” terminals of the potentiostat (Autolab PGSTAT100) to the cathodic half-cell, and the “working” and “sense” terminals to the anodic compartment [23,24]; the potential differences refer to the potential of the reducing agent half-cell relative to that of the metal. Gold disks (2 mm) and homemade Ag/AgCl_{sat} were used as working and reference electrodes, respectively. Pt served as counter electrode in the Cu-containing half-cell, while graphite was used with dimethylamine borane (DMAB), to avoid the well-known noble metal catalysis of the reagent's hydrolysis [25,26]. In the galvanic cell, spontaneous current transients and open circuit potentials (OCP) are recorded by short-circuiting the Au electrodes and connecting both compartments through a salt-bridge; data was acquired using a National Instruments PCI-4065 digital multimeter card, with a custom-written LabView program [27].

The composition of Cells 1–5 derives from previous reports of Cu-DMAB electroless systems [4,28]. The pH was regulated to 11.6, using KOH and triethanolamine as buffer, with tetraazadodecane ligating Cu(II) to prevent precipitation [28,29]. A thermostatic water bath maintained the temperature at 55 ± 0.2 °C (with room temperature as comparison). Cu electrodes were prepared by electroless deposition, while thicknesses were determined through a stripping method previously described [27].

3. Results and discussion

Chronoamperometric experiments in the bipolar cell (Cell 2) allowed the study of applied potential differences (ΔE) on the copper-

^{*} Corresponding author. Fax: +44 161 275 4598.

E-mail address: robert.dryfe@manchester.ac.uk (R.A.W. Dryfe).

¹ Present address: School of Chemistry, University of Bristol, Bristol BS8 1TS, UK.

Table 1
OCP magnitudes at different times and the efficiency after 1800 s, in Cell 3, at 22 and 55 °C.

T/°C	OCP ₀ /V	OCP _{30s} /V	OCP _{1800s} /V	Q _s /Q _{od}
22	0.78	0.62	0.34	0.47
55	0.69	0.44	0.34	0.80

DMAB system. Fig. 1A shows that the deposit thickness after 10 min in Cell 2 increases markedly with potential, from no detectable deposition at ΔE values above 0.20 V, to over 0.50 μm at values more negative than -0.60 V. At $\Delta E = -0.69$ V, the thickness is equal to that of the electroless bath (Cell 1, dashed line). Although this potential coincides with the magnitude of the OCP measured in Cell 3, in the latter case deposits were much thinner after 10 min (solid triangle). This implies that, as expected from MPT, the galvanic cell's OCP is a good indicator of the driving force of the electroless process; however, an external energy input is needed to maintain the rate when the half-reactions are separated (see below).

In contrast to Cell 2, where ΔE is externally held constant throughout the experiment, the conditions in Cell 3 vary as deposition occurs. To understand the differences between Cells 2 and 3, OCP magnitudes were studied as a function of time (Fig. 1B). This was done by periodically interrupting deposition for a few seconds. As with all measurements in the galvanic cell, triplicate experiments were performed and average values are presented.

The OCP in Cell 3 drops significantly within the first 30 s (by 0.25 V), with considerably slower change with time afterwards. This coincides with the induction time observed in the equivalent electroless bath [27], indicating an influence of the deposit, in the copper half-cell, on the OCP. This drastic initial drop could explain the behaviour seen in Fig. 1A: if instead of the initial OCP, that obtained after 10 min is used for comparison (open inverted triangle), the thickness obtained in Cell 3 is closer to the bipolar trend. This can be attributed to the deposition of Cu on the Au electrode in the cathodic compartment and its consequent effect on the thermodynamics of Cu deposition. The open circles in Fig. 1B result from Cell 4, which contains a Cu electrode in the cathodic half-cell. They show that the initial OCP is close to that of Cell 3 after 30 s, when the Au electrode in the latter is covered by Cu; the behaviour of both cells is very similar after 30 s. The change in the driving force for Cu deposition with the evolution of the surface reveals the deficiencies of MPT as this theory does not consider the effects of the substrate on the half-reactions.

Cell 1

Copper-DMAB electroless bath.

0.030 M CuSO ₄
0.065 M DMAB
0.3 M triethanolamine
0.045 M 1,5,8,12-tetraazadodecane

Cell 2

Bipolar cell equivalent to Cell 1.

Ag/AgCl	0.065 M DMAB 0.3 M triethanolamine	0.030 M CuSO ₄ 0.3 M triethanolamine 0.045 M 1,5,8,12-tetraazadodecane	Ag/AgCl

Cell 3

Galvanic cell equivalent to Cell 1.

Au	0.065 M DMAB 0.3 M triethanolamine	0.030 M CuSO ₄ 0.3 M triethanolamine 0.045 M 1,5,8,12-tetraazadodecane	Au

Cell 4

Cu electrode in the Cu-containing compartment of Cell 3.

Au	0.065 M DMAB 0.3 M triethanolamine	0.030 M CuSO ₄ 0.3 M triethanolamine 0.045 M 1,5,8,12-tetraazadodecane	Cu

In the electroless bath, the decrease of the deposition driving force is countered by an increase due to the catalytic nature of copper towards DMAB oxidation. As seen in Fig. 1B, an increase of ca. 0.25 V is observed by replacing Au with Cu in the DMAB compartment (Cell 5). An analogous trend to that of Cell 3 is produced with time; however, as the initial potential is higher, the OCP is always higher in Cell 5, in agreement with the faster rate and higher efficiencies previously observed in this type of cell [27]. The increase in OCP due to DMAB oxidation on Cu almost exactly counters the decrease in OCP associated with Cu deposition on Cu. In all cases a slow decrease in OCP is seen with time, suggestive of progressively poorer DMAB oxidation kinetics. The rate of adsorption and substrate effects has been noted previously [30–32]. Homma et al. have theoretically rationalised the faster oxidation of DMAB on Cu compared to metals with lower electron affinity [33]; Au is such a metal. Reported DMAB electro-oxidation currents are over an order of magnitude higher on Cu than on Au electrodes [29]. These results demonstrate the interdependence of the half-reactions, with the evolution of the Cu deposit directly affecting DMAB oxidation; as noted above, the assumption of independent reactions is one of the major drawbacks of MPT.

Fig. 2A presents the effect of temperature, showing thickness versus potential at room temperature (22 °C, triangles) and 55 °C (dots). Higher ΔE values are required at the lower temperature to obtain similar thicknesses. At 22 °C, deposition does not occur at potentials above 0.00 V, approximately 0.2 V below the onset at 55 °C. Likewise, the thickness obtained in Cell 1 at 55 °C was not obtained in the bipolar cell at 22 °C, even when applying almost twice the potential difference required at 55 °C (-1.3 V vs. -0.7 V).

The OCP measured using Cell 3 at the two temperatures (Table 1) is similar at the start and after 30 min of deposition (it is in fact initially higher at 22 °C). After 30 s, however, the decrease in OCP is significantly smaller at room temperature (ca. 0.15 V) than at 55 °C, indicating a longer induction time, i.e. the electrode is not covered by Cu after 30 s, consistent with the three-fold fall in rate suggested by Fig. 2A.

Deposition efficiency was studied in the bipolar cell by comparing the deposit thickness with the charge passed (Fig. 2B). Three distinct regions are present at 55 °C: above 0.20 V, the ratio of the stripping and deposition charges is close to zero, as deposition is negligible; between 0.20 V and -0.20 V a sharp and steady increase in efficiency is observed, reaching a value of ~ 0.9 below -0.20 V. As mentioned above, this latter efficiency agrees with that of Cell 3. The agreement in efficiency in this potential region between the galvanic and bipolar cells indicates that the efficiencies of the former are a good approximation to that of the electroless bath; i.e. in this window, the bipolar cell produces films that match in thickness those of the bath.

A 0.2 V offset is observed between the efficiency plots for the different temperatures and a more gradual increase is observed at room temperature than at 55 °C. Table 1 shows a significant difference of efficiency in Cell 3: at 22 °C it is below 50%, indicating a clear influence of side reactions that do not contribute to deposit growth with hydrogen evolution being the most likely cathodic side reaction in this system [23,27].

Cell 5

Cu electrode in the DMAB-containing compartment of Cell 3.

Cu	0.065 M DMAB 0.3 M triethanolamine	0.030 M CuSO ₄ 0.3 M triethanolamine 0.045 M 1,5,8,12-tetraazadodecane	Au

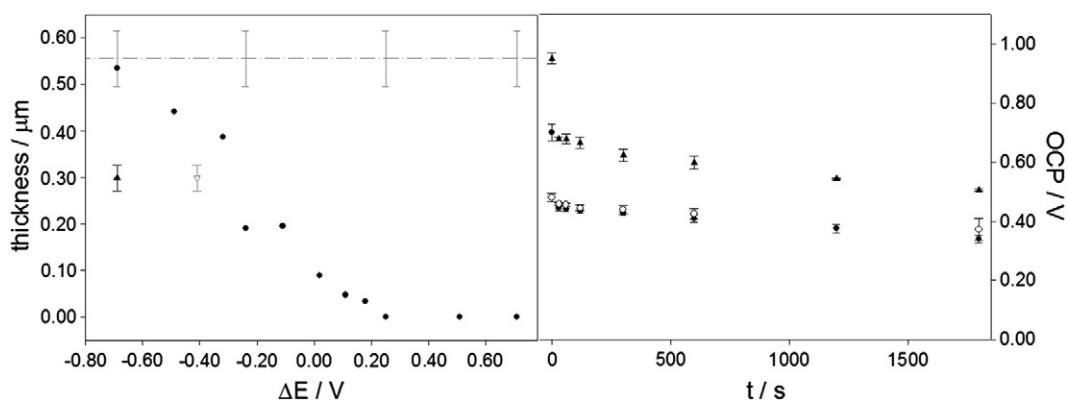


Fig. 1. A. Thickness as a function of applied potential (solid dots), after 10 min using Cell 2; Cell 1 (dashed line) and Cell 3 (solid triangle), is shown for comparison. The open inverted triangle uses the potential after 10 min in Cell 3, rather than the initial OCP used for the solid one. B. Magnitude of the open circuit potential with time in Cell 3 (solid dots), 4 (open circles) and 5 (solid triangles).

4. Conclusions

It has been widely assumed that electroless deposition occurs via independent redox reactions, and the mixed potential theory can describe the process. The results presented here show that this is an over-simplification. Interdependence of the deposition and oxidation half-reactions has been suggested previously; the use of the galvanic and bipolar cells demonstrates that in the system under study (Cu-DMAB) the separation leads to decreased reaction kinetics due to changes in cell potential caused by surface effects. Both DMAB oxidation and Cu deposition are surface-sensitive reactions, strongly affected by the coverage of the Au substrate with Cu overlayers.

Additionally, the deposit thickness decreased with decreasing temperature at equal potentials and the Faradaic efficiency was halved by lowering the temperature from 55 °C to 22 °C; this observation demonstrates that the deposition half-reaction is affected by temperature, giving way to side reactions which decrease efficiency.

Acknowledgements

We thank EPSRC for support (grant: EP/D04717X/1) and Dr. A.I. Campbell for assistance with LabView.

References

1. E. Malel, D. Mandler, *J. Electrochem. Soc.* 155 (2008) D459–D467.
2. N.A. Luechinger, E.K. Athanassiou, W.J. Stark, *Nanotechnology* 19 (2008) 445201–445206.
3. A. Vaskelis, J. Jaciauskiene, I. Stalnioniene, E. Norkus, *J. Electroanal. Chem.* 600 (2007) 6–12.
4. S. Balci, A.M. Bittner, K. Hahn, C. Scheu, M. Knez, A. Kadri, C. Wege, H. Jeske, K. Kern, *Electrochim. Acta* 51 (2006) 6251–6257.
5. Y. Shacham-Diamand, Y. Sverdlov, V. Bogush, R. Ofek-Almog, *J. Solid State Electrochem.* 11 (2007) 929–938.
6. J.F. Rohan, D.P. Casey, B.M. Ahern, F.M.F. Rhen, S. Roy, D. Fleming, S.E. Lawrence, *Electrochem. Commun.* 10 (2008) 1419–1422.
7. C. Wagner, W. Traud, *Z. Elektrochem.* 44 (1938) 391.
8. I. Ohno, O. Wakabayashi, S. Haruyama, *J. Electrochem. Soc.* 132 (1985) 2323–2330.
9. M. Paunovic, D. Vitkavage, *J. Electrochem. Soc.* 126 (1979) 2282–2284.
10. Y.S. Kim, H.J. Sohn, *J. Electrochem. Soc.* 143 (1996) 505–509.
11. S.M. El-Raghy, A.A. Abo-Salama, *J. Electrochem. Soc.* 126 (1979) 171–176.
12. M. Spiro, *A Critique of the Additivity Principle for Mixed Couples*, Kluwer Academic/Plenum Publishers, New York, 2001.
13. B.J. Feldman, O.R. Melroy, *J. Electrochem. Soc.* 136 (1989) 640–643.
14. R. Schumacher, J.J. Pesek, O.R. Melroy, *J. Phys. Chem.* 89 (1985) 4338–4342.
15. H. Wiese, K.G. Weil, *Ber. Bunsen Ges. Phys. Chem.* 91 (1987) 619–626.
16. L.M. Abrantes, J.P. Correia, *J. Electrochem. Soc.* 141 (1994) 2356–2360.
17. A. Bittner, M. Wanner, K.G. Weil, *Ber. Bunsen Ges. Phys. Chem.* 96 (1992) 647–656.
18. I. Ohno, *Mater. Sci. Eng. A* 146 (1991) 33–49.
19. G. Loget, J. Roche, A. Kuhn, *Adv. Mater.* 24 (2012) 5111–5116.
20. J.P. Guerrette, S.M. Oja, B. Zhang, *Anal. Chem.* 84 (2012) 1609–1616.
21. C. Ulrich, O. Andersson, L. Nyholm, F. Bjorefors, *Angew. Chem. Int. Ed.* 47 (2008) 3034–3036.
22. G. Loget, A. Kuhn, *Anal. Bioanal. Chem.* 400 (2011) 1691–1704.
23. D. Plana, G. Shul, M.J. Stephenson, R.A.W. Dryfe, *Electrochem. Commun.* 11 (2009) 61–64.
24. D. Plana, F.G.E. Jones, R.A.W. Dryfe, *J. Electroanal. Chem.* 646 (2010) 107–113.
25. M. Chatenet, F. Micoud, I. Roche, E. Chainet, *Electrochim. Acta* 51 (2006) 5459–5467.
26. M. Lelental, *J. Catal.* 32 (1974) 429–433.
27. D. Plana, A.I. Campbell, S.N. Patole, G. Shul, R.A.W. Dryfe, *Langmuir* 26 (2010) 10334–10340.
28. R. Jagannathan, M. Krishnan, *IBM J. Res. Dev.* 37 (1993) 117–123.
29. C.D. Iacovangelo, *J. Electrochem. Soc.* 138 (1991) 976–982.
30. D. Plana, P. Rodriguez, M.T.M. Koper, R.A.W. Dryfe, *Electrochim. Acta* 56 (2012) 7637–7643.
31. A. Sargent, O.A. Sadik, *Langmuir* 17 (2001) 2760–2767.
32. A. Sargent, O.A. Sadik, L.J. Matienzo, *J. Electrochem. Soc.* 148 (2001) C257–C265.
33. T. Homma, A. Tamaki, H. Nakai, T. Osaka, *J. Electroanal. Chem.* 559 (2003) 131–136.

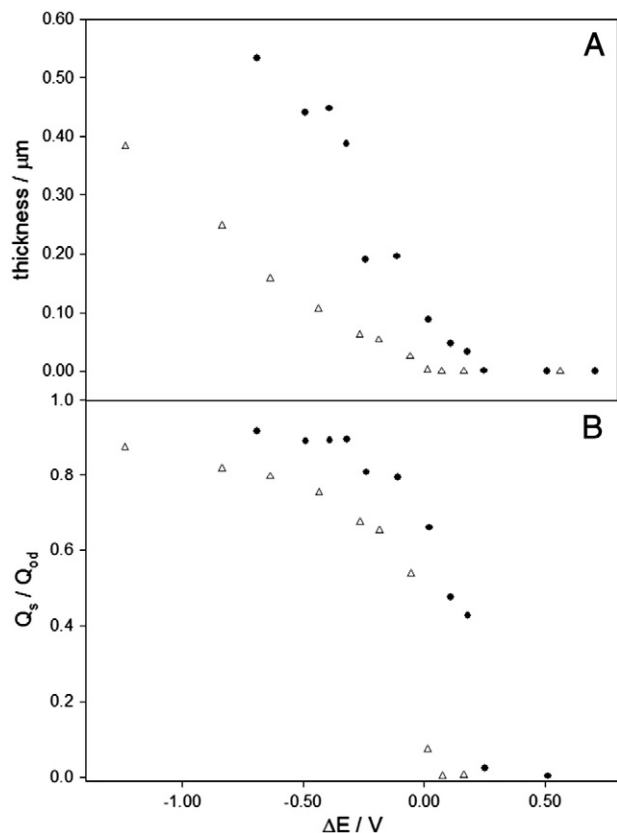


Fig. 2. Thickness (A) and efficiency (B) in Cell 2 as a function of potential, at 55 °C (dots) and 22 °C (triangles).