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Electric and electrochemical properties of surface films formed on copper in the presence of bicarbonate anions

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VTT Manufacturing Technology

In STUK this report was supervised by **Juhani Hinttala**

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ABSTRACT

Copper is used as an outer shield of cast iron canisters planned for storage of spent nuclear fuel. The copper shield is responsible for the corrosion protection of the canister. The aim of the present work was to study the influence of bicarbonate (HCO_3^-) anions on the stability of the copper oxide film. The work consists of a brief literature survey and an experimental part, in which voltammetry, electrochemical impedance spectroscopy and dc resistance measurements via the Contact Electric Resistance (CER) technique were used.

The studies reported in the literature indicated that HCO_3^- ions increase the solubility of copper in the stability region of Cu(II). Thus they render the oxide film formed on copper susceptible to local damage and to localised corrosion at high potentials. Unfortunately, despite the great importance of bicarbonates in copper corrosion, most of the environments used in the electrochemical and corrosion studies are not comparable with repository conditions. In the existing studies either the bicarbonate concentrations or pH of the solutions were too high. In addition, no such studies were available, in which not only the effect of carbonate ions, but also possible synergetic effects of them with other aggressive ions would have been clarified.

The voltammetric results of the experimental part of this work point to a bilayer structure of the anodic film on copper in neutral solutions containing HCO_3^- ions. The transport of ionic defects through a thin continuous p-type semiconductor layer was concluded to be the rate limiting step of the anodic oxidation of copper in the stability region of monovalent copper and in the mixed oxide (Cu(I)/Cu(II) oxide) region. Films formed in the divalent copper region did not show well-pronounced semiconductor behaviour. Substantial evidence was found in the voltammetric, CER and impedance results for the increased defectiveness of the anodic film in the Cu(II) region. The oxidation rate of copper in the divalent region was suggested to be limited by interfacial charge transfer and transport of ions through the very defective and/or porous anodic layer.

The present results strongly indicate that bicarbonate ions render the Cu/anodic film system susceptible to metastable pitting and related localized corrosion phenomena at positive potentials. High positive potential may however not be relevant in repository conditions. Accordingly, it can be suggested that bicarbonate ions alone are not likely to pose a serious hazard to the stability of copper oxide films on the shield of the canister.

SIRKIÄ, Pekka, SAARIO, Timo, MÄKELÄ, Kari, LAITINEN, Timo, BOJINOV, Martin. (VTT Valmistustekniikka). Bikarbonaatti-ionien vaikutus kuparin pintafilmien sähköisiin ja sähkökemiallisiin ominaisuuksiin. STUK-YTO-TR 157. Helsinki 1999. 22 s.

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TIIVISTELMÄ

Käytetty ydinpolttoaine on suunniteltu varastoitavaksi valurautasäiliöihin, joiden ulkopinnalle tulee kuparivaippa. Kuparivaippa toimii säiliön korroosiosuojana. Tämän työn tavoitteena oli selvittää bikarbonaatti-ionien (HCO_3^-) vaikutus kuparin pintaa suojaavien oksidifilmien stabiilisuuteen. Työ koostuu lyhyestä kirjallisuusselvityksestä ja kokeellisesta osasta, jossa käytettiin voltammetriaa, sähkökemiallista impedanssitekniikkaa ja kontaktivastusmittaus-tekniikkaa.

Kirjallisuudessa esitettyjen tulosten mukaan HCO_3^--ionit lisäävät kuparin liukoisuutta kahdenarvoisen kuparin (Cu(II)) stabiilisuusalueella ja altistavat näin kuparin oksidifilmin paikalliselle vaurioitumiselle ja korroosiolle voimakkaasti hapettavissa olosuhteissa. Useimmat tehdyistä sähkökemiallisista ja korroosiotutkimuksista eivät ole käytetyn koeympäristön osalta verrattavissa loppusijoitusolosuhteisiin. Olemassaolevissa tutkimuksissa joko bikarbonaattikonsentraatio tai liuoksen pH ovat olleet liian korkeita. Lisäksi yhtään sellaista tutkimusta ei löydetty, jossa olisi selvitetty bikarbonaatti-ionien ja muiden aggressiivisten ionien mahdollista synergistä vaikutusta.

Kokeellisen osuuden voltammetriatulokset viittaavat siihen, että kuparin pintaan neutraaleissa liuoksissa bikarbonaatin läsnäollessa syntyvä pintafilmi on rakenteeltaan kaksikerroksinen. Yhdenarvoisen kuparin (Cu(I)) ja sekaoksidin (Cu(I)/Cu(II)) alueella hapettumisen ja korroosionopeuden rajoittavaksi tekijäksi osoittautui ionihilavirheiden kuljetus oksidin ohuen pintakerroksen läpi. Tämä pintakerros käyttäytyy kuten p-tyyppinen puolijohde. Kahdenarvoisen kuparin stabiilisuusalueella muodostuneet filmit eivät osoittaneet selviä puolijohdeominaisuuksia. Sekä voltammetria-, impedanssi- että kontaktivastustulokset osoittivat, että kahdenarvoisen kuparin alueella muodostunut oksidifilmi sisältää huomattavasti enemmän hilavirheitä kuin yhdenarvoisen kuparin alueella muodostunut oksidifilmi. Cu(II)-alueella kuparin hapettumisnopeutta rajoittaa rajapinnan yli tapahtuva varauksensiirto sekä ionien kuljetus huokoisen ja/tai runsaasti hilavirheitä sisältävän oksidifilmin läpi.

Tässä työssä saadut tulokset viittaavat siihen, että voimakkaasti hapettavissa olosuhteissa bikarbonaatti-ionit tekevät kuparin oksidin alttiiksi metastabiilille pistesyöpymiselle ja siihen liittyvälle paikalliselle korroosiolle. On kuitenkin todennäköistä, että näin voimakkaasti hapettavia olosuhteita ei esiinny loppusijoitusolosuhteissa. Niinpä voidaan olettaa, että bikarbonaatti-ionit eivät yksistään muodosta vakavaa uhkaa kuparikapselin oksidifilmien stabiilisuudelle.

CONTENTS

ACKNOWLEDGEMENTS

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1 INTRODUCTION

Understanding the stability of the passive films forming on copper is of great importance when considering the use of copper as an outer shield of cast iron canisters for storage of spent nuclear fuel. The copper shield is responsible for the corrosion protection of the canister construction. Nitrites, chlorides, sulphides and carbonates have been suggested to affect the stability of the oxide films on copper and to promote localised corrosion. However, a consistent model for the growth and stability of copper oxide films has not been available, which has made a mechanistic understanding of the influence of these detrimental anions difficult.

On the basis of our previous experimental work, the oxide film formed on Cu in $Na_2B_4O_7$ solutions at 80 °C was depicted as consisting of a conductive layer and a very thin semiconductive layer. The aim of the present work is to study and discuss the influence of bicarbonate (HCO_3^-) anions on the stability of the copper oxide film. The work consists of a brief literature survey and an experimental part, in which voltammetry, electrochemical impedance spectroscopy and dc resistance measurements via the Contact Electric Resistance (CER) technique were used as the main techniques.

2 LITERATURE SURVEY

Electrochemical measurements in slightly alkaline solutions have shown that the passivation of the copper surface involves the formation of cuprous oxide and cupric oxide together with cupric hydroxide surface compounds. Above a certain threshold potential, which depends largely of the solution composition and pH, the breakdown of the oxide film and the initiation of copper pitting has been reported [1]. The electrochemical behaviour of Cu in alkaline solutions is rather complex, but some information about the relative contributions of all these reactions has been obtained by performing voltammetric measurements.

2.1 Voltammetric studies

Voltammetric measurements can be used not only to obtain an overview of the electrochemical behaviour of the studied material at different potentials, but also to obtain preliminary kinetic information about the reactions occurring on the metal surface. The polarisation curves of copper in bicarbonate solutions can be divided into four different sections as shown in Fig. 1a.

Section I consists of the first anodic current peak, which is followed by the passivation of the copper surface in section II. According to Drogowska et al. [29], these two regions are connected to the formation of an inner Cu_2O layer of the oxide film according to the reaction below.

$$2\ Cu + H_2O = Cu_2O + 2H^+ + 2\ e^- \qquad (1)$$

Drogowska et al. made also a measurement in which they formed the oxide film on the copper surface in the upper part of the section II and then reduced it. The measured Q_{red}/Q_{ox} ratio was found to be close to 1, indicating that no soluble species are released to the solution during the formation of an oxide film in the region of monovalent copper. Furthermore, they reported that the formation of cuprous oxide is thermodynamically as well as kinetically more likely than the formation of copper carbonates. The authors reported also that with increasing temperature the height of the first anodic peak increases and the potential shifts to more negative values [2].

Section III comprises the second anodic peak and a broad oxidation area where the current is independent of the potential. The possible reactions occurring in this region can be written as:

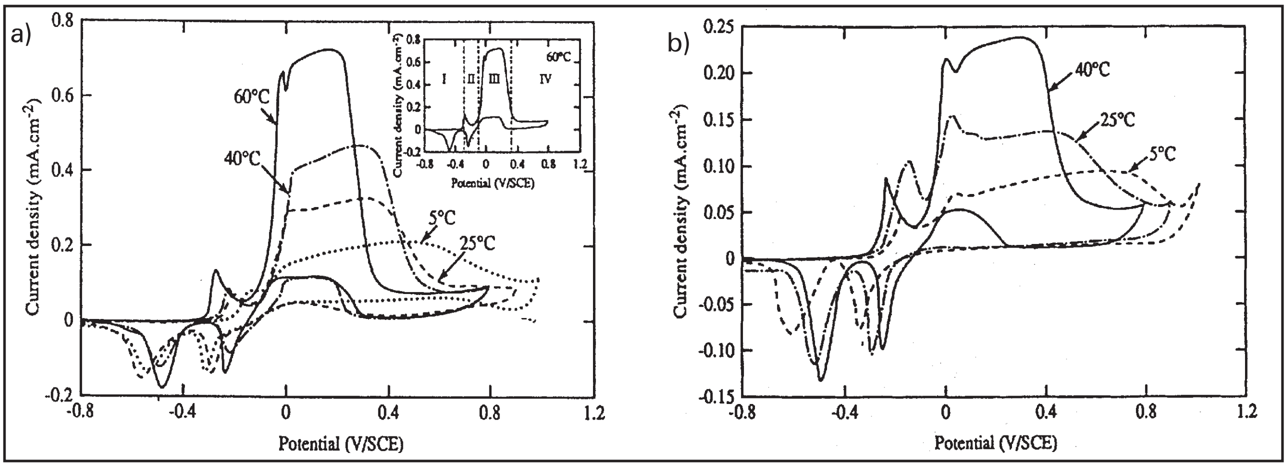

Fig. 1. *(a) Cyclic voltammograms for a Cu disc electrode rotated at 1000 rpm, sweep rate of 5 mVs^{-1} at 5, 25, 40 and 60 °C **a)**: in 0.1 m $NaHCO_3^-$ solution (pH 8), **b)**: in a 0.05 m $NaHCO_3$ solution (pH 8) [2].*

$$Cu_2O + H_2O = 2CuO + 2\ H^+ + 2\ e^- \quad (2)$$

$$Cu_2O + 3H_2O = 2\ Cu(OH)_2 + 2\ H^+ + 2\ e^- \quad (3)$$

and

$$Cu_2O + 2HCO_3^- = 2CuCO_3 + H_2O + 2\ e^- \quad (4)$$

$$CuCO_3 + HCO_3^- = [Cu(CO_3)_2]^{2-} + H^+ \quad (5)$$

Within Section III passive film is growing and may compose of copper carbonates, whose structure can approach that of malachite ($CuCO_3*Cu(OH)_2$) or azurite ($2CuCO_3*Cu(OH)_2$) if the pH of the solution is higher than 10.5. Malachite can react with bicarbonate ions forming highly soluble copper complex ions through reactions (6) and (7).

$$\begin{aligned} &CuCO_3*Cu(OH)_2 + HCO_3^- \\ &= 2\ [Cu(CO_3)_2]^{2-} + 2\ H_2O + H^+ \quad (6)\end{aligned}$$

$$\begin{aligned} &CuCO_3*Cu(OH)_2 + HCO_3^- \\ &= 2\ [Cu(CO_3)(OH)_2]^{2-} + H^+ \quad (7)\end{aligned}$$

On the other hand, copper carbonates ($CuCO_3$) as such or Cu(I) carbonate complexes have not been detected nor reported [2,3].

The temperature influences significantly the broad oxidation region in Section III as shown in Fig. 1. The figure clearly shows that the anodic currents increase with increasing temperature. The authors reported also that the reduction efficiency during the negative going sweeps fell from 100% to 11 % with increasing temperature. Interaction between bicarbonate and Cu(II) ions resulting in soluble complexes may explain the observed, significantly different anodic behaviour of copper in solutions containing bicarbonates compared to that of other aqueous electrolytes. In the absence of carbonates, Cu(II) compounds on the copper surface assured an extensive range of passivity [3,4].

Section IV in Fig. 1 shows the secondary passivation of the copper electrode surface before oxygen evolution begins. Increasing temperature narrows the second oxidation region (Section III) and reciprocally makes the secondary passivation region wider as shown in Fig. 1a. Drogowska et al. have reported this to result from increased copper dissolution-precipitation rate with temperature. Furthermore, the temperature increase of the bicarbonate solution increases the amount of current flowing through the oxide film. This suggests that the film becomes less protective towards general corrosion [3,4].

The typical reduction peaks of CuO and Cu_2O are detected during the negative going sweeps. Several authors have reported also an anodic current peak during the reverse sweep. A clear anodic peak can be seen during the reverse sweep in Figs 1 and 2 roughly between $-0.2\ V < E < 0.3\ V$. This has been reported to be an indication of the reactivation of the electrode surface despite of the fact that the surface remained covered with Cu_2O film [3–5].

In addition to temperature, the electrolyte flow rate has an effect on the shape of the voltammograms. Stirring does not affect significantly the height of the first anodic peak whereas the sections II and III seem to be remarkably dependent on hydrodynamics. This indicates that the rate of base metal electrodissolution process is promoted by chemical dissolution of the passivating surface layer [1,3,5]. When the stirring and pH is kept constant and concentration of HCO_3^- increased, the measured anodic currents are higher i.e. the amount of soluble Cu(II) species in the solution increases [3].

2.2 Effect of bicarbonate concentration and pH on passive film on copper surfaces

Thomas et al. [6,7] have shown that in air-saturated solutions at ambient temperature the oxide film formed on copper is protective in 0.01 m $NaHCO_3$. Nevertheless, at high enough positive potentials the oxide film broke down and high currents were measured. This supports again the idea that a possible breakdown occurs through the reaction with cupric hydroxide film rather than the cuprous oxide film as indicated in the previous chapter. Thus the oxide films with different valency formed on the copper surface exhibit different characteristics towards anions.

As the bicarbonate concentration is increased, the oxide film is less protective towards general corrosion, probably due to the increasing formation of soluble copper carbonate complexes. This increasing solubility of copper complexes explains the measured increasing corrosion currents through the cuprous oxide film with increasing bicarbonate concentration as shown in Fig. 1 [2]. The results suggest that the bicarbonate ions do not interfere with Cu_2O formation, but Cu^{2+} ions are stabilised by the complexing action of HCO_3^-. This was confirmed by the observation that a higher bicarbonate anion concentration caused an increase in the anodic current, but the cathodic currents were not significantly affected

The estimated oxide thickness on the copper samples depended only slightly on the electrolyte concentration (0.1–0.001 M $NaHCO_3$) but depended mostly on the time the sample was kept at each potential. A more significant change in the film thickness was observed as the temperature was increased from 5 to 60 °C (from 1.6 nm to 4.6 nm, respectively) [2].

Not only the bicarbonate concentration but also the pH of the solution affects the breakdown of the oxide film and the pitting phenomena on copper surfaces. The anodic behaviour of copper in dilute $NaHCO_3$ solutions (pH 8) indicates that corrosion proceeds at localised areas rather than in pits and continues as a quasi-homogeneous Cu dissolution through the anodic film [2]. Behaviour of the copper surface is different if the carbonate concentration is increased. The voltammograms of copper in two bicarbonate solutions with two different pH-values are shown in Fig. 2. According to Sanchez et al. the pitting potential of copper is 0.4 V vs. SCE at pH 8.7 and 0.53 V vs. SCE at pH 11. They reported that a number of current fluctuations were measured in the voltammogram at potentials more positive than 0.4 V vs. SCE as shown in Fig. 2 [1]. Typically these fluctuations are related to partial breakdown and reforming of the oxide film.

Sanchez et al. investigated copper surfaces with SEM after potential cycling of the specimens. They found out that in 0.1 m $NaHCO_3$ solutions a milder pitting corrosion and much lower pit density was observed on the surfaces than when the samples were exposed to solution with higher pH-value. On the other hand, as the potential sweep was reversed before the pits were observed, no clear Cu pitting was established and the measurements showed a nearly homogeneous copper electrodissolution through the anodic layer.

The increasing amount of soluble Cu(II) species with higher concentration of carbonate ions in the solution generated by reactions (5),(6) and (7) could be explained by the increase in the HCO_3^- surface concentration [1]. Sanchez et al. stated that for the $NaCO_3$+$NaHCO_3$ solutions the local acidification implies a local increase in the concen-

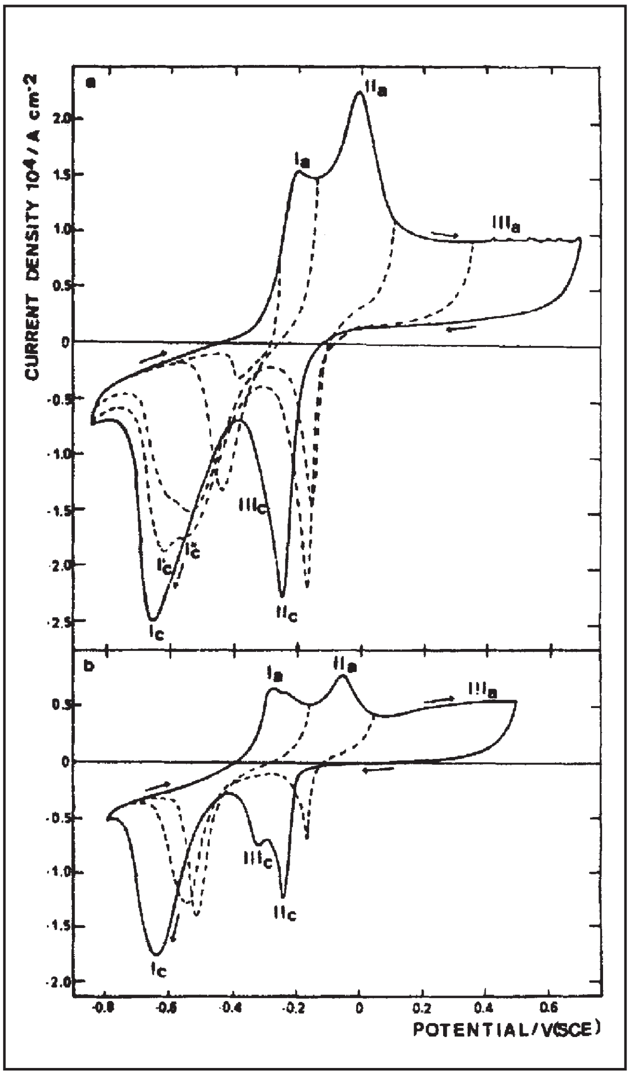

Fig. 2. Voltammogramms of copper in $NaHCO_3$ + Na_2CO_3 solutions at 10 mVs-1: a) 0.09 m $NaHCO_3$ + 0.01 m Na_2CO_3, pH 9.1; b) 0.03 m $NaHCO_3$ + 0.07 m Na_2CO_3, pH 11 [1].

tration of HCO_3^- ion in such a way that it should be considered as the actual aggressive ion for Cu pitting. This fact explains the pH dependence of the pitting potential [1].

Ribotta et al. [3] stated that in lower pH solutions HCO_3^- behaves as an aggressive ion, but with increasing solution pH the total dissolution rate of the base metal is determined by the combined effects of bicarbonate and pH of the solution. This implies that with low pH value and high carbonate concentration in the solution, pitting is observed on the copper surface. On the other hand, the surface is less prone to experience pitting when carbonate concentration is low in low or high pH solutions [3,8].

2.3 Comments on the relevance of the test environments

Despite the great importance of bicarbonates in copper corrosion, most of the environments used in the electrochemical and corrosion studies are not comparable with repository conditions. In the existing studies either the bicarbonate concentrations or pH of the solutions are too high. In addition, no such studies are available in which not only the effect of carbonate ions, but also possible synergetic effects of these species with other aggressive ions would have been clarified. The joint actions of different ions are theoretically extremely difficult to model.

3 EXPERIMENTAL PART

The experimental part was focused on finding possible evidence of local damage to the oxide films on copper in the presence of bicarbonate ions.

3.1 Materials, experimental conditions and equipment

Phosphorus microalloyed copper (Cu OFP) containing 99.992 wt-% Cu and 45 ppm P (Outokumpu Poricopper Oy) was used as the test material in all the experiments. The experiments were performed in a static titanium cladded autoclave. The electrolyte was deaerated and pressurised to 2 MPa using a mixture of Ar+3% H_2. The working electrodes were polished using 4000 grit emery paper and rinsed with MILLI-RO® 15 water before use. A Pd electrode saturated with hydrogen was used as a reference and was assumed to behave as a Reversible Hydrogen Electrode (RHE). All the potentials in this work are reported on the reversible hydrogen electrode scale. The solutions were made of p.a. $Na_2B_4O_7$, p.a. $NaHCO_3$ and MILLI-RO® 15 purified water. The CER equipment was supplied by Cormet Ltd. Potentiostatic and potentiodynamic conditions were ensured using a Wenking LB 81M potentiostat and a Hi-Tek Instruments PPR1 waveform generator. Voltammetric and impedance measurements were performed by a Solartron ECI 1287/FRA 1260 system controlled by ZPlot / CorrWare software (Scribner) in a frequency range 0.01 Hz…10 kHz at an AC amplitude of 10 mV (rms). Capacitance vs. potential curves were registered at a sweep rate of 1 mVs^{-1} and a frequency of 970 Hz.

3.2 Results and discussion

3.2.1 Voltammetric behaviour

A cyclic voltammogram of Cu OFP in 0.1 M $Na_2B_4O_7$ +1.7 mM HCO_3^- is shown in Fig. 3a. The shape of the curve is qualitatively similar to that measured in pure 0.1 M $Na_2B_4O_7$ [9], except for the anodic excursion observed during the negative going sweep in the potential range 1.0…0.65 V.

The currents measured during negative going potential sweeps after different oxidation times at different potentials are shown in Figs 3b…4b. The potential 0.6 V corresponds to the stability region of monovalent copper, 0.75 V to the mixed oxide (Cu(I)/Cu(II) oxide) region and 1.0 V to the stability region of divalent copper. After oxidation at E = 0.6 V for more than 1 h, two different reduction peaks are observed, suggesting the formation of two different layers in the film. These peaks are followed by a tail, presumably due to the reduction of copper ions present in the solution. The charge stored in the peak at higher potentials (0.3…0.35 V) is less influenced by the oxidation time than that stored in the peak at lower potentials (E < 0.2 V). This points to a bi-layer structure, in which only one of the layers grows appreciably in thickness with time. Numerical integration of the curve registered after 3 h of oxidation shows that the thickness of the part reduced at 0.3 V is ca. 3 times higher than that reduced at ca. 0.1 V. After oxidation at 0.75 V a third reduction peak appears at 0.6…0.65 V due to the formation of divalent Cu in the film.

An anodic excursion is observed during the negative-going potential sweep at 0.55…0.85 V after oxidation at 1.0 V, in accordance with the result shown in Fig. 3a. This is a strong indication of local damage of the oxide film, i.e. susceptibility to pitting of the material. It is worth noting that the amount of oxide reduced at 0.3...0.4 V is significantly smaller after oxidation at 1.0 V than at 0.6 V. This fact together with the fact that the ratio of the cathodic charge to the anodic charge is smaller points to the release of a higher amount of soluble products at 1.0 V.

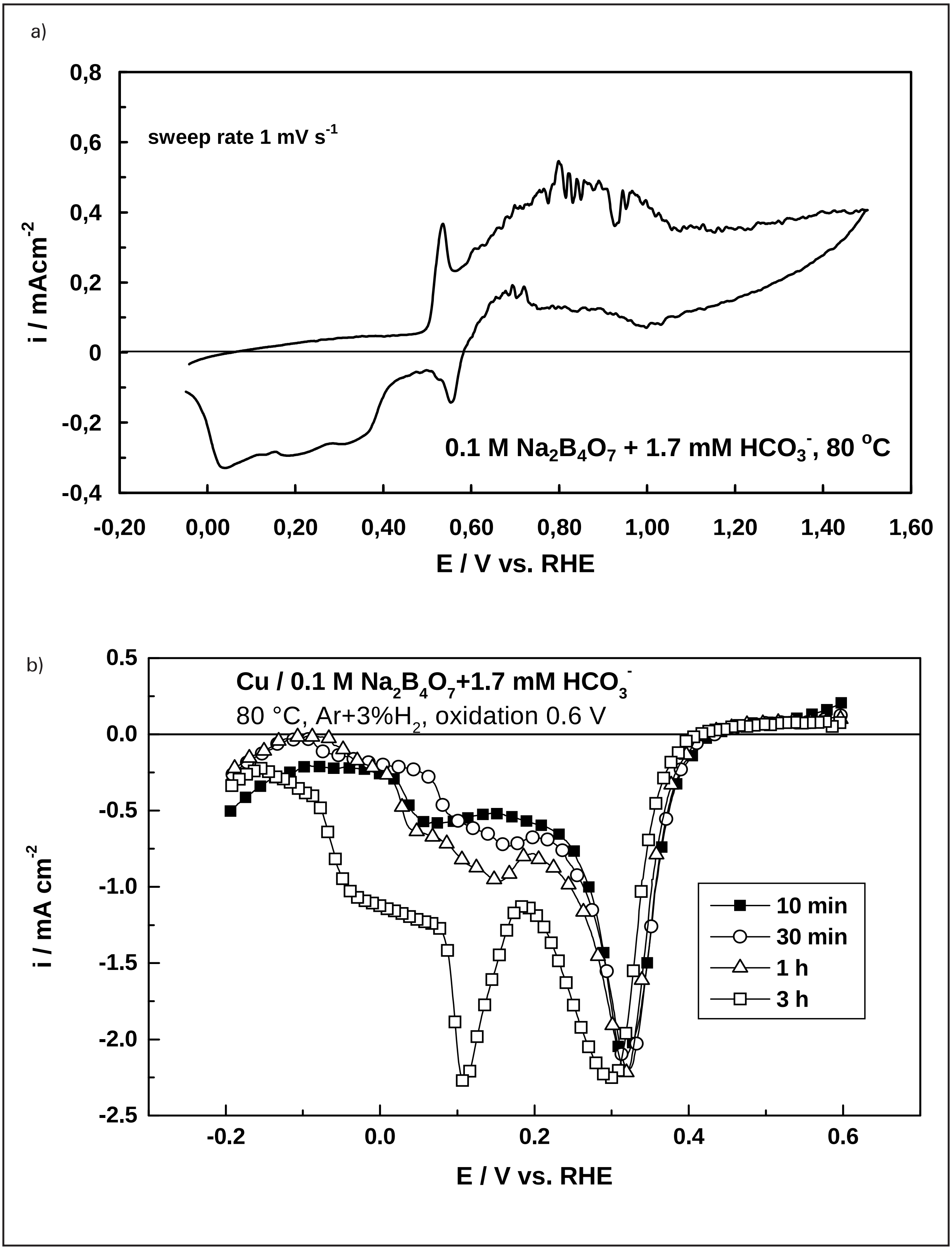

Fig 3. *Polarisation curve* ***a)*** *and negative-going potential sweeps after different oxidation times at* ***b)*** *+0.6 V for Cu OFP in 0.1 M* $Na_2B_4O_7$ *+ 1.7 mM* HCO_3^- *at 80 °C and 2 MPa Ar+3%* H_2*. Sweep rate 1 mVs*$^{-1}$*.*

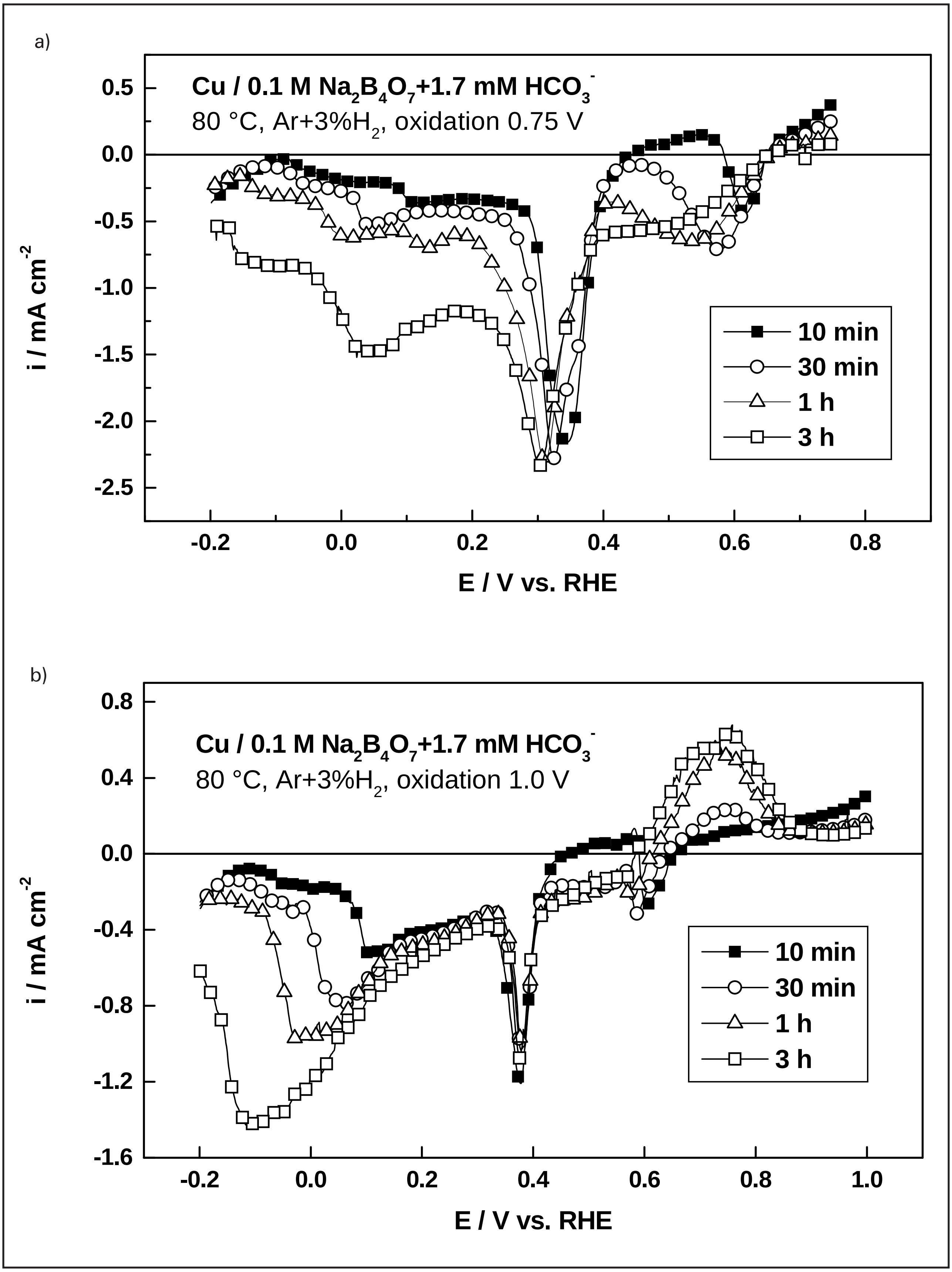

Fig 4. *Negative-going potential sweeps after different oxidation times at* ***a)*** *0.75 V and* ***b)*** *1.0 V for Cu OFP in 0.1 M $Na_2B_4O_7$ + 1.7 mM HCO_3^- at 80 °C and 2 MPa Ar+3% H_2. Sweep rate 1 mVs^{-1}.*

3.2.2 Electronic resistance of the oxide film formed on copper

The electronic resistance of the oxide film formed on Cu in 0.1 M $Na_2B_4O_7$ containing 1.7 mM HCO_3^- ions during a positive-going potential sweep is shown in Fig. 5a. It is in close agreement with the corresponding result in HCO_3^- -free 0.1 M $Na_2B_4O_7$ [10,11]. After the formation of a steady state film at E = 0.6 V, the resistance exhibits a value (see Fig. 5b) that is about ten-fold when compared to the corresponding value in pure 0.1 M $Na_2B_4O_7$ [10,11]. This might be due to the formation of a thicker or less defective semiconductor part of the layer in the stability region of monovalent copper in the presence of HCO_3^- ions. When the potential is cycled between 0.6 V and 0.9 V, the resistance at E = 0.9 V shows about the same values as in pure 0.1 M $Na_2B_4O_7$. This points to more profound changes in the structure of the film as a function of

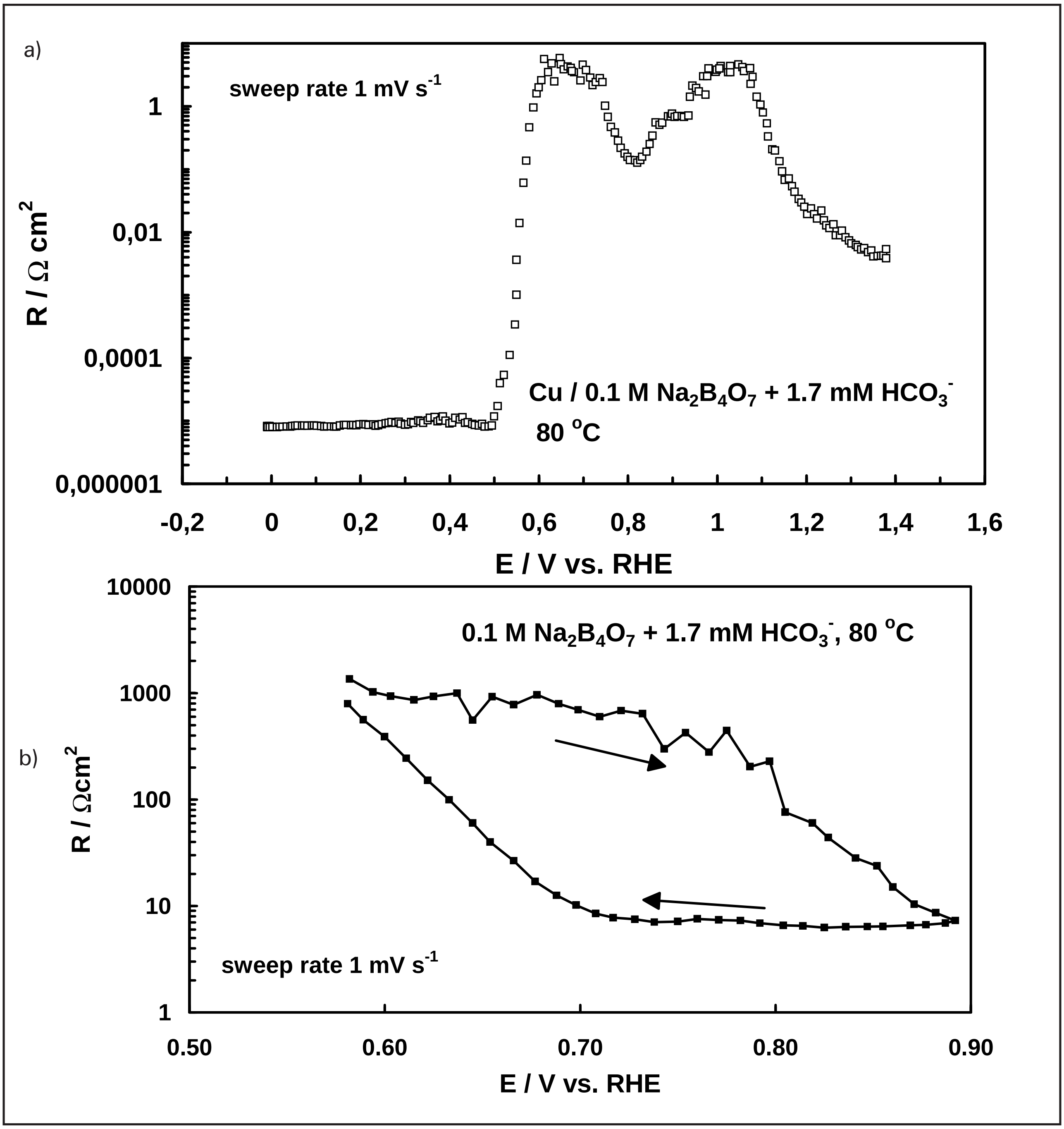

Fig. 5. *Electronic resistance* ***a)*** *of the film formed on Cu during a positive-going potential sweep and* ***b)*** *during a cyclic potential sweep after oxidation at 0.6 V for 0.5 h in 0.1 M* $Na_2B_4O_7$ *+ 1.7 mM* HCO_3^- *at 80 °C and 2 MPa Ar+3%* H_2*.*

potential than in the case of pure 0.1 M $Na_2B_4O_7$. These changes may be connected with the formation of defects in the film or its partial destruction, which is in agreement with the anodic excursion in the i-E curve discussed above (Fig. 4b).

After oxidising Cu in the presence of HCO_3^- ions at 0.75 V and at 1.0 V and switching to open circuit, the electronic resistance first increases with decreasing potential (Fig. 6). However, the R-t curve following oxidation at 1.0 V shows a clear minimum when the potential has decayed to 0.6…0.7 V. This kind of minimum is very weak in the case of pure $Na_2B_4O_7$ [10], which again points to a more defective structure of the film in this potential region in the presence of HCO_3^- ions when compared to pure tetraborate.

3.2.3 Electrochemical impedance response of the oxide film formed on copper

Figures 7 a…c show the electrochemical impedance spectra of Cu oxidised at 0.6 V(a), 0.75 V (b) and 1.0 V (c) for 3…17 h. The results point to two dominating processes in the stability region of monovalent copper and in the mixed oxide (Cu(I)/Cu(II) oxide) region. The process resulting in the time constant at higher frequencies could be rela-

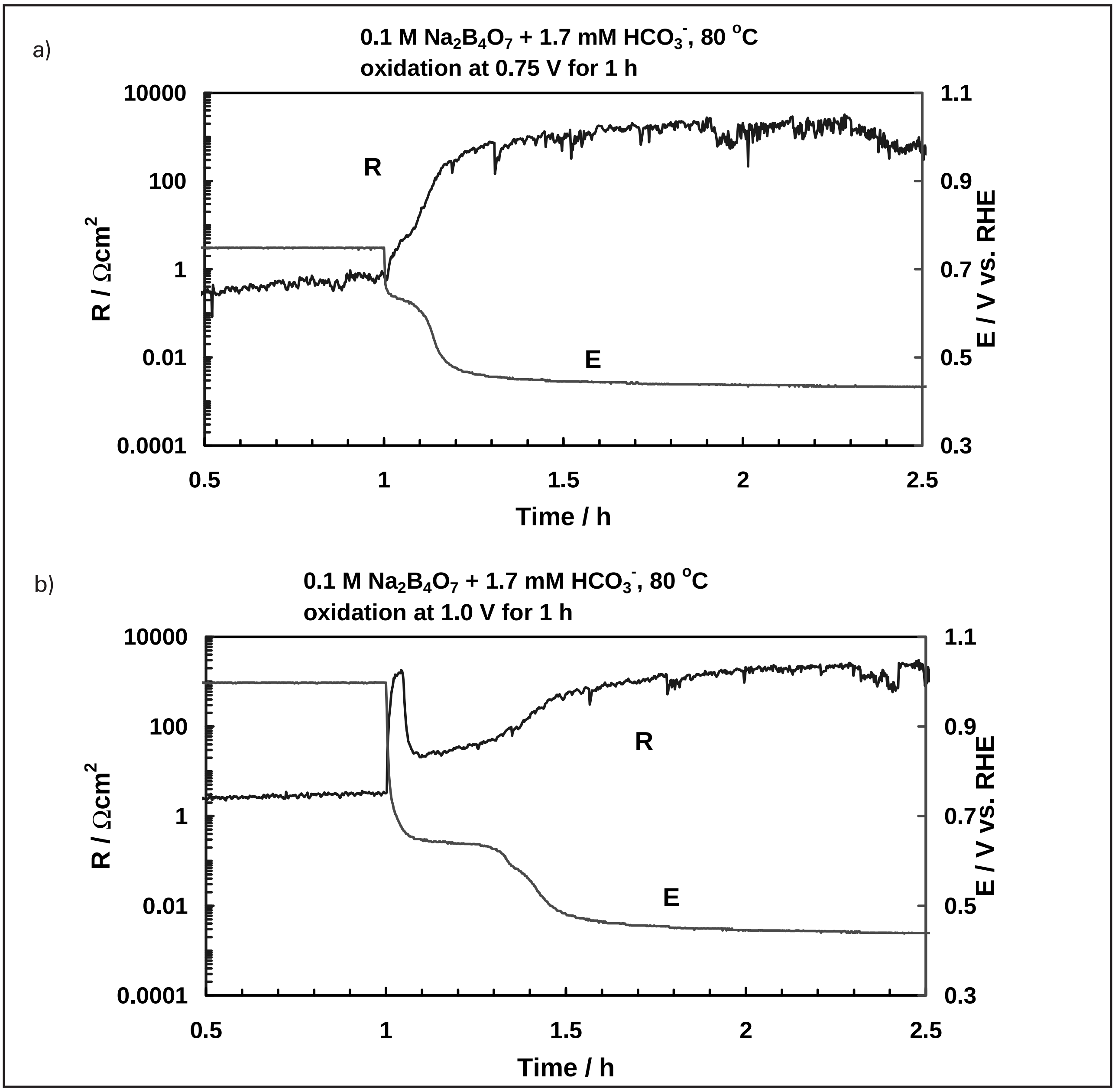

Fig. 6. *Open circuit potential decay curves and the corresponding resistance vs. time curves for Cu oxidised for 1 h at **a)** 0.75 V and **b)** 1.0 V in 0.1 M* $Na_2B_4O_7$ *+ 1.7 mM* HCO_3^- *at 80 °C and 2 MPa Ar+3%* H_2.

ted to the electronic properties of the semiconductor part of the film, while that at lower frequencies is a transport process. For the film formed in the stability region of divalent copper, the contribution of the semiconductor part was no more discernible and some evidence for a transport process in a porous medium is seen.

The spectra shown in Figs 7 a…b (oxidation at 0.6 and 0.75 V, i.e. in the monovalent and the mixed oxide region) can be described with the following transfer function

$$Z = R_{el} + 1 / (1/R_t + j\omega C) + \sigma \tanh [(j\omega\tau_d)^{0.5}] / (j\omega)^{0.5}$$

where R_{el} is the electrolyte resistance, R_t and C are charge transfer resistance and high-frequency capacitance, respectively, σ is the Warburg constant and τ_d is the time constant of the transport process. As the transport process can be described by a finite-length Warburg impedance [12], it most probably occurs in the barrier part of the anodic film. At 1.0 V, the determination of the time constant of the transport process (τ_d) was impossible because of the unrealistically low measurement frequencies needed (Fig. 7c). That is why only the values of the Warburg constant (σ) were calculated for this potential. Furthermore, the exponent of the Warburg function at 1.0 V was found to be

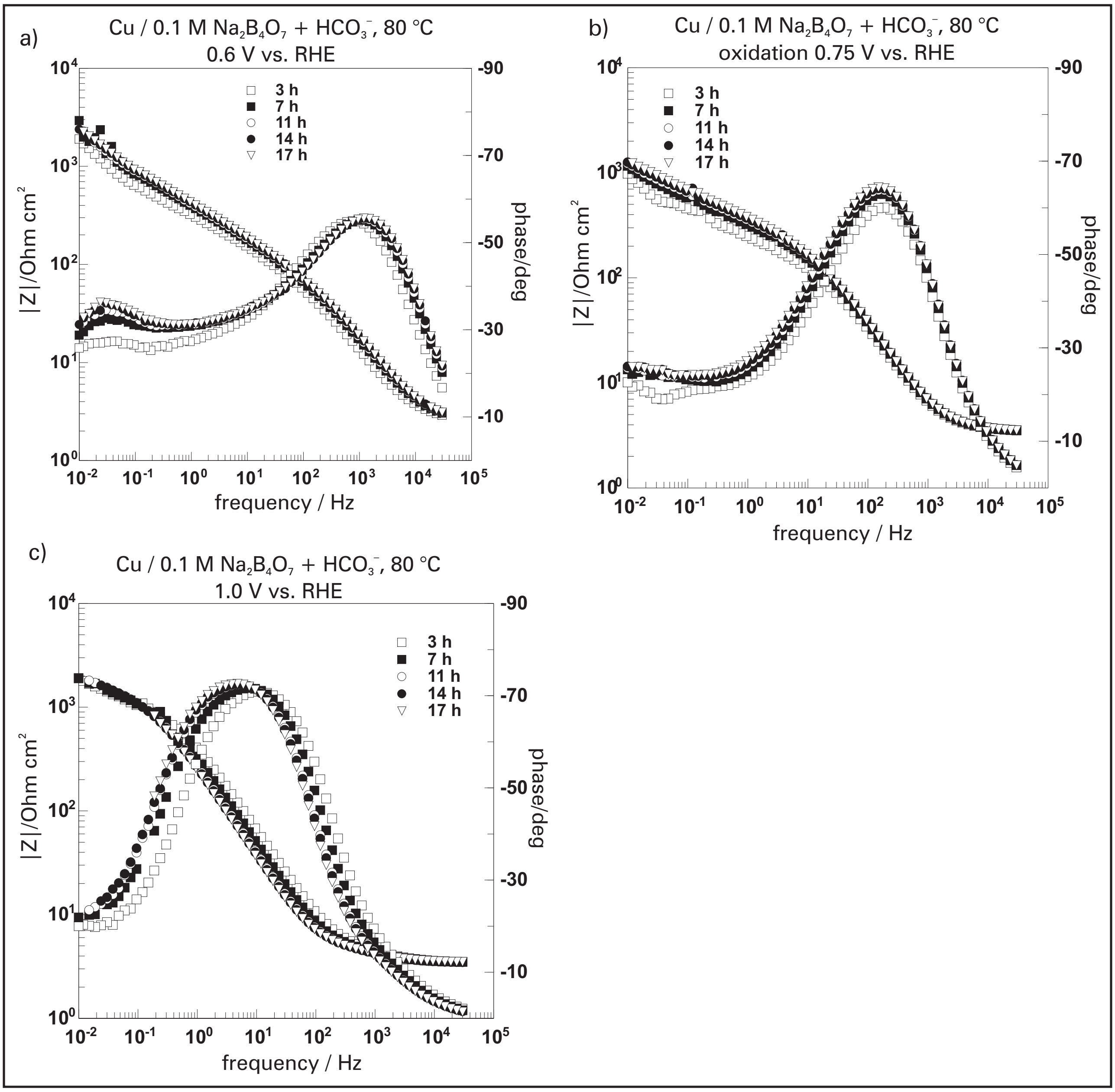

Fig. 7. *Electrochemical impedance spectra of Cu oxidised at* ***a)*** *0.6 V,* ***b)*** *0.75 V and* ***c)*** *1.0 V in 0.1 M* $Na_2B_4O_7$ *+ 1.7 mM* HCO_3^- *at 80 °C and 2 MPa Ar+3%* H_2 *pressure for 3…17 h .*

Table I. *Best-fit values of the Warburg constant σ, the diffusion time constant τ_d, the charge transfer resistance R_t and the high-frequency capacitance C for Cu oxidised at 0.6, 0.7 and 1.0 V in 0.1 M $Na_2B_4O_7$ + 1.7 mM HCO_3^- for 3…17 h.*

	σ / Ω cm^2 s$^{-1/2}$			τ_d / s		R_t / Ω cm^2			C / μFcm^{-2}		
t / h	**0.6 V**	**0.75 V**	**1.0 V**	**0.6 V**	**0.75 V**	**0.6 V**	**0.75 V**	**1.0 V**	**0.6 V**	**0.75 V**	**1.0 V**
3	511	232	500	37.7	79.8	70	60	720	6.2	11	81
7	739	272	320	51.1	129	66	80	1080	4.76	22	102
11	982	284	340	59.2	177	66	90	1100	4.62	20	100
14	1373	293	340	62.3	199	66	90	1120	4.55	21	102
17	1424	303	320	72.3	195	70	100	1100	4.45	20	105

considerably less than 0.5 implying e.g. transport in a porous medium [13]. The best-fit values of the parameters **σ,** τ_d, R_t and C are collected in Table I for all potentials.

The values of the charge transfer resistance practically do not change with time at 0.6 V, but increase up to 11 h oxidation at 0.75 V and 1.0 V. The capacitance values at 0.6 V decrease slowly with time and can by order of magnitude be associated with a thin space charge layer, whereas at 0.75 V the capacitance values practically do not change after 7 h of oxidation and are considerably greater, i.e. the space charge layer is much thinner or more defective. At 1.0 V, the capacitance values can be identified with those of a double layer, i.e. no evidence is found for a space charge layer. The Warburg constant increases continuously with time at 0.6 V probably indicating a decrease in the concentration and/or diffusion coefficient of the transported defects. This points to a certain stabilization process of the layer in the stability region of monovalent copper. The Warburg constant values are considerably lower and stay approximately constant both at 0.75 and 1.0 V implying a faster transport rate in the stability region of divalent copper. Thus the layer contains probably a higher concentration of defects in this region than in the region of monovalent copper.

The plots of C^{-2} vs E (i.e. Mott-Schottky plots) for films formed on Cu at 0.75 V and 1.0 V during oxidation for 1 and 16 h are shown in Fig. 8. In all the cases a linear portion in the curves can be recognised at $E < 0.65$ V, i.e. in the region where the film is composed mainly of monovalent copper. Any quantitative conclusions from the linear part are based on the assumptions that the defect concentration remains approximately constant over a narrow potential range and that the dielectric constant of the film does not change. The acceptor density decreases with time which is in line with the values of the Warburg constant collected in Table 1 for the potential of 0.6 V. What is more important, the acceptor density of the film in the monovalent region is higher in the case when the film was first formed at $E = 1.0$ V than at 0.75 V. This again points to the formation of a more defective film at positive potentials and hence to an increased susceptibility to localised corrosion.

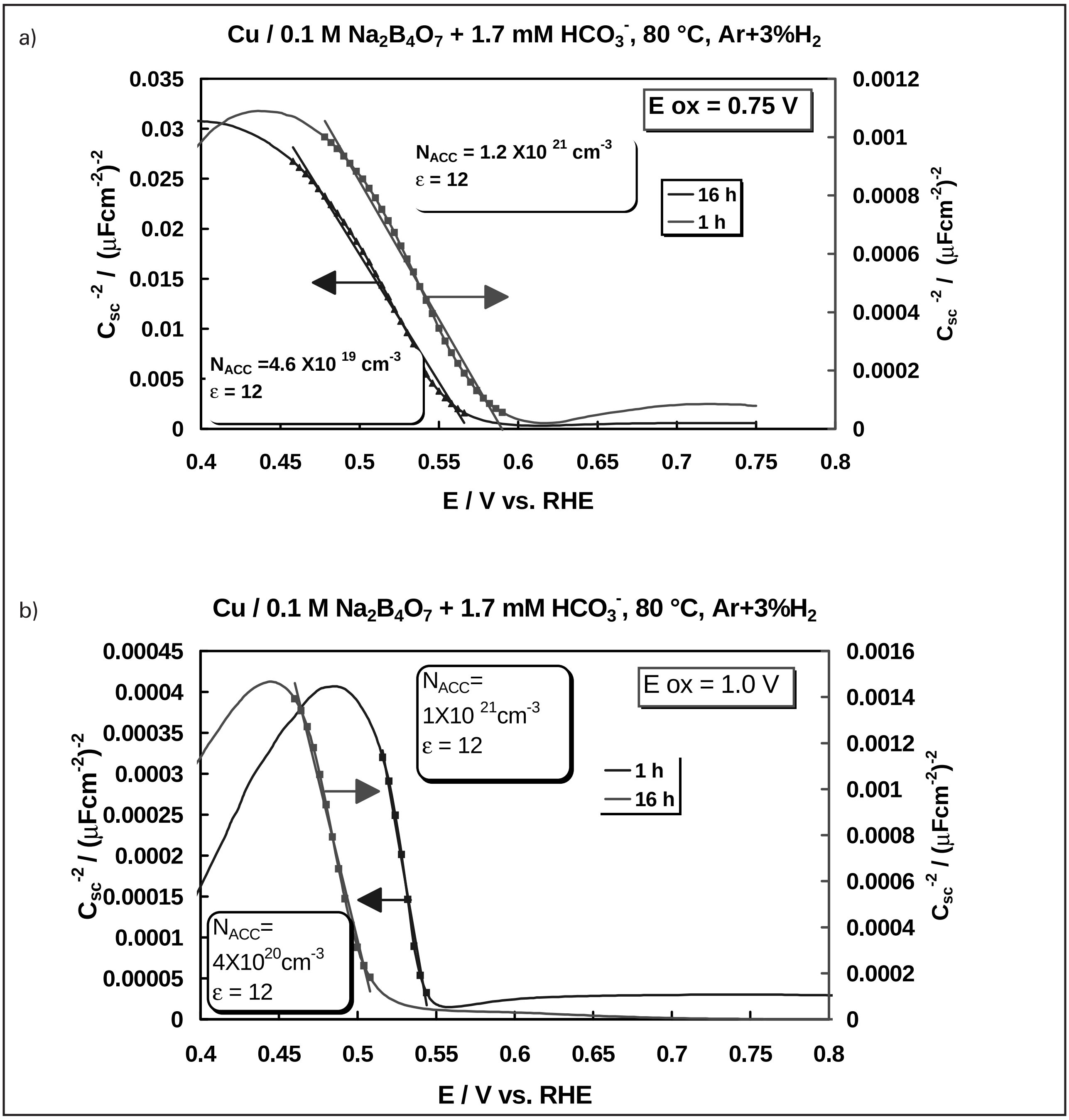

Fig. 8. *Mott-Schottky plots for films formed on Cu during oxidation at* ***a)*** *0.75 V and* ***b)*** *1.0 V in 0.1 M $Na_2B_4O_7$ + 1.7 mM HCO_3^- at 80 °C for 1 and 16 h.*

4 CONCLUSIONS

The studies reported in the literature indicate that HCO_3^- ions increase the solubility of copper in the stability region of Cu(II). Thus they render the oxide film formed on copper susceptible to local damage and thus to localised corrosion at positive potentials. Unfortunately, environments in most of the studies reported in the literature are not comparable with repository conditions.

The results obtained in the experimental part of this work point to a bilayer structure of the anodic film on copper in neutral solutions containing bicarbonates. In the stability region of monovalent copper and in the mixed oxide (Cu(I)/Cu(II) oxide) region, the transport of ionic defects through a thin continuous p-type semiconductor layer is the rate limiting step of the anodic oxidation of copper. Anodic films formed in the stability region of divalent copper, do not show well-pronounced semiconductor behaviour. Substantial evidence was found in the voltammetric, CER and impedance results for the increased defectiveness of the anodic film in the divalent copper region. The anodic oxidation rate in the divalent copper region is presumably limited by interfacial charge transfer and transport of ions through the very defective and/or porous anodic layer. Thus bicarbonates render the Cu/anodic film system more susceptible to metastable pitting and related localized corrosion phenomena at positive potentials. High positive potential may however not be relevant in repository conditions. Accordingly, it can be suggested that bicarbonate ions alone are not likely to pose a serious hazard to the stability of copper oxide films on the shield of the canister.

5 SUMMARY

Copper is used as an outer shield of cast iron canisters planned for storage of spent nuclear fuel. The copper shield is responsible for the corrosion protection of the canister. The aim of the present work was to study and discuss the influence of bicarbonate (HCO_3^-) anions on the stability of the copper oxide film. The work consists of a brief literature survey and an experimental part, in which voltammetry, electrochemical impedance spectroscopy and dc resistance measurements via the contact electric resistance (CER) technique were used as the main techniques.

The studies reported in the literature indicated that HCO_3^- ions increase the solubility of copper in the stability region of Cu(II). Thus they render the oxide film formed on copper susceptible to local damage and to localised corrosion at positive potentials. Unfortunately, despite the great importance of bicarbonates in copper corrosion, most of the environments used in the electrochemical and corrosion studies are not comparable with repository conditions. In the existing studies either the bicarbonate concentrations or pH of the solutions were too high. In addition, no such studies were available, in which not only the effect of carbonate ions, but also possible synergetic effects of these species with other aggressive ions would have been clarified.

The voltammetric results obtained in the experimental part of this work point to a bilayer structure of the anodic film on copper in neutral solutions containing bicarbonate ions. The transport of ionic defects through a thin continuous p-type semiconductor layer was concluded to be the rate limiting step of the anodic oxidation of copper in the stability region of monovalent copper and in the mixed oxide (Cu(I)/Cu(II) oxide) region. Films formed in the divalent copper region did not show well-pronounced semiconductor behaviour. Substantial evidence was found in the voltammetric, CER and impedance results for the increased defectiveness of the anodic film in the divalent copper region. The oxidation rate of copper in the divalent region was suggested to be limited by interfacial charge transfer and transport of ions through the very defective and/or porous anodic layer.

The present experimental results strongly indicate that bicarbonate ions render the Cu/anodic film system more susceptible to metastable pitting and related localized corrosion phenomena at positive potentials. High positive potential may however not be relevant in repository conditions. Accordingly, it can be suggested that bicarbonate ions alone are not likely to pose a serious hazard to the stability of copper oxide films on the shield of the canister.

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