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Electrochemical investigation and *ab initio* computation of passive film properties on copper in anaerobic sulphide solutions

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ABSTRACT

Electrochemical measurements based on the point defect model and *ab initio* calculations were employed to investigate the properties of passive films formed on copper in anaerobic sulphide-containing solutions at different temperatures. P-type semiconductor characteristics were observed at potentials more positive than $-0.75 V_{SCE}$, which is consistent with copper vacancies being the dominant defect, but n-type behaviour was observed at lower potentials. The density of copper vacancies (approximately 10^{22} cm^{-3}) increases with temperature and formation potential, and the diffusion coefficient of copper vacancies lies within the range of 10^{-15} to $10^{-14} \text{ cm}^2/\text{s}$ based on *ab initio* computations and electrochemical measurements.

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1. Introduction

Because of its thermodynamic immunity to corrosion in deoxygenated water, copper has been selected as a canister material in various high-level nuclear waste (HLNW) isolation programs (such as those in Sweden, Finland, and Canada) [1,2]. The HLNW containers will be fabricated with an inner layer of cast iron for structural support and an outer shell of oxygen-free copper for corrosion protection (30–50 mm in thickness), and the design service life is 10^5 – 10^6 years [2–6]. However, granitic repositories are extremely complex, slightly alkaline (pH 8–10) environments with high concentrations of aggressive chloride (0.1–1.4 M), limited oxygen, and widely varying temperatures [7,8]. They also generally contain bisulphide ion (HS^-), which is a known activator of the corrosion of copper [9,10], at concentrations of up to about 0.1 mM. After closure of the disposal repository, the canister will experience different environmental scenarios, spending its first few decades in an oxic environment followed by a long-term anoxic period. Initially, oxygen will be trapped in the bentonite buffer between the canister surface and granitic rock. Once this oxygen has been consumed, the more likely corrosive agents in the groundwater to which the copper canisters will be exposed

include bisulphide, polysulphide, and possibly polysulphur oxyanions, depending upon the prevailing redox potential. Under deep repository conditions, the dominant species is expected to be bisulphide with a concentration of 10^{-7} – 10^{-4} M in the groundwater [7]. These agents are derived from microbial activity (i.e., the sulphate activity of sulphate-reducing bacteria) or from mineral dissolution (i.e., pyrite, FeS_2 , which is the salt of Fe^{2+} and S_2^{2-}) [11,12]. These reduced sulphur species can induce an anodic reaction ($2\text{Cu} + \text{HS}^- \rightarrow \text{Cu}_2\text{S} + \text{H}^+ + 2\text{e}^-$) at a potential that is substantially more negative (by 500–600 mV) than that of Cu_2O formation and hydrogen evolution, so that hydrogen evolution becomes a viable partial cathodic reaction in the corrosion of copper in anoxic environments [13,14]. Moreover, the corrosion potential finally reaches a value within the range of -0.80 to $-1.00 V_{SCE}$, depending upon the concentration of sulphide [15]. The corrosion of the copper canister is also greatly affected by the temperature of the environment. In typical high-level nuclear waste repositories, the temperature varies significantly with both location and time and with the type of waste being isolated (e.g., spent nuclear fuel vs vitrified high level waste); an increase in the temperature up to 363 K is expected to occur up to 10 years after closure followed by a decrease to 303 K after approximately 2000 years [7].

Another favourable property of copper is the spontaneous formation of thin (nanometre-scale) oxide layers on copper surfaces exposed to an oxidizing environment. In the anaerobic aqueous sulphide solutions that exist in granitic repositories, however,

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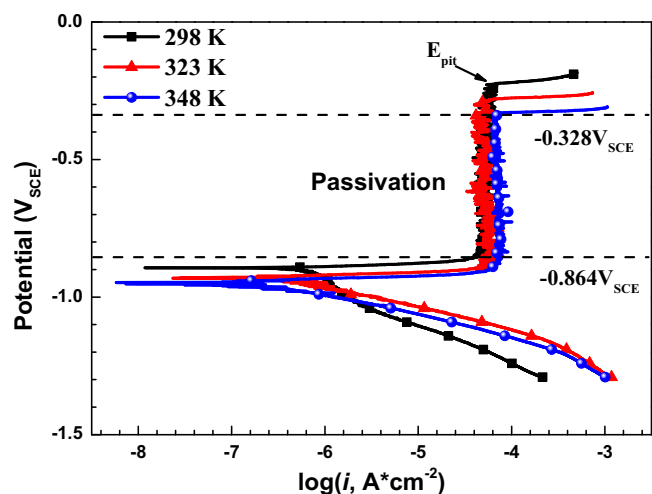


Fig. 1. Potentiodynamic polarization curves for copper in deaerated 0.1 M NaCl + 5×10^{-4} M Na₂S·9H₂O solution at different temperatures, i represented the current density and the potential scanning rate employed was 0.1667 mV/s.

copper is found to form a steady-state passive film comprising Cu₂S [16–18], although that result is also controversial. First-principles calculations based on density functional theory (DFT) that enquire into the stabilities and electronic structures of the Cu_xS ($1.2 < x < 2.0$) system over a wide stoichiometric range also indicate that Cu₂S becomes stable in a low-chalcocite structure [19]. However, Cu_xS has a highly complicated, strongly temperature-dependent crystal structure. Chalcocite (Cu₂S) forms three phases at different temperatures: a monoclinic phase (low-chalcocite) at temperatures below 377 K, a hexagonal phase (high-chalcocite) between 377 and 709 K, and a cubic phase (cubic-chalcocite) at temperatures above 709 K [20,21]. Wang [22] and Sigman [23] examined the crystal structure and growth direction of Cu₂S nanowire arrays on copper surfaces at room temperature, in order to investigate the stability and photocatalytic characteristics of Cu₂S microcrystals. The monoclinic nanowires preferentially aligned along the Cu₂S c-axis and were characterized by a layered structure.

Recently, several researchers [24–28] have studied the mechanism and kinetics of passive film growth on copper in sulphide-containing solutions. The mechanism is postulated to involve competition between sulphide diffusion in the solution and the interfacial reaction rates on the copper surface. The types of films that develop appear to depend on the sulphide concentration, sulphide flux at the copper surface, and chloride concentration in the solution. The kinetic results revealed two types of growth processes that depend on [HS⁻]; parabolic growth at high sulphide concentrations (5.0×10^{-4} M) and linear growth at lower concentrations (5.0×10^{-5} M). The parabolic growth is postulated to reflect diffusion of Cu⁺ ions through the passive matrix or along grain boundaries in the passive barrier layer, whereas the linear film growth appears to be controlled by HS⁻ diffusion and yields a porous, non-protective film. However, to our knowledge, other growth laws, such as that afforded by the Point Defect Model (PDM) [29–33] were not examined. The PDM accounts for both logarithmic (commonly described as “parabolic”) and linear growth laws in the same theoretical framework [33].

For many years, researchers have suspected that passive film breakdown depends on the presence and distribution of point defects (cation and anion vacancies and metal interstitials) in the film as well as on the electrolyte composition, potential, and temperature [29–32]. The PDM, which has been developed by Macdonald and his collaborators over the past thirty years, postulates

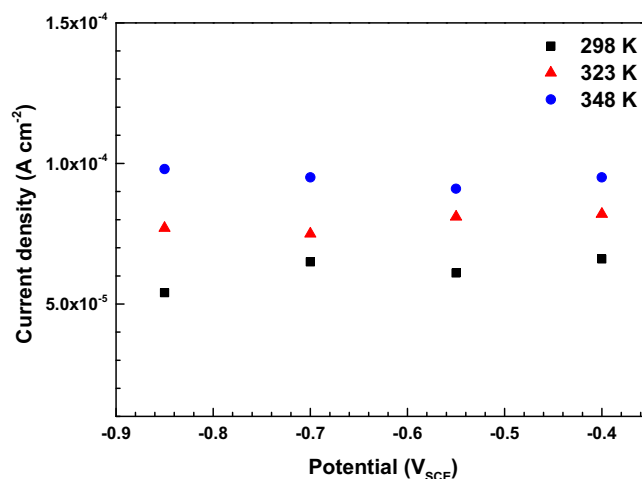


Fig. 2. Steady-state passive current density of copper under potentiostatic polarization for 2 h in deaerated 0.1 M NaCl + 5×10^{-4} M Na₂S·9H₂O solution at different temperatures, current density stabilized at approximately 5 min after applying the potential.

that the defect types that are present in the barrier layer can be distinguished by the semiconductor characteristics of a defective barrier layer of the passive film [29]. This model explains the mechanism of the growth, dissolution, and breakdown of passive films [30,31]. It also accounts for the homeostasis and transient properties and the nucleation of localized corrosion induced by passivity breakdown on many metals and alloys in contact with aqueous solutions [30,32]. Previously, we measured the near-normal distribution of the critical breakdown potential and measured the critical cation vacancy concentration for passivity breakdown ($\xi = 1.09 \times 10^{15}$ cm⁻²) of copper in anaerobic sodium sulphide solutions having different chloride concentrations and pH values [34]. Our results satisfactorily agree quantitatively with the PDM predictions, providing convincing evidence that the PDM describes the passivity breakdown on copper in sulphide- and chloride-containing groundwater. However, we note that Shoosmith et al. [24,25,27] deny the possibility of passivity breakdown on copper in contact with sulphide-containing, granitic groundwater, because their experiments indicate that copper is not passive, in contradiction with our own results [34]. However, these studies were performed under slightly different conditions, so that this controversy remains to be resolved.

In the PDM, pits are initiated by condensation cation vacancies at the metal–barrier layer (m/bl) interface, due to an aggressive anion-induced enhancement of the cation vacancy flux across the barrier layer. The growth rate of the condensate depends not only upon the flux of cation vacancies across the barrier layer but also on the rate of annihilation of the cation vacancies at the m/bl interface via cation injection from the substrate metal. Shoosmith et al. [16,27] assumed that cation vacancies are transported primarily via diffusion, rather than migration, thereby accounting for parabolic film growth kinetics. Under migration conditions (high electric field strength), however, the flux of cation vacancies can be written as $J = \chi\gamma DH\varepsilon$, where χ is the charge, D is the cation vacancy diffusivity, H is the vacancy concentration, ε is the electric field strength within the barrier layer, and $\gamma = F/RT$ (F is Faraday's constant and R and T represent the universal gas constant and Kelvin temperature, respectively). Because the electric field strength is independent of the film formation potential, the flux of cation vacancies across the barrier layer varies only with the concentration and diffusivity of the cations, with the concentration being established at the bl/s interface in response to the absorption of aggressive anions (e.g., Cl⁻) into surface oxygen vacancies followed by cation vacancy gen-

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