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Abstract

This report presents influence of water and copper salt on the anodic dissolution of metallic copper in a eutectic solvent of choline chloride and ethylene glycol (DES) in a 1:2 molar ratio. The mechanism of copper dissolution anodically was investigated using anodic linear sweep voltammetry (LSV) and electrochemical impedance spectroscopy (EIS). Atomic force microscope (AFM) was used to examine the morphology and topography of the surface after electrochemical dissolution course. The addition of 1, 4, 8, 16 and 20 vol.% of water cause pitting and has no significant impact on the electrochemical behavior, in particular the shape of anodic linear sweep voltammetry remains unchanged. The more profound effect was seen from the microscopic analysis. The addition of 0.1 and 0.81 M CuCl₂ into this eutectic solvent resulted in relatively high resistance at the interfacial region where charge transfer occurs during anodic dissolution of metallic copper using impedance responses. The results confirmed that water will not affect anodic dissolution behavior and the chemistry of dissolution in the deep eutectic solvent.

Keywords: Anodic dissolution; anodic linear sweep study; deep eutectic solvent; impedance

1. Introduction

Anodic dissolution is a broad topic involves a process of atomic dissolution of metals in an attempt to reduce surface roughness and also metal processing.¹⁻³ Anodic dissolution has usually been carried out in concentrated acids at current densities between 0.01 and 0.5 A cm⁻².⁴ Anodic dissolution is an extremely successful process for polishing and metal finishing process.⁵,⁶ However, there are major drawbacks and practical problems associated with the methodology, including the electrolyte bashes, especially in aqueous media that are highly corrosive and toxic
and extensive gas evolution (with associated low current efficiency) also occurs during the process.\textsuperscript{7,8}

Anodic dissolution of metallic copper in both aqueous media, deep eutectic solvents (DESs) and ionic liquids (ILs) has drawn attention of many research groups.\textsuperscript{9} Copper bulk metal has been utilized in a number of applications, including, pre-coating, electro-catalysis, electronic devices.\textsuperscript{10,11} In aqueous solutions, it has been extensively studied at both deposition and dissolution levels and the mechanism of copper dissolution in aqueous solutions is well-documented.\textsuperscript{4,12}

Additives can concentrate at the electrode solution interface and affect the chemistry of dissolution and deposition processes. In a recent review, Abbott et al. studied the electrode solution interface as a mixture of ionic and molecular components.\textsuperscript{13} To govern the rate of metal deposition and dissolution, addition of additives such as brighteners and viscosity modifiers are often conducted. There is a compromise between the charge density and dipole moments of the constituents of an electrolyte as a result of applied potential. In other words, in one side ions or dipolar species and the other side there is a charged electrode surface. Clearly, the addition of dipolar species in the form of water and charged species in the form of metal salts will affect the Nernstian half-wave potential, the double layer structure and the rate of dissolution and super saturation which can be achieved. Metals and neutrals will also affect the speciation of the metal complex which forms and its resulting solubility.\textsuperscript{14}
Ionic liquids (ILs) are molten salts below 100 °C that composed mostly of organic ions and inorganic anions, in particular Cl⁻ and PF₆⁻. Electropolishing of various metals in an electrolyte based on DESs as a new type of ionic liquid has been investigated in many report. Recently, electropolishing of stainless steels, titanium, cobalt, nickel and aluminum in DESs has been successfully carried out.

The DESs contain nonsymmetrical ions that make the DESs to have low lattice energy, resulting in low melting point. They can be prepared by the complexation of a quaternary ammonium salt with a metal salt or hydrogen bond donor (HBD). The charge delocalization occurring through hydrogen bonding between for example a halide ion and the hydrogen-donor moiety is responsible for the decrease in the melting point of the mixture relative to the melting points of the individual components.

Deep eutectic solvents (DESs) are considered as promising electrolytes for metal processing, in particular electropolishing process, which can be used in chemical synthesis for industrial and commercial applications due to their superior advantages of easy preparation, reasonable conductivity, low melting point, benign, low cost of preparation and wide potential stability. Generally, the anodic dissolution processes are in strong relationship with the cathodic processes.

This work is aimed at systematically investigating the effect of additives, such as metal salts, and water on electrochemical dissolution of copper bulk metal in choline-based chloride deep eutectic solvent. The results obtained here will help to understand the mechanistic view of the anodic dissolution of copper and the factors that govern the whole electrochemical dissolution
process. The metallic copper can then be used as a counter electrode to provide copper ion in situ in the process of coating a substrate by copper.

2. Experimental and Materials

Preparation of the deep eutectic solvent (Ethaline) was carried out by mixing choline chloride, (ChCl) (Aldrich, 99%) and ethylene glycol, EG (Aldrich, > 99%) in a molar ratio of 1:2 (1 ChCl: 2 EG). Afterwards, the mixture was heated at 60 °C and stirring continuously until a homogeneous liquid produced (Ethaline). The copper wire was purchased from Alfa Aesar with (99.9%, Alfa Aesar, USA).

Preliminary tests were performed using both stationary, such as cyclic voltammetry and linear sweep voltammetry. The Autolab PGSTAT 12 controlled by GPES software that fitted with an FRA impedance module was used for the galvanostatic and the AC impedance measurements. The acquisition impedance spectra were conducted in the frequency range of 1–65,000 Hz with the AC signal of small amplitude of 10 mV. A three electrode cell system comprising of 1.0 mm diameter metal disc Cu working electrode, sealed in glass, a platinum flag (1 cm², area) as a counter electrode and Ag/AgCl (0.1 M in 1 ChCl: 2 EG) reference electrode was used at 20 °C and at 5 mV s⁻¹ scan rate.

In the morphology investigation, atomic force microscopy (AFM) was utilized. A digital instruments nanoscope IV dimension 300 (Veeco) atomic force microscope with a 100 mm scanning head contact mode was used for image acquisition. Software of nanoscope version 6.13 during image acquisition in air was used.

3. Results and discussion
3.1. In pure Ethaline

Fig. 1 shows the LSV of copper electrode in pure ethaline. The initial sharp rising of the linear sweep is likely due to the formation of a Cu$^+$ species, e.g. [CuCl$_2$]$^-$. As the layer of ionic liquid at the electrode surface becomes enriched in Cu$^+$ species, which has a low solubility compared to Cu$^{2+}$ in these solvents, a layer of crystalline material precipitates (i.e. CuCl formed which is sparingly soluble) onto the electrode surface, resulting in the sharp drop in current density. Shortly afterwards, the system returns to a diffusion controlled steady state. The sudden decrease in the current, while most likely. Due to the huge IR drop as a result of salt film formation (i.e. concentrated ion region) on the surface, there is a characteristic passivation at the electrode surface.$^{19}$

3.2. Water

Fig. 1 exhibits the influence of percent of H$_2$O added on the electrochemical dissolution process of metallic copper wire in choline chloride/ethylene glycol electrolyte at 5 mV s$^{-1}$. It is interesting to notice that addition of water up to 10 Vol.% into Ethaline does not affect significantly on the initial oxidative charge. Herein, the effect of water addition on two electrochemical parameters; current and potential are explained. With regarding current, there is a significant impact of water addition up to 16% and 20 vol.% water, recording a current density of 41 and 45 mA cm$^{-2}$, respectively. The value of current was recorded for copper in pure Ethaline at 34 mA cm$^{-2}$ and nearly unchanged with other additions. This was due to conductivity increasing, in other words, the viscosity decreasing. The potential also underwent shifting where at all additions of water the potential shifted toward more negative side compared to fresh one. This can be attributed to contribution of both oxide layer and saturation of interface with chloride ion.$^{15}$
From this result, one can conclude that the initial dissolution process was not limited by mass transport. It is also in accordance with the mechanism of the dual salt dissolution where the mass transport of species through the salt film impacts the rate of dissolution than species diffusing through the solution. The anodic current increasing slightly would be due to changes in the layer which forms on the electrode surface and the salt layer could change predominantly from chloride to remarkable amounts of oxide.

Several impurities were studied that not only impact the physico-chemical properties of ILs, but also have indirect influence on the overall chemistry of electrochemical processes. For example, 1-methylimidazole as an impurity in the imidazolium-based ionic liquids acts as a poison of catalysts. Furthermore, viscosity is one of the physico-chemical properties of electrolyte from which one can decide the eligibility for the electrochemical applications. Seddon et al. showed that viscosity increasing as a result of chloride increasing of ILs. In another study, it was shown that even the hydrophobic ILs adsorb water strongly, but to less extent compared to hydrophilic ones.

The influence of water on anodic dissolution of copper in Ethaline has to be clarified because water is not avoidable in this electrolyte. Fig. 2 shows the AFM images of copper dissolved in Ethaline in the presence of water. On the other hand, the presence of water leveled the copper surface but with higher roughness values compared to the native copper sheet. All these can be ascribed to the conductivity increasing as a consequence of viscosity decreasing. Thereby, it resulted in water involvement in the complex formation of copper.
It is well-known that most anodic dissolution reaction is accompanied by the evolution of gas which has a detrimental effect on the whole process (low current efficiency). In the presence work, it is likely that Cl\textsubscript{2} and H\textsubscript{2} liberate at anode and cathode, respectively, originating from three sources; two of these from ethaline components: Cl\textsubscript{2} is caused by ChCl and the H\textsubscript{2} comes from trace water and ethylene glycol (EG). Therefore, electrochemical parameters have to be optimized carefully, such as potential, current and electrolyte composition are of vital importance.

### 3.3. Copper salt addition

The role of two different concentrations of CuCl\textsubscript{2}.2H\textsubscript{2}O i.e. 0.10 M and 0.81 M on metallic copper dissolution at 5 and 50 mVs\textsuperscript{-1} is shown in Fig. 3. At first glance, the influence of 0.1 M salt is indistinguishable from the fresh solution at the low scan rate, whereas in the 0.81 M (close to saturation) a slight difference can clearly be observed. In this experiment two different scan rates were applied in order to know about the effect of scan rate on the anodic dissolution in the presence of huge amount of copper ion at the interface. It is well-know that at the low scan rate thicker diffusion layer exists. More clearly, 0.81 M CuCl\textsubscript{2} will use up 1.62 M of free Cl\textsuperscript{-} (i.e. 2 chlorides for each copper ion). A slight decreasing in the oxidative current can be seen but the passivation potential is uninfluenced. More interesting observation is that the limiting current ($E > 0.5$ V) decreases when addition of copper ions is performed. This is likely if the layer was either thicker or denser and precluded the ion migration to and from the electrode surface.

This salt addition into the deep eutectic solvent in the metallic copper dissolution electrochemically was also examined using electrochemical impedance spectroscopy. This technique can be exploited for studying the mechanism of electrochemical process at the interface region.\textsuperscript{1} Fig. 4 shows the response of copper dissolution in pure Ethaline in the existence of 0.81
M CuCl₂.2H₂O at 20 °C. In general, there is a similarity of overall shapes of the spectra but the semicircle sizes are obviously different. At -0.4 V, when copper exist in the Ethaline, a semicircular response is seen owing to copper deposition on the electrode surface, however, at -0.2 V two semicircles are noticed probably resulted from both dissolution and deposition processes. From electrochemical impedance spectroscopy as a powerful technique, one can deal with the mechanism of electrochemical reactions, in particular the dissolution processes. It is worth-mentioning that to differentiate between two comparable electrochemical processes at an electrode surface, a decisive region is taken into consideration from the response at low frequency region where the mass transportation is dominating process. At the high frequency region, there is response for charge transfer at the electrolyte/electrode interface. For polarisable electrodes, applications of potential and electrode material determines the double layer capacitance.

However, in the current study, the copper piece is non-polarizable electrode so that the capacitance value depends upon the electrode materials (i.e. copper) to less extent since it acts as reactant that participates in the electrochemical dissolution process. In the dissolution process, the dissolution of electrode surface results in the formation of a film which continuously change in the thickness and also in the composition as well when the potential is altered. Therefore, the thicker the film thickness and composition change strongly relies on the potential value, especially, the more anodic potential needs. It is obviously seen that as the potential was swept toward positive side, the semi-circles are faced charge transfer resistance. Although the more positive means high over-potential, the presence of copper salt made the interfacial region to be saturated with copper ion. Thereby, this phenomenon suppressed the dissolution of copper sheet.
4. Conclusions

Summarily and descriptively, in this study the following conclusions can be shown:

- The existence of water in the choline chloride/ethylene glycol mixture is not effective regarding the electrochemistry of metallic copper dissolution which can be taken into consideration as advantageous of this interesting deep eutectic solvent.
- The metallic copper dissolution electrochemically is successful in the deep eutectic solvent which can be exploited in electroplating copper on other substrates using sacrificed copper counter electrode.
- The impact of addition of copper salt on electrochemical dissolution of metallic copper results in slight anodic current suppression.
- It is also documented that copper ions coming from copper salt undergo deposition at negative potential and re-dissolved when the potential is swept back toward positive side.
- The presence of copper salt, especially at 0.81 M CuCl$_2$.2H$_2$O makes the interfacial region to be saturated with copper ion causing suppression of metallic copper dissolution as confirmed from the LSV and EIS.

Acknowledgments

The authors gratefully acknowledge the financial support for this study from the University of Sulaimani, Kurdistan-Iraq & Ministry of Higher Education and Scientific Research, Kurdistan Regional Government/Iraq.

Conflicts of Interest: The authors declare no conflict of interest.
References

1. A. P. Abbott, J. Hartley, W. O. Karim, and K. S. Ryder, *Prog. Nat. Sci. Mat. Int.*, **25**, 595 (2015).

2. A. P. Abbott, G. Frisch, and K. S. Ryder, *Annu. Rev. Mater. Res.*, **43**, 335 (2013).

3. E. L. Smith, A. P. Abbott, and K. S. Ryder, *Chem. Rev.*, **114**, 11060 (2014).

4. J. Huo, R. Solanki, and J. McAndrew, *J. Appl. Electr.*, **34**, 305 (2004).

5. W. O. Karim, J. A. Juma, K. M. Omer, Y. M. Salih, K. H. Hamaaziz, and S. B. Aziz, *J. Electr.*, **88**, 447 (2020).

6. A. P. Abbott, G. Frisch, J. Hartley, and K. S. Ryder, *Green Chem.*, **13**, 471 (2011).

7. M. Datta, *IBM J Res. Dev.*, **37**, 207 (1998).

8. B. Du, *J. Appl. Electrochem.*, **34**, 1215 (2004).

9. A. Kityk, V. Protsenko, F. Danilov, O. Kun, and S. Korniy, *Surf. Coat. Tech.*, **375**, 143 (2019).

10. M.-T. Zhang, Z. Chen, P. Kang, and T. J. Meyer, *J. Am. Chem. Soc.*, **135**, 2048 (2013).

11. D. DeCiccio, S. Ahn, S. Sen, F. Schunk, G. Palmore, and C. Rose-Petruck, *Electrochem. Commun.*, **52**, 13 (2015).

12. B. Du and I. I. Suni, *J. Electrochem. Soc.*, **151**, C375 (2004).

13. A. P. Abbott, K. J. McKenzi, and K. S. Ryder "Technical Aspects" in Electrodeposition of metals from Ionic Liquids (Eds. F. Edres and A. P. Abbott), Wiley VCH (2007).

14. J. Hartley, G. C. Forrest, K. Singh, S. J. Gurman, K. S. Ryder, A. P. Abbott, and G. Frisch,
Inorg. Chem., 53, 6280 (2014).

15. A. P. Abbott, G. Capper, K. J. Mckenzie, A. Glidle, and K. S. Ryder, Phys. Chem. Chem. Phys., 8, 4214 (2004).

16. A. P. Abbott, K. S. Ryder, and U. Konig, Trans. IMF, 86, 196 (2008).

17. W. O. Karim, A. P. Abbott, S. Cihangir, and K. S. Ryder, Trans IMF, 96, 200 (2018).

18. J. B. Mathieu, D. Landolt, J. Electrochem. Soc., 125, 1044 (1978).

19. J. A. Hammons, A. J. Davenport, S. M. Ghahari, M. Monir, J.-P. Tinnes, M. Amri, N. Terrill, F. Marone, R. Mokso, and M. Stampanoni, J. Phys. Chem. B, 117, 6724 (2013).

20. W. Han and F. Fang, Int. J. Mach. Tool Manuf., 139, 1 (2019).

21. A. Stark, M. Ajam, M. Green, H. G. Raubenheimer, A. Ranwell, and B. Ondruschka, Adv. Synth. Catal., 348, 1934 (2006).

22. L. L. Lazarus, C. T. Riche, N. Malmstadt, and R. L. Brutchey, Langmuir, 28, 15987 (2012).

23. K. R. Seddon, A. Stark, and M.-J. Torres, Pure Appl. Chem., 72, 2275 (2000).

24. J. A. Widegren, A. Lasecke, and J. W. Magee, Chem. Comm., 12, 1610 (2005).
Figure 1. LSVs of pure metallic copper disc electrode in pure Ethaline and in Ethaline/water at 20 °C and at scan rate of 5 mVs⁻¹.
Figure 2. AFM images of metallic copper (a), after galvanostatic dissolution at 27.3 mA cm$^{-2}$ at 20 °C in pure Ethaline for 85 s (b) and in pure Ethaline for 850 s (recorded in air at a scan rate of 0.5 Hz, 256 lines).
Figure 3. LSVs of pure metallic copper disc electrode in pure Ethaline and in 0.1 M and 0.81 M CuCl$_2$.2H$_2$O/Ethaline at 20 °C and two sweep rates: 5 (left) and 50 mV s$^{-1}$ (right).
Figure 4. Electrochemical impedance spectra of pure metallic copper in pure Ethaline (left) and in 0.81 M CuCl$_2$·2H$_2$O Ethaline (right) at 20 ºC and at various potentials with AC amplitude of 10 mV in the frequency range of 1–65000 Hz.