

Current oscillations during copper electrodisolution under solution sparging in acidic NaCl solutions

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Abstract

Potentiostatic current oscillations were observed during electrodisolution of a helical coiled copper wire electrode in acidic sodium chloride when nitrogen was sparged through the solution. The oscillations were studied as a function of solution pH, chloride ion concentration and sparging rate over the potential range of 0.2 to 0.7 V versus Ag/AgCl (3 M NaCl). The surface morphology of the copper was observed during the oscillatory process using *in situ*, real-time optical microscopy, and the formation of a surface film was correlated with the oscillations.

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1. Introduction

Oscillations in current during copper electrodisolution in acidic solution have been observed for a long time. Oscillations have been reported in aqueous chloride, phosphate, and acetate-based solutions, and recently in trichloroacetic and trifluoroacetic acid solutions, as well as nonaqueous carbonate-based hexafluorophosphate [1–7]. Various mechanisms have been proposed to explain the oscillations. The two most widely accepted mechanisms involve surface controlled processes [8,9] and autocatalysis [4,10]. One must recognize that the complex nature of the oscillations allows for the coexistence of different mechanisms. Also, it is unlikely that a single model could explain all types of oscillations. Of the electrolytes mentioned above, chloride is known to produce a variety of oscillatory phenomena. The formation of a black film on the copper surface has been closely related to the presence of the oscillations. However, more investigation is needed to further elaborate the existing models. A complete

description of the process is a difficult problem and still an open field.

Of the oscillations reported for copper in chloride electrolytes, rotating disc or rotating ring electrodes have been most widely used. It is believed that the presence of oscillations is related to the dynamical conditions obtained by electrode rotation. Itagaki et al. have used a channel flow double electrode (CFDE) technique [11]. This paper reports on current oscillations that were observed with a helical coiled copper wire electrode during solution sparging with nitrogen; dynamical conditions that are different from those obtained by rotating electrodes or flow techniques. These oscillations add a new dimension to the electrochemical oscillatory phenomena for copper electrodisolution in low pH, high chloride concentration electrolytes.

Also, the formation of an anodic or surface film on the copper electrode is associated with the presence of the oscillatory behavior, as has been observed by other researchers [1–5,8–19]. During each oscillatory peak period, the film morphology changed. Film morphology dynamics have been reported to be associated with oscillations since the late 1960s [20]. Recently, Wang and coworkers have utilized holography to observe dynamic changes associated with potentiostatic current oscillations of iron [21–23]. In the present report, *in situ*, real-

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time optical microscopy has been utilized. The correlation between the surface changes and the oscillatory phenomena is expected to provide some clues about the origin of oscillations during copper electrodisolution.

2. Experimental

2.1. Materials

The copper electrodisolution was conducted in an H-type electrochemical cell (120 mm width \times 75 mm height \times 42 mm diameter, Lab Glass, Vineland, NJ, catalog number LG-4330, Fig. 1). Each cell compartment capacity was 60 ml. The compartments were connected through a -100 coarse-fritted porous glass disc. One compartment contained the auxiliary electrode (AE) and the other compartment contained the working and reference electrodes. Each compartment was fit with a Teflon™ plug that had been machined to hold the electrodes and a N_2 inlet tube in place. The working electrode (WE) was a copper wire helical coil made from 1.024 mm diameter (18 gauge) \times 7.3 cm length, 99.99% purity wire (Fisher, catalog number 15-545-2B). The immersed area of the electrode was calculated to be 2.35 cm^2 . The copper wire was conditioned with 80 grit SiC paper to remove any surface oxidation layer, and then smoothed with 600 grit ultra fine paper. The coil was made by wrapping the wire around a 3 mm diameter metal rod for 6 turns. The coil was rinsed with doubled distilled water and dried with a tissue before use. The AE was a 0.5 cm diameter, 23 cm long platinum wire coil (Bioanalytical Systems, BAS, MW-1033). The reference electrode (RE) was Ag/AgCl (3 M NaCl) (BAS, MF-2052).

Coiled electrodes are often supplied and used to provide increased surface area and as a space savings method (e.g., the commercial platinum auxiliary electrode used in this study is supplied as a coiled electrode). Many combination pH–glass

electrodes have the external Ag/AgCl reference electrode coiled around the internal Ag/AgCl reference electrode. Karantonis and co-workers have previously utilized copper coil electrodes in their studies of relaxation oscillatory electrochemical cells [24,25].

The electrolyte used in this study was NaCl that was acidified with nitric acid. The ACS reagent-grade chemicals were purchased from Spectrum. Double distilled water was used to prepare all solutions. The glass pH electrode was an Orion combination 91-04 electrode which was connected to an Orion digital ionalyzer model 501 meter.

The nitrogen used in this experiment was supplied by Airgas (Roadnor, PA). No further attempts were made to purify the nitrogen. The flow rate was measured by a soap bubble gas flow meter, constructed from a 25-ml graduated glass pipette. N_2 sparging was begun 2 min before the potential was applied, unless otherwise stated, to ensure that only trace levels of dissolved oxygen remained in solution.

2.2. Cell preparation and apparatus

A volume of 30 ml electrolyte was added to each compartment of the H-cell, and 2 min were allowed for the solution height in both compartments to reach the same level. The WE and the RE were placed in one compartment, with a 2-cm distance between them. The AE was placed into the other compartment of the H-cell. The compartment with WE and RE was mounted on a C3 cell stand (BAS), and other compartment containing the AE was clamped onto a ring stand. The polypropylene N_2 sparging tube (2 mm o.d.) was inserted into the cell compartment containing the WE and RE. The tube orifice was positioned at the cell bottom, and half-way between the electrodes. The distance between the tube and the WE was ~ 1 cm. All experiments were performed with a CH-604A electrochemical analyzer (CH Instruments) which was interfaced to a personal computer. Current–time (I – t) measurements were recorded at a sampling interval of 0.001 s. The open-circuit potential (OCP) of the cell was -0.28 ± 0.02 V.

The *in situ*, real-time optical microscopic images were obtained with an Intel® Play™ QX3™ Plus Computer Microscope [26]. The microscope was removed from its base, mounted in a horizontal position next to the cell and focused through the glass cell wall on the copper coil. Digital images were obtained at $60\times$ magnification.

3. Results and discussion

Fig. 2 shows anodic dissolution curves at applied potentials from 0.2 to 0.7 V and a N_2 sparging rate of $1.3 \text{ cm}^3 \text{ s}^{-1}$ over a 1000-s (typical) potential pulse. The noise-level is attributed to disturbance of the WE surface as a result of Cu oxidation and mass transfer processes. At a potential of 0.2 V, no oscillations were observed (Fig. 2a). At 0.3 V oscillations were present over the time interval of 15 s to 536 s of the potential pulse. The magnitude and frequency steadily decreased (Fig. 2b). When the potential was increased to 0.4 V the oscillations were sustained until 1166 s (of a 1500 s potential pulse, Fig. 2c). A

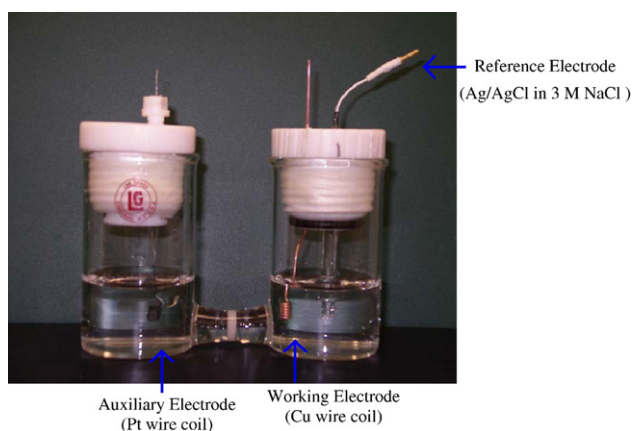


Fig. 1. H-type electrochemical cell (120 mm width \times 75 mm height \times 42 mm diameter). Each compartment capacity is 60 ml. Compartments are connected through a -100 coarse-fritted porous glass disc. Working electrode is Cu wire coil. Reference electrode is Ag/AgCl (3 M NaCl). Auxiliary electrode is Pt wire coil.

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