The Electro-Deposition/Dissolution of CuSO$_4$ Aqueous Electrolyte Investigated by In Situ Soft X-ray Absorption Spectroscopy


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ABSTRACT: The electrodeposition nature of copper on a gold electrode in a 4.8 pH CuSO$_4$ solution was inquired using X-ray absorption spectroscopy, electrochemical quartz crystal microbalance, and thermal desorption spectroscopy techniques. Our results point out that the electrodeposition of copper prompts the formation of stable oxi-hydroxide species with a formal oxidation state Cu$^{+}$ without the evidence of metallic copper formation (Cu$^{0}$). Moreover, the subsequent anodic polarization of Cu$_2$O$_aq$ yields the formation of CuO, in the formal oxidation state Cu$^{2+}$, which is dissolved at higher anodic potential. It was found that the dissolution process needs less charge than that required for the electrodeposition indicating a nonreversible process most likely due to concomitant water splitting and formation of protons during the electrodeposition.

INTRODUCTION

Among other methods, copper thin films can be deposited by physical vapor deposition (PVD), chemical vapor deposition (CVD), and sputtering but they had been shown to be expensive procedures. Electrodeposition is an attractive method used to prepare a variety of materials allowing precise control of the chemical composition and structure of the electrodeposited material.$^1$ Electrodeposition of copper plays an important role in a multitude of applications; for example replacing aluminum with copper in semiconductor technology$^2$ thanks to its ability to cover imperfections,$^3$ high electrical conductivity (higher than aluminum),$^4$ and because it works as an effective thermal expansion barrier. In addition electrodeposited copper is used extensively as an interconnect via filler material on printed circuit boards (PCBs) and as an electrode in Li-ion batteries applications$^5$ or as electrocatalyst$^6$ in chemical energy conversion and storage. Moreover, the anodic deposition of copper species onto a conductive substrate through the formation of an insoluble electroactive film of oxides or oxi-hydroxide$^7$ is of prime nature in applications such as electrocatalysis or in the fabrication of oxide ceramics and metal oxide semiconductors.

It is well accepted that the overall reaction of copper deposition and dissolution in acidic conditions involves two electron transfers and is described simply as follow:

$$\text{Cu}^{2+} + e^- \rightleftharpoons \text{Cu}^+ \quad (1)$$

$$\text{Cu}^+ + e^- \rightleftharpoons \text{Cu}^0 \quad (2)$$

where a cupric ion is reduced to form metallic copper and the other way around; a metallic atom is oxidized to produce a cupric ion where the assumption is that the copper is completely oxidized or reduced. Nevertheless, the processes that govern these reactions are not well understood. Galvanostatic measurements suggested that the redox process between Cu$^{2+}$ and Cu$^{+}$ is rate controlling, while Cu$^{+}$ exists in reversible equilibrium with Cu$^{0}$ at the electrode surface due to the fact that the overpotential, at a constant current density, changes in a similar way as an equivalent circuit composed of a resistance in parallel with a capacitance.$^8$ Kinetic studies of Cu deposition and dissolution revealed that the redox process...
between Cu\(^{2+}\) and Cu\(^+\) is rate controlling with reaction 2 being intrinsically faster than reaction 1 yielding an irreversible process with an exchange current density \(i_{0,2} \gg i_{0,1}\) and reaction 2 faster than reaction 1. Therefore, under deposition conditions the current associated with reaction 2 cannot be larger than that associated with reaction 1 in a stationary state. In contrast, Cu\(^+\) exists in a reversible equilibrium with Cu\(^0\) at the surface at low potential polarization, yielding a posterior diffusion of the adsorbed copper (Cu\(_{ads}\)) to the lattice (Cu\(_{lattice}\)). At higher polarization both reactions are irreversible hindering the dissolution of Cu\(^+\) in the electrolyte because the reaction 2 is faster than reaction 1 yielding Cu\(^2+\). On the other hand, under anodic polarization, when the Cu\(^+\) ion concentration reaches a certain level, the Cu\(^+\) ions form Cu\(^{2+}\) and Cu\(^0\) according to this reaction:

\[
Cu^0 \rightarrow Cu^{+} + e^- \tag{3}
\]

\[
2Cu^{+} \rightarrow Cu^{2+} + Cu^0 \tag{4}
\]

where it is assumed that Cu\(^+\) prompts a disproportionation redox reaction 4 yielding the dissolution of copper in form of Cu\(^{2+}\). However, it has been reported some time ago\(^{11}\) that possible oxide intermediates may be formed during the electrodeposition process, where the oxygen is supplied by the water.\(^{12}\) This oxidation state contradicts the generally accepted mechanism introduced by Mattson and Bockris,\(^{8}\) which does not take into account the existence of intermediates as oxides or oxy-hydroxide species. This discrepancy is because Cu\(^+\) is not stable in acidic (pH < 3.5) conditions undergoing a rapid equilibrium with Cu which explains why copper is electrodeposited as a metal.\(^{13}\) Accordingly, the formation of copper oxide/hydroxide intermediates cannot be quenched in acidic conditions hindering the total understanding of their electroformation and deposition.

Hereby, we use a combination of advanced \emph{in situ} X-ray absorption spectroscopy (XAS) and quartz crystal microbalance (QCM) under potentiostatic control to reveal the electronic structure and, thereby, the complex reactions that govern the electrodeposition process of copper in acidic media (4.8 pH). To the best of our knowledge, no comprehensive systematic experiments in the characterization of the electronic structure at the Cu L-edges have been performed during electrodeposition/dissolution of copper. It was found that the electrodeposition and dissolution processes in acidic media involve the formation of nonmetallic copper, most likely in form of oxi-hydroxide.

## METHODS

**Beamline.** \emph{In situ} synchrotron radiation-based experiments were performed at the beamline 20A1 of the National Synchrotron Radiation Research Center (NSRRC) in Hsinchu (Taiwan). This beamline has one horizontal and one vertical focusing mirror, as well as a grating monochromator with four different gratings and a refocusing toroidal mirror. It covers energy spectral range from 60 to 1250 eV (soft X-ray range), with an average resolution of 5000. For the experiments a grating with a groove density of 1200 l/mm was used yielding a resolution of 3000 and 8 \(\times 10^{10}\) photons/s flux with a beamspot of \((1.5 \times 1)\) mm\(^2\).

**In Situ Electrochemical Cell.** The flow liquid cell was operated inside the main chamber of the beamline 20A1 endstation at a background pressure of \(\sim 10^{-8}\) mbar while aqueous solutions circulated on the back side of a 100 nm thick Si\(_3\)N\(_4\) membrane (from the company Norcada, Canada), which is used to separate the liquid phase from the vacuum in the main chamber where the detector (channeltron) is placed. The continuous flow of liquid was assured with a positive displacement micro pump (120SP series from BioChem Fluidics, USA). On the Si\(_3\)N\(_4\) membrane a 20 nm thin film of Au was sputtered and used as working electrode (see below for electrode preparation by sputtering method). The main body of the cell is made of polyether ether ketone (PEEK) which is an electrical insulator and chemically inert. The cell is completed of two extra electrodes used as reference and counter (platinum wire).\(^{14}\) Note that the election of Pt pseudoreference electrode is due to space constritions in the electrochemistry cell. The potential was calibrated to Ag/AgCl following the procedure described by Kasem et al.\(^{15}\)

**Au-Thin Film Working Electrode Preparation.** The Au working electrode was deposited by sputtering with a Cressington 208HR sputter coated machine on a Si\(_3\)N\(_4\) 100 nm thick membrane from the company NORCADA. First of all, an adhesion layer of Ti (99.99%, Elektronen-Optik-Service GmbH, Dortmund, Germany), 3 nm nanometer thick, was deposited in a 0.1 mbar Ar atmosphere at a current of 40 mA during 30 s. After that a 20 nm film of Au (99.99%, Elektronen-Optik-Service GmbH, Dortmund, Germany) was deposited by sputtering in a 0.1 mbar Ar atmosphere at a current of 40 mA for 140 s. This approach yields the formation of a homogeneous polycrystalline thin film used as working electrode.\(^{16}\) The X-ray transmission through this membrane is estimated to \(\sim 74\%\) of the incoming intensity at the edge of interest (the signal intensity is attenuated to around \(\sim 92\%\) of initial intensity through 100 nm of Si\(_3\)N\(_4\) and \(\sim 80\%\) through 20 nm Au). The accurate surface area of the working electrode is around \(\sim 0.016\) cm\(^2\).

**Electrolyte Preparation.** The electrolyte was prepared by diluting 0.798 g of CuSO\(_4\) (Sigma-Aldrich, anhydrous powder, 99.99%) in 1 L of Milli-Q water (18.2 M\(\Omega\)) at room temperature (RT), 25 °C. The electrolyte was continuously saturated with pure N\(_2\) gas by bubbling, which minimizes the presence of other dissolved gases in the liquid. The electrolyte is acidic with a 4.8 pH.

**Potentiostat.** The potentiometric control was assured with a VersaSTAT4, Princeton Applied Research, which allows different potentiometric and amperometric control as well as impedance spectroscopy among others.

**Electrochemical Quartz Crystal Microbalance (EQCM).** Commercially available calibrated quartz crystals (AT-cut 9 MHz) were used as working electrode (with an effective surface of around \(\sim 0.020\) cm\(^2\)) for the \emph{in situ} mass measurements and resistance variations. The quartz crystals were coated with a gold layer (200 nm) on Ti film, and they were used as received from the manufacturer. These crystals were placed in a PEEK cell with a special holder with a 90 \(\mu\)L reservoir for the electrolyte. The system was operated with an analyzer QCM922A (SEIKO EG&G) which allows measurements from 9 to 27 MHz with a resolution of 0.01 Hz and 0.01 \(\Omega\) at 25–27 MHz range using the third overtone of a 9 MHz crystal. The mass change from the initial stage is determined by the resonance frequency variation using the Sauerbrey equation, which yields a mass-frequency sensitivity of 1 ng/Hz. Using this setup 5 mM CuSO\(_4\) electrolyte (4.8 pH) was continuously flowed in the electrochemical cell at a flow rate of 0.8 mL/min avoiding the depletion of the ions or changes in the electrolyte concentration. The electrodes in the cell were the quartz crystal coated with Au (working electrode), platinum.
wire (counter electrode) and a Ag/AgCl reference electrode. This technique allows the monitoring of variations in the redox current, charge transfer, frequency and resistance depending in the applied potential making this technique a powerful tool for the characterization of electrodeposited materials. For easier interpretation the variation in the frequency is directly converted into mass using constant parameters, in dynamic flow, and the Sauerbrey equation.

**TPD Measurements.** TPD analysis was performed in samples electrodeposited in a gold foil (25 μm thick with 99.985% metal purity from the company Alfa Aesar, Germany) from 5 mM CuSO4 electrolyte at a potential of −0.7 V vs Ag/AgCl (CV plateau region dominated by ions diffusion) during 300 s. The desorption measurement was conducted on a self-constructed TPD/TDS setup equipped with a IR furnace from Behr (IRF 10) and QMS 200 quadrupol mass spectrometer from Pfeiffer Vacuum. The sample was pretreated for 12 h under HV condition. The desorption was performed at a heating rate of 25 °C/min until 525 °C. As background correction, a blank measurement (reactor without sample) for each m/z ratio is subtracted from the mass spectrometry data.

## RESULTS AND DISCUSSION

Changes in the resonance frequency, current, and resistance were monitored depending on the applied potential by means of an in situ EQCM, with a quartz/gold resonant electrode yielding a direct observation of the mass change, electrochemical reactions, growth kinetics, and interfacial properties (viscocity and density) under liquid environments. Figure 1 shows the changes in the redox current, charge transfer, mass (frequency), and resistance in both potentiostat/galvanostat devices as a function of the applied potential (cyclic voltammogram, CV). The CV in Figure 1 is related to the electrodeposition of copper in 5 mM CuSO4. Variations in the process current at a given potential were correlated to the variation in the mass, resistance, and charge transfer in the Au working electrode. At −0.28 V vs Ag/AgCl the cathodic current starts to increase indicating a process ascribed to the electroreduction of Cu+ and its electrodeposition as the increase in the mass proves (see Figure 1). At higher cathodic polarization there is a large plateau region dominated by ion diffusion. Reversed sweep into the anodic polarization yields the formation of an anodic peak corresponding to the oxidation-electrodissolution of the deposited copper into the solution, which is indicated by a decrease in the mass. In addition, the density of the current at higher anodic polarization tends to zero, at higher cathodic polarizations, indicating the complete dissolution of the electrodeposited copper as well. Changes in the resistance shows that the electrodeposited material presents higher contact resistance than the pristine sputtered Au electrode. Taking into account that the bulk resistance of metallic copper is lower (16.78 nΩ·m, at 20 °C) than that of gold (25.00 nΩ·m), the electrodeposited copper should not be particularly in metallic form. The implication of this fact is that the electrodeposited material should contain a complex mix of metallic and/or oxidized copper as the fact that low concentrations of oxygen in the bulk yields high conductivity, like in copper metals, indicating a rich oxygen environment. Therefore, the electrodeposited copper oxide is a p-type semiconductor yielding the formation of a Schottky barrier junction at the solid-electrolyte interface affecting the charge transfer due to the formation of a space charge region.

The electrodeposited mass, the resistance and charge transferred to the system start to increase until the potential is reversed and raised up to a potential of −0.18 V vs Ag/AgCl, establishing the existence of two regions for the overall process: the first one ascribed to the electroreduction of Cu2+ to Cu+ and the subsequent formation of cuprous oxide and the second one dominated by a oxidation/dissolution process.

Changes in the current (anodic oxidation) indicate the existence of an oxidized state in the form of Cu2+ or CuO at the interface involving bonds with O and/or OH groups yielding, at around −0.18 V vs Ag/AgCl, a drop in the mass resistance and charge. Note that, the onset-potential difference between mass (frequency) and resistance results from the heterogeneous structure, island growing, and noninteracting characteristics. The reduction in the resistance at anodic polarization is ascribed to different processes that occur simultaneously like: (i) the dissolution of the electrodeposited copper and the consequent demising of the layer thickness (the total resistance is inversely proportional to the electrodeposited copper oxide thickness). (ii) Due to disproportionation reactions that form metallic copper or other surface oxides with lower resistance than the electrodeposited copper oxide. One interesting effect is revealed by the lack of reversibility in the total charge transferred to the system as the difference between the electrodeposited drove charge (109 mC) and the final transferred charge after the dissolution (54 mC), which indicates the existence of a nonreversible process during the electrodeposition. Roughly, during the cathodic reduction process the electrodeposited copper requires two times the total charge drive due to reoxidation/dissolution processes. Therefore, during the electrodeposition other process, like water splitting and the hydrogen evolution reaction (HER), should occur, thereby requiring more electrons per Cu atom electrodeposited. These processes cannot be compensated by copper precipitation, which yields a strong pH increase. Thus, the anodic peak in the inverse scan is associated with the stripping process of the deposited copper. The charge related to the copper electrodeposition is higher than that corresponding to the electro-oxidation process. This behavior can be attributed to the participation of a competing reduction process of H2O or H+ during the electrodeposition to molecular
hydrogen, the HER. A portion of the generated hydrogen diffuses away from the electrode interface and hence the charge is missing during the anodic scan.

Even the information provided by the in situ EQCM is really valuable, changes in the mass, current, charge and resistance at a given potential can be ascribed to different reasons, such as adsorption/desorption, oxidation/reduction, or deposition/dissolution. After all, although EQCM is a powerful method, details in the atomistic information related to the electronic structure are systematically missed. Therefore, these measurements were complemented with in situ X-ray absorption spectroscopy in fluorescence mode (XAS-FY) using the above-mentioned in situ flow cell in the beamline 20A1 of the NSRRC. The XA spectra yield information on the electronic transitions from core levels to unoccupied valence states.28 Note that the thin layer of electrodeposited material (in the hundreds of nanometer range) assures that these electrodeposited electrodes are not susceptible to self-adsorption effects.29 In transition metals L_{2,3} spectra are dominated by the excitation of 2p electrons to unoccupied 3d states (LUMOS) providing information about the electronic structure and coordination environment of these complexes. Cu L-edge spectra can be used to determine unambiguously the oxidation state of Cu and the coordination environment of these complexes. Cu L-edge peaks can be used to determine unambiguously the oxidation state of Cu and the coordination environment of these complexes. 

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Table 1. Peaks Assignment of Different Copper Oxides

<table>
<thead>
<tr>
<th>oxidation state</th>
<th>main peak position (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu⁰</td>
<td>932.7,34 933.7,31 934.5,33 934.8,32 933.7,31</td>
</tr>
<tr>
<td>Cu⁺</td>
<td>932,32 933.7,31 934,32 934.5,34 933.7,31 933.8,36 931.3,37 934,38 933.7,31 933.6,38 931.3,37 934.38 933.7,31 933.6,38</td>
</tr>
<tr>
<td>Cu²⁺</td>
<td>934.32 930.14 931.3,33 931.31 931.34 931.0,36 931.3,36 933.8,37 931.3,37 930.8,37</td>
</tr>
</tbody>
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Figure 2. Cu L_{2,3} spectra depending on the applied potential as well as the current in 5 mM CuSO₄ with Pt as counter and Ag/AgCl as reference electrodes. Each spectrum was recorded in 1 min using a continuous potential variation rate of 0.833 mV/s yielding a potential resolution of 0.05 V. For a better interpretation some significant spectra were selected at different points of interest: (a) +0.18 V, (b) -0.10 V, (c) -0.50 V, (d) +0.70 V, (e) +0.35 V, (f) +0.88 V, and (g) +0.88 V.

For a better interpretation some significant spectra were selected at different points of interest: (a) +0.18 V, (b) -0.10 V, (c) -0.50 V, (d) +0.70 V, (e) +0.35 V, (f) +0.88 V, and (g) +0.88 V.
Usually, the assignment of Cu\(^{+}\) and Cu\(^{2+}\) had been ascribed to cuprous and cupric oxides in the form of Cu\(_2\)O and CuO respectively. However, TPD indicates that oxidation is induced by OH groups yielding the formation of formally (oxi)-hydroxide species.\(^{42}\) The resulting solid is either a mixed-valent oxi-hydroxide surface film on a stoichiometric bulk or possibly a bulk oxi-hydroxide. This intermediate product is still reactive indicating the existence of Cu\(^{+}\) and Cu\(^{2+}\) oxi-hydroxide surface compounds\(^{43}\) or to the coexistence of CuO\(_x\)-Cu(OH)\(_x\) hydrous nature.\(^{44}\) In addition to this fact, there is a formation of a Cu\(_2\)O and mixed Cu\(_2\)O/Cu(OH)\(_2\) layer in alkaline and neutral electrolytes in concordance with the Pourbaix diagram. Under acidic conditions and anodic polarization the oxide species are inherently adsorbates constituting the initial state of an eventual bulk-phase oxidation. During the cathodic cycle, it is more likely the coexistence of Cu—O than Cu—OH groups indicative of the presence of oxygen bounded atoms. These two phases (adsorbed oxygen and oxide) are the precursors of the formation of an oxide multilayer and ultimately a bulk copper-oxide becoming favored the O\(_{ads}\) versus the OH\(_{ads}\) in acidic media, which diminishes the activity of OH\(^{-}\). Thus, the ordered O\(_{ads}\) structure is stabilized in acidic media by hydrogen bonding with hydronium ions\(^{32}\) proceeding the transformation of Cu(OH)\(_2\) to CuO.\(^{46}\)

It is evident from the in situ XAS-FY measurements that copper is electrodeposited from CuSO\(_4\) in the form of Cu\(^{+}\) as the prominent peak at 933.6 eV (L3) proves. This fact together with the TPD measurement indicates that the electrodeposited copper exists in the form of oxo-hydroxide (Cu\(_x\)O\(_{aq}\)), which is deposited under cathodic polarization as the EQCM measurements proved. In addition, the formation of a less conductive layer than Au is supported by the EQCM resistance measurements. Accordingly, the electrodeposition of Cu\(_x\)O\(_{aq}\) involves the reduction of Cu\(^{2+}\) ions to Cu\(^{+}\) species which precipitate as Cu\(^{+}\) and due to the concomitant electrochemical discharge of H\(_2\)O to H\(^+\), generating Cu\(_2\)O\(_{aq}\) and thus increasing locally the pH at the vicinity of the electrode. Thus, in acidic conditions, copper cations are involved in the two-step reduction mechanism. This process is described as

\[
\text{Cu}^{2+} + e^{-} \rightarrow \text{Cu}^{+}
\]

(5)

\[
2\text{Cu}^{+} + \text{H}_2\text{O} \rightarrow \text{Cu}_2\text{O}_{aq} + 2\text{H}^+
\]

(6)

yielding the formation of stable Cu\(^{+}\) which is an insoluble solid according to the Pourbaix diagram\(^{13}\) indicating a gradual increasing in the local pH\(^{47}\) which is not compensated by the Cu\(_2\)O precipitation. This process is shown in Figure 4 involving 2e\(^-\), for the reduction of Cu\(^{2+}\) to Cu\(^{+}\) and the reduction of water into H\(^+\). On the reverse scan, anodic polarization causes the oxidation/dissolution of Cu\(_2\)O\(_{aq}\). The cathodic charge is thereby not fully recovered due to diffusion hydrogen transport away from the interface. Taking into account this fact and the in situ XAS-FY measurements the oxidation/dissolution processes are described as

\[
\text{Cu}_2\text{O}_{aq} \rightarrow \text{Cu}^{0} + \text{CuO}_{aq}
\]

(7)

\[
\text{Cu}_2\text{O}_{aq} \rightarrow \text{CuO}_{aq} + e^{-}
\]

(8)

\[
\text{CuO}_{aq} + 2\text{H}^+ \rightarrow \text{Cu}^{2+} + \text{H}_2\text{O}
\]

(9)

At moderate anodic polarization the Cu\(_x\)O\(_{aq}\) species can be disproportionated to Cu\(^{0}\) (which is not easy to detect owing to the presence of the other phases, especially cuprous oxides due to peak overlapping, see Table 1) and CuO\(_{aq}\) reaction 7, indicating why the resistance decreases during the anodic cycle. The reaction can also directly proceed to CuO\(_{aq}\) mediating one e\(^-\) charge reaction 8. Therefore, soluble Cu\(^{2+}\) ions reduce the

Figure 3. TPD measurements of an electrodeposited Cu electrode onto a Au foil showing the desorption of H\(_2\)O/OH (m/z = 18) and O\(_2\) (m/z = 32) from room temperature (20 °C) up to 520 °C.

Figure 4. Electrodeposition and dissolution processes derived from the in situ XAS-FY, EQCM, and TPD characterization.
amount of electrodeposited mass in the WE as the EQCM indicates. Thus, the oxidation is an irreversible process that forms CuO$_{aq}$ which is dissolved at higher anodic polarization yielding Cu$^{2+}$ and H$_2$O inducing the continuously dissolution of this material until the electrode is completely depleted of copper due to reaction 9, process that is shown in Figure 4 as well. It is noteworthy that the charge necessary to drive the dissolution is only one electron in contrast with the two electrons necessary for the electrodeposition, which is supported by the charge measurements done with the in situ EQCM. Therefore, the irreversibility is due to concomitant water splitting that is of different effectiveness when the potential is anodic or cathodic cycled as consequence of different electrode oxidation state.

**CONCLUSIONS**

Recent advances in spectroscopy aim to provide new insights in the knowledge of the electrochemical processes. Classically, the electrodeposition/dissolution of copper has been described by the interpretation of variations in macroscopic magnitudes as changes in the charge, current, or impedance. However, changes in these magnitudes cannot be related unequivocally to transformations in the electronic structure or chemical composition of these materials. Here, a combination of in situ advanced XAS, EQCM, and TPD proved that the electrodeposition of copper in acidic media involves the formation of Cu$^+$ in the form of a stable solid without the evidence of the formation of any copper metallic species (Cu$^0$), at least within the detection limit due to the superposition of the cuprous oxide peak. Moreover, the dissolution of copper, leads to the condensation of CuO$_2$ that subsequently dissolved as Cu$^{2+}$ ions as the in situ XAS-FY and EQCM proved. Consequently, these results provide new insights in the understanding of copper electrodeposition and dissolution processes revealing the role of the HER reaction in the formation of copper oxo-hydroxide groups. Furthermore, these experiments contribute significantly to the interpretation of the complex reaction scenario governed by performing the operando valence state determination of the above electrodeposited oxo-hydroxide complexes. Kinetic processes govern this reaction scenario. Both the condensation chemistry of Cu species under varying local pH and the potential-induced deposition-dissolution reactions are combinations of solid–liquid interface processes. Deposition and electocrystallization reactions are intertwined with poly condensation reactions controlled by the local pH. The present article reveals in exemplary fashion how a projection of the kinetic processes onto a set of experimental conditions can look like. The ambient reaction temperature slows down all diffusion-controlled equilibration processes and tends to preserve gradient-induced inhomogeneity in the material. The result is a high energy material with residual chemical reactivity. We tried to operate within steady state experiments at each data point to minimize transient phenomena as additional complication. We note that changes in overall pH, the temperature and the agitation will quantitatively affect the findings. The qualitative sequence of events as represented in Figure should, however be independent from the kinetic boundary conditions. Future works will elucidate the sensitivity of the present findings against parameter and concentrate there in temperature and overall pH effects.

A general conclusion is that electrodeposition of a metal under a defined set of conditions may not lead to a homogeneous film material. The complexity of the reaction sequences call for the parasitic inclusion of nonequilibrium species of which more types may exist than anticipated from solution chemistry as consequence of the here demonstrated overlay deposition processes with electrocatalytic transformations of the electrolyte species. The effects of aging freshly deposited films, of high electrocatalytic activity and the pronounced effects of thermal post treatment of such materials find their chemical explanation in the complexity of the initial deposition reactions.

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**Notes**

The authors declare no competing financial interest.

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**REFERENCES**

