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Electrochemical methods to study hydrogen production during interaction of copper with deoxygenated aqueous solution

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ABSTRACT

In some countries, spent nuclear fuel is planned to be encapsulated in canisters with a copper shell for corrosion protection, for further disposal in geologic repositories. The possibilities for corrosion after oxygen depletion must be evaluated, even if copper is considered to be immune in oxygen-free water. To follow the interaction of copper with deoxygenated aqueous solution, open-circuit potentiometric and electrochemical impedance measurements have been coupled to in-situ detection of cupric ion, dissolved molecular hydrogen and oxygen concentrations using electrochemical sensors. A kinetic model that considers the production of hydrogen as a catalytic process, the rate of which is proportional to the surface coverage of an intermediate species formed during interaction between copper and the solution is used to interpret the results. Kinetic parameters are estimated by a simultaneous fit of the experimental impedance spectra, the open circuit potential and cupric ion concentration as depending on temperature (22–70 °C) and exposure time (up to 720 h) to the model equations. Using the obtained values and a balance equation of hydrogen production on copper and its diffusion out of the cell through its walls, the kinetic parameters of this process are estimated by fitting dissolved molecular hydrogen concentration vs. time data at the three temperatures.

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1. Introduction

In some countries, Sweden and Finland, for example, spent nuclear fuel is planned to be encapsulated in canisters with a cast iron insert for mechanical strength and an outer copper shell for corrosion protection. The canisters are to be placed for final disposal in a geologic repository. The thickness of the copper shell is planned to be 50 mm. For this wall thickness, a corrosion rate of $0.5\,\mu m\,y^{-1}$ would lead to a canister lifetime of 10^5 years. The oxygen entrapped in the repository after closing it will cause corrosion of the copper shell, but after its depletion the corrosion is assumed to stop, since copper is considered to be immune to corrosion in oxygen-free water. After the consumption of oxygen in the repository, there are, however, some possibilities for continued corrosion. Dissolved sulfides can react with copper, form copper sulfide and liberate hydrogen [1]. Thermodynamic calculations [2] have indicated a possibility of copper corrosion in highly saline oxygen-free water at low pH values. For extremely high chloride concentrations, $5\,mol\,kg^{-1}$, corrosion may even occur at pH values close to neutral [3].

More recently, a series of studies has been performed, the results seemingly supporting the notion that copper corrodes at a non-negligible rate with water alone as the oxidant [4–8]. The experiments have mainly measured gaseous hydrogen via the pressure increase in a chamber that was connected to the test chamber via a Pd membrane that is permeable to hydrogen alone. The rate of hydrogen evolution has then been used to calculate the amount of oxidized copper. This amount would thus mean that the copper canisters corrode to a considerably larger extent than predicted by calculations based on well recognized thermodynamic data. Subsequently, attempts have been made to reproduce the results with similar experimental set-ups [9–12]. As the experiments deviate from general thermodynamic expectations, their interpretations have also been strongly questioned [13,14]. Summarizing, in view of the recent experiments performed by Hultquist and co-workers [4–8], independent studies [9,10] and also measurements reported within the SKB research program [11,12,15,16], there is a need to further explore the conservative estimates of hydrogen formed during interaction of copper surfaces with water, and more generally, deoxygenated neutral aqueous solutions.

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Accordingly, the main purpose of the present work is to obtain in-situ estimates of the concentration of dissolved molecular hydrogen formed during interaction of copper with a deoxygenated borate buffer solution, and further to couple those measurements with in-situ characterization of the system using electrochemical methods: zero current chronopotentiometry, detection of soluble divalent copper using an ion-selective electrode and identification of the electrochemically detectable steps of the interaction process using electrochemical impedance spectroscopy. The obtained results are used for the validation and verification of the kinetic model for the interaction of copper with deoxygenated aqueous solution presented earlier [17,18], which bears some analogy to another recent model for hydrogen evolution on copper in borate solution [19]. Our model is in turn updated to take into account the interaction of divalent copper with borate [20,21] and includes a catalytic model for the hydrogen generation. The kinetic parameters are estimated by a simultaneous fit to the model equations of the experimental impedance spectra, the measured open circuit potential and cupric ion concentration as depending on exposure time and temperature. Using the obtained values and a balance equation of hydrogen production on copper and its diffusion out of the cell through its walls, the kinetic parameters of this process are estimated by fitting the experimental dissolved molecular hydrogen concentration vs. time data. A discussion on the relative importance of different processes during interaction of copper with water solution is presented.

2. Model description

2.1. Main chemical reactions and rate equations

A quantitative kinetic model of Cu interaction with deoxygenated borate buffer has been advanced based on measurements of current vs. potential curves, impedance spectra and soluble Cu concentration during polarization in the interval of potentials -0.25/+0.1 V with respect to the corrosion potential for up to 3000 h of exposure [17,18]. Within the framework of the model, it was assumed that copper is covered by three types of adsorbates – water, adsorbed hydroxyl and copper (I) hydroxide (CuOH). The formation of two types of oxygen-containing adsorbates during the initial stages of Cu oxidation has been hypothesized by Droog et al. [22] on the basis of voltammetric and ellipsometric measurements. Further support for the formation of two distinct types of oxidized species comes from measurements of current transients on scratched Cu electrodes in aqueous solutions with pH from 0 to 14 [23,24]. Evidence for two types of adsorbed hydroxide ion on Cu has been gathered more recently also by in-situ SERS [25]. It is possible that on specific parts of the surface, OH_{ad} pulls copper atoms above the surface plane in analogy to what has been reported for Cl_{ad} [26]. Moreover, adsorbed CuOH has been regarded as an important intermediate exhibiting catalytic activity towards the oxygen reduction reaction on copper in neutral solutions by King et al. [27] and has been speculated to be responsible for the enhancement of hydrogen evolution on Cu by Martins and Arvia [28]. In addition, both in-situ STM measurements and thermodynamic calculations have shown that in the pre monolayer oxidation region, OH_{ad} (and perhaps also $CuOH_{ad}$) is more stable than Cu_2O or adsorbed water [29–31].

On the other hand, several works [32–37] have emphasized the persistence of divalent copper after the dissolution and/or reduction of the native oxide layer. In one of these works, in particular [32], it has been proposed that CuOH can be formed also by the reduction of an intermediate which could represent subsurface oxygen trapped below the surface copper atoms (Cu^*) that retain the configuration of Cu_2O. Further, Gil et al. [37] have proposed that reduction of cupric oxide goes through the production of an adsorbate species Cu*(I), an intermediate that later transforms to copper (I) oxide.

The chemistry of the model is expressed via the following equations:

$$H_2O_{ad} \underset{k_{-1}}{\overset{k_1}{\rightleftarrows}} OH_{ad}(\theta_1) + H^+ + e^- \tag{1}$$

$$OH_{ad}(\theta_1) + Cu \underset{k_{-2}}{\overset{k_2}{\rightleftarrows}} CuOH_{ad}(\theta_2) \tag{2}$$

$$CuOH_{ad}(\theta_2) \underset{k_{-3}}{\overset{k_3}{\rightleftarrows}} Cu^{2+}_{aq} + OH^- + e^- \tag{3}$$

where θ_1 and θ_2 are the respective surface coverages of the OH_{ad} and $CuOH_{ad}$ intermediate species. For the sake of mathematical consistency, Reaction (3) is written in the oxidation direction, although the line of reasoning in the previous paragraph implies that it takes place in the reduction direction. Even if literature is not unanimous as to whether the detected CuOH is an adsorbed species that exists as individual molecules on the surface or a 2-D condensed phase that acts as a precursor to Cu(I) oxide, at this stage of the modeling we preferred to assume that an adsorbed species is present. This assumption can be verified a posteriori via the calculated surface coverage values (see below). Another important simplification is that no gradient of the concentration of divalent copper ions between the interface and the bulk is considered, i.e. the transport of divalent copper is not a rate limiting step. The validity of this assumption relies on the fact that no extra low-frequency time constant corresponding to a transport process was detected in the impedance spectra. The aim is to get a reduced set of equations in order to be able to calculate statistically meaningful values of the kinetic parameters by a quantitative comparison of the model predictions with the electrochemical data obtained in the present work.

We start with the assumptions of exponential dependence of the rate constants of the reaction steps involving charge transfer (k_i, i = 1,-1, 3,-3) on potential:

$$k_1 = k_1^0 \exp(b_1 E),\ \ k_{-1} = k_{-1}^0 \exp(-b_{-1} E),\ \ k_3 = k_3^0 \exp(b_3 E),$$
$$k_{-3} = k_{-3}^0 \exp(-b_{-3} E),\quad b_i = \frac{\alpha_i F}{RT} \tag{4}$$

where α_i(i = 1,-1, 3 and -3) are the respective charge transfer coefficients for the individual reaction steps. Using a Langmuir-type of isotherm for the adsorbed intermediates, the following charge and material balances are obtained on the basis of the set of Eqs. (1)–(3):

$$\frac{I}{F} = k_1(1-\theta_1-\theta_2) - k_{-1}\theta_1 + k_3\theta_2 - k_{-3} c_{Cu^{2+}_{aq}} \tag{5}$$

$$\begin{aligned} \beta\frac{d\theta_1}{dt} &= k_1(1-\theta_1-\theta_2) - k_{-1}\theta_1 - k_2\theta_1 + k_{-2}\theta_2 \\ \beta\frac{d\theta_2}{dt} &= k_2\theta_1 - k_{-2}\theta_2 - k_3\theta_2 + k_{-3} c_{Cu^{2+}_{aq}} \end{aligned} \tag{6}$$

where β is the concentration of surface sites available for adsorption of intermediate species. It is worth mentioning that in the case of processes taking place at partly oxidized metal electrodes, the physical meaning of both β and θ_i are usually widened, i.e. it is deemed possible that the overall process could extend to a depth larger than a monolayer. The above assumption was implied in the treatment of Al dissolution [38,39], whereas

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