

The Oxygen Evolution Reaction Drives Passivity Breakdown for Ni–Cr–Mo Alloys

Alfred Larsson,* Andrea Grespi, Giuseppe Abbondanza, Josefin Eidhagen, Dorotea Gajdek, Konstantin Simonov, Xiaoqi Yue, Ulrich Lienert, Zoltan Hegedüs, Arno Jeromin, Thomas F. Keller, Mattia Scardamaglia, Andrey Shavorskiy, Lindsay R. Merte, Jinshan Pan,* and Edvin Lundgren

Corrosion is the main factor limiting the lifetime of metallic materials, and a fundamental understanding of the governing mechanism and surface processes is difficult to achieve since the thin oxide films at the metal–liquid interface governing passivity are notoriously challenging to study. In this work, a combination of synchrotron-based techniques and electrochemical methods is used to investigate the passive film breakdown of a Ni–Cr–Mo alloy, which is used in many industrial applications. This alloy is found to be active toward oxygen evolution reaction (OER), and the OER onset coincides with the loss of passivity and severe metal dissolution. The OER mechanism involves the oxidation of Mo^{4+} sites in the oxide film to Mo^{6+} that can be dissolved, which results in passivity breakdown. This is fundamentally different from typical transpassive breakdown of Cr-containing alloys where Cr^{6+} is postulated to be dissolved at high anodic potentials, which is not observed here. At high current densities, OER also leads to acidification of the solution near the surface, further triggering metal dissolution. The OER plays an important role in the mechanism of passivity breakdown of Ni–Cr–Mo alloys due to their catalytic activity, and this effect needs to be considered when studying the corrosion of catalytically active alloys.

1. Introduction

Metallic materials are essential to our modern society as structural materials in most industries, infrastructures, energy, and transportation sectors, and they are desired due to their high strength, ductility, thermal and electrical conductivity, and possibility for their machining and forming. The main limiting factor of metallic materials is material degradation due to corrosion in aqueous media,^[1] resulting in global annual costs of over 3% of industrialized nations' gross domestic product,^[2,3] causing a significant environmental footprint and even disasters.^[4,5] However, many metals and alloys exhibit a phenomenon, so-called passivity, due to the spontaneous formation of a few nanometer-thin and continuous passive oxide film on the surface, which greatly reduces the corrosion rate so that the material can be used in corrosive environments for extended periods of time.^[1] Passivity has been described

A. Larsson, A. Grespi, G. Abbondanza, E. Lundgren
Lund University
Division of Synchrotron Radiation Research
Lund 221 00, Sweden
E-mail: alfred.larsson@sljus.lu.se
J. Eidhagen, X. Yue, J. Pan
KTH Royal Institute of Technology
Division of Surface and Corrosion Science
Stockholm 100 44, Sweden
E-mail: jinshanp@kth.se
J. Eidhagen
Alleima (former Sandvik Materials Technology)
Sandviken 811 81, Sweden

D. Gajdek, L. R. Merte
Malmö University
Materials Science and Applied Mathematics
Malmö 205 06, Sweden
K. Simonov
Swierim AB
Department of Materials and Process Development
Kista 164 07, Sweden
U. Lienert, Z. Hegedüs
DESY Photon Science
22607 Hamburg, Germany
A. Jeromin, T. F. Keller
Centre for X-ray and Nano Science (CXNS)
Deutsches Elektronen-Synchrotron DESY
22607 Hamburg, Germany
T. F. Keller
Department of Physics
University of Hamburg
22607 Hamburg, Germany
M. Scardamaglia, A. Shavorskiy
MAX IV Laboratory
Lund University
Lund 221 00, Sweden

 The ORCID identification number(s) for the author(s) of this article can be found under <https://doi.org/10.1002/adma.202304621>

© 2023 The Authors. Advanced Materials published by Wiley-VCH GmbH. This is an open access article under the terms of the Creative Commons Attribution License, which permits use, distribution and reproduction in any medium, provided the original work is properly cited.

DOI: 10.1002/adma.202304621

by the point defect model (PDM), which considers the electrochemical and chemical reactions at the metal/oxide and oxide/electrolyte interfaces, the generation and annihilation of point defects, and the ionic transport across the oxide film. The PDM can explain the oxide growth as well as the breakdown of passivity for many material systems.^[6–9] A typical example of a material system exhibiting passivity is stainless steel, where Cr added as an alloying element spontaneously oxidizes and forms a protective oxide film on the surface, hindering ionic transport and thus acting as a kinetic barrier to further oxidation and corrosion.^[10–12] The passivating properties and the corrosion resistance of advanced alloys, and therefore a more sustainable society, depend on the structure, chemistry, and electronic properties of the passive films and the metal lattice underneath.^[13–17]

In some harsh conditions, stainless steel does not meet the material requirements, and instead, Ni-based alloys are used, which have excellent mechanical properties and corrosion resistance.^[18–20] Ni is commonly alloyed with Cr and Mo, where Cr is known to increase the general corrosion resistance due to the formation of a Cr_2O_3 oxide film on the surface,^[20–24] while the role of Mo is debated. Reports suggest that Mo suppresses the dissolution of Cr,^[20,23–24] stabilizes the passive film in the case of local corrosion attack known as pitting corrosion.^[19,25,26] favoring the Cr_2O_3 formation,^[27–29] and has beneficial properties when it comes to re-passivation of the surface.^[26,30,31] Ni alloys are less extensively studied than stainless steel, and there is still a lack of understanding of the corrosion mechanisms. Commonly used electrochemical techniques for studying passivity and corrosion of stainless steel may not be directly applicable to Ni-based alloys because the measured electrochemical current is not only due to corrosion reactions.^[32] NiO and MoO_2 are good catalysts for the oxygen evolution reaction (OER),^[33–39] which adds another dimension of complexity to understanding the degradation of Ni–Cr–Mo alloys since OER is known to be coupled with dissolution and degradation in other related materials.^[40–45] The oxidation and corrosion of Ni alloys have previously been studied with electrochemical measurements,^[20,31] X-ray photoelectron spectroscopy (XPS),^[23,27–29,46–48] scanning tunneling microscopy,^[21,30,49] time-of-flight secondary-ion mass spectrometry,^[50,51] transmission electron microscopy and energy loss spectroscopy,^[52,53] operando neutron reflectivity,^[54,55] and in-line inductively coupled plasma mass spectrometry,^[56,57] providing valuable information of the electrochemical behavior, the passive film, and metal dissolution. However, results obtained from separate experiments do not always correlate well with each other, particularly due to very different experimental conditions. For example, in commonly used XPS measurements, the sample is placed under ultrahigh vacuum (UHV) conditions. Hence, the correlation of XPS results with experiments performed in electrolyte or ambient conditions is not straightforward. A fundamental and complete understanding is also missing regarding how the chemistry and structure of the passive film evolve in realistic aqueous conditions and how that correlates with the onset of dissolution, which determines the breakdown of passivity.

In this work, we have carried out a comprehensive in situ study where we combine several synchrotron techniques to characterize the surface region of a Ni–Cr–Mo alloy immersed in NaCl electrolyte during electrochemical polarization at stepwise increased anodic potentials, as shown in **Figure 1**. X-ray reflectivity

(XRR) and ambient-pressure XPS (AP-XPS) were used to investigate the thickness and chemistry of the passive film. Grazing-incidence X-ray diffraction (GI-XRD) was used to determine the change in the metal lattice underneath the oxide film. X-ray fluorescence (XRF) was used to quantify the concentration of dissolved elements in the electrolyte. X-ray absorption near-edge structure (XANES) was used to study the chemical state of the species dissolved into the electrolyte and the chemical state of corrosion products formed on the surface. The XRR, XRF, and GI-XRD were integrated into one setup, while XANES and AP-XPS were measured in separate experiments. Combining these techniques allowed us to study the corrosion process, detect the passivity breakdown in situ, and correlate it with the onset of the OER from data measured in NaCl electrolytes of both pH 7 and pH 2.

2. Results

Figure 2 shows the electrochemical behavior of the Ni–Cr–Mo alloy in a 1 M NaCl solution at pH 7 and pH 2 to highlight the presence of OER. As seen in **Figure 2a**, the alloy exhibits a stable passive range with low current densities in the range of $\mu\text{A cm}^{-2}$, up to ≈ 600 mV vs Ag/AgCl at pH 7 and ≈ 900 mV at pH 2, respectively. At higher potentials, the current density increases, appearing like passivity breakdown. The thermodynamic onset for OER at pH 7 and 2, calculated with the Nernst equation $E_{\text{red}} = 1023 - 59 \cdot \text{pH}$ (mV vs Ag/AgCl), is also marked in **Figure 2a**. The values, 610 mV at pH 7 and 905 mV at pH 2, which agree well with the potentials at which the current increases, suggest that the OER takes place. Even if Cl ions are present in high concentration, the chlorine evolution reaction (CER) can be neglected since the standard potential is 1161 mV vs Ag/AgCl, which is outside the potential range used in **Figure 2**. Also, the onset potential of CER is not pH dependent since protons don't take part in the reaction as in OER, (this is further discussed in the Supporting Information).^[58] The difference in the electrochemical behavior can also be seen in **Figure 2b** where the sample was increasingly polarized with different scan rates. As can be seen from the faster scan rates, the difference between pH 2 and 7 is more pronounced, and the curves do not converge at higher potentials, as is seen for the slow scan rates. Metal dissolution, which requires the transport of cations through the oxide film on the surface, is suppressed at higher scan rates due to slow kinetics compared to OER. At higher scan rates, there is also less time to alter the local pH during OER, which will be discussed in more detail later. This is why a separation between the polarization curves measured in pH 7 and pH 2 can be observed for the faster scan rate.

The semiconducting property of the passive film was investigated through Mott–Schottky analysis, as shown in **Figure 2c**. The Mott–Schottky plots show a positive slope in the lower potential region and a negative slope in the higher potential region, typically observed for passive films on Cr and Ni–Cr alloys consisting of Cr_2O_3 .^[59,60] The negative slope at higher potentials is characteristic of a p-type semiconductor, which is the potential region relevant to this study. For a p-type semiconductor, the point defects are cation vacancies, and the defect density can be calculated from the slope of the linear region of the

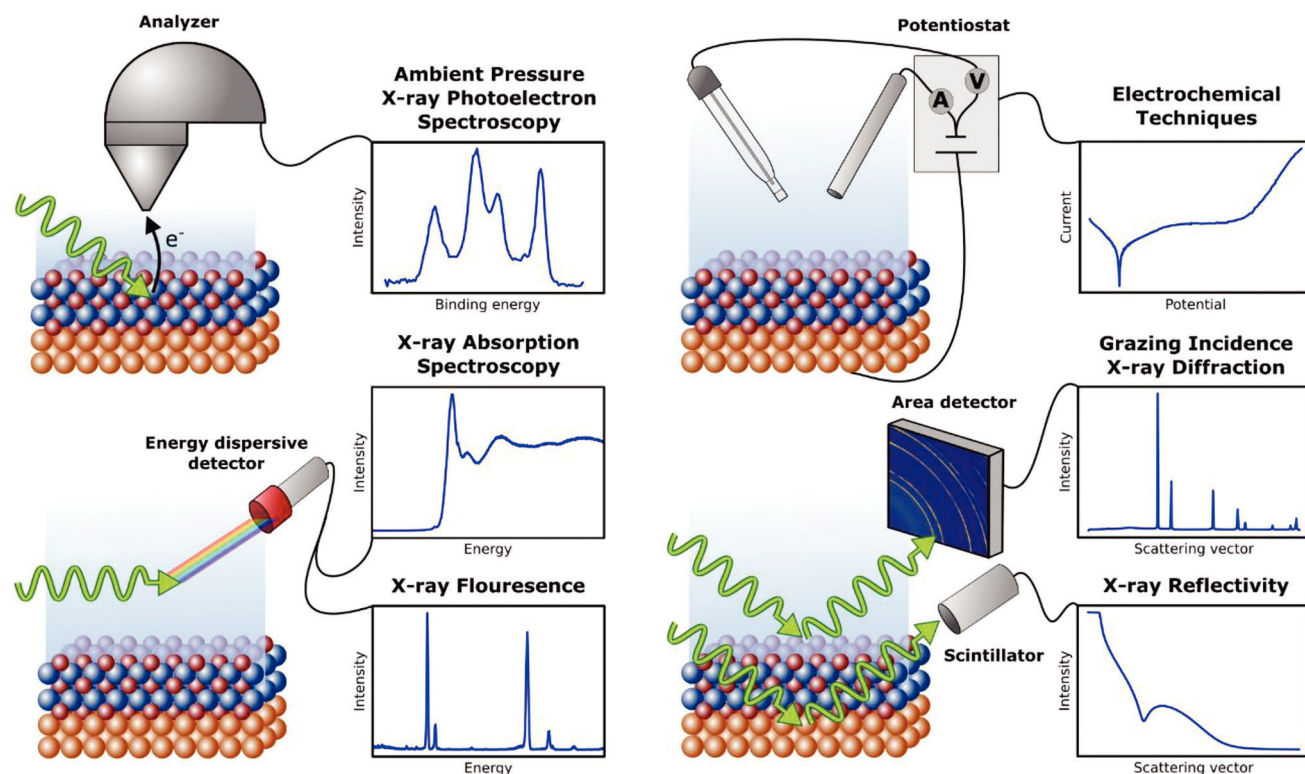


Figure 1. Experimental techniques. A schematic representation of the combination of experimental techniques used during this work. The orange atoms represent the metal, blue the metal cations, and red the oxygen anions in the oxide layer. XRR, XRF, and GI-XRD were integrated into one experimental setup. XANES and AP-XPS were measured in separate experiments.

Mott–Schottky plot. The defect density is slightly higher for the film formed at pH 2 than for pH 7.

The electrochemical impedance spectroscopy (EIS) Nyquist plot in Figure 2d shows part of a semicircle modeled with an equivalent circuit (see the Figure S10f, Supporting Information). At 800 mV, the charge transfer resistance was significantly lower in pH 7 than in pH 2, with values of 3.5 kΩ and 21.8 kΩ, respectively. This large discrepancy diminishes at higher applied anodic potentials, as shown in Figure 2e,f, where the EIS response becomes close to equivalent at 1000 mV. The charge transfer resistance drops significantly at these high anodic potentials where the current density due to OER is larger. At potentials of 900 mV and above, an inductive loop is observed in the Nyquist plot, implying that metal dissolution takes place.^[61] These EIS spectra were modeled with the equivalent circuit shown in Figure S10g (Supporting Information). The convergence of the EIS data goes in line with the observed convergence of the polarization curve at high anodic potentials, as shown in Figure 2a. As mentioned above, this is due to the local change of pH near the surface, which will be discussed in more detail below. The fitting parameters for the EIS data can be found in the Supporting Information.

Figure 3 shows the composition and thickness of the surface oxide in the passive range. The oxide thickness and composition were calculated from the AP-XPS data and presented versus the potential, as shown in Figure 3a,b. At OCP and in the passive range, the oxide film is thicker at pH 7 than at pH 2. The oxide film is also richer in Cr³⁺ oxide at pH 7 at OCP. As the sample is

anodically polarized, the oxide film grows thicker and becomes enriched in Mo⁶⁺ oxide. Also, the hydroxide layer grows thicker, which can be due to further hydroxylation of the oxide surface or hydroxylation of dissolved ions according to the PDM.^[6] In addition, the fact that the steady-state oxide thickness is smaller at pH 2 indicates higher dissolution rates of the oxide at pH 2 compared to pH 7 in the passive range. From the oxide composition, it can be deduced that a thinner oxide at pH 2 at OCP and in the passive range is due to enhanced dissolution of Cr³⁺ since the oxide at pH 2 contains less Cr³⁺. XRR was also used as a complementary method to quantify the oxide thickness under real operando conditions, and the data is shown in Figure 3c. The difference in oxide thickness for the different pH values is also seen in the results extracted from modeling the XRR data, shown in Figure 3d. The oxide is thinner at OCP, and in the passive range for low pH, and as the anodic potential increases, the oxide film grows thicker. A schematic model of the surface region used for the interpretation of the XPS and XRR results is shown in Figure 3e.

Figure 4 shows the passive film breakdown seen from the in situ surface analysis. A dramatic change in the surface chemistry of the alloy is observed at 800 mV for pH 7 and 900 mV at pH 2, corresponding approximately to the respective onset of passivity breakdown. This is evident from the AP-XPS spectra in Figure 4a,b. At these potentials, a significant increase in the Cr(OH)₃ and Mo⁶⁺ oxide peaks is seen with a corresponding decrease in all metallic and other oxide

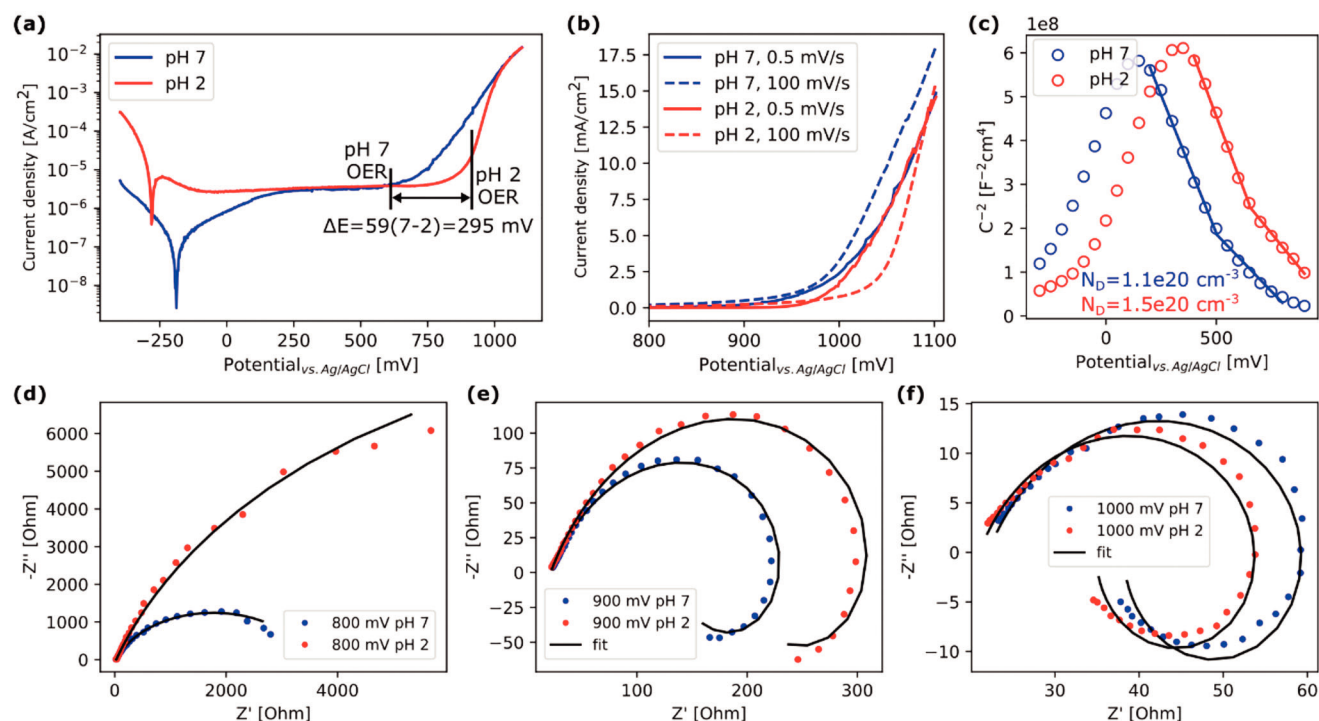


Figure 2. Electrochemical behavior. a) Polarization curves of the Ni–Cr–Mo alloy in 1 M NaCl at pH 7 and pH 2 measured with a sweep rate of 0.5 mV s^{−1}. Thermodynamic potentials for OER are indicated. b) Polarization curves measured at 0.5 mV s^{−1} and 100 mV s^{−1}, respectively, in 1 M NaCl at pH 7 and pH 2, plotted on a linear current scale. c) Mott–Schottky plots of Ni alloy measured after polarization at 900 mV for 30 min. d,e) Nyquist plot of EIS data for Ni alloy in 1 M NaCl at pH 7 and pH 2 at 800 mV, 900 mV, and 1000 mV vs Ag/AgCl, respectively.

components. This means that the Mo⁶⁺/Cr(OH)₃ layer became so thick (≈5 nm, which is the AP-XPS probing depth under these conditions described in the Supporting Information) that no photoelectrons from the underlying material can escape. This change in surface chemistry correlates with an increase of one order of magnitude in the current density, as shown in Figure 4c,d. The correlation between the drastic increase in current and the formation of a thick layer of Mo⁶⁺/Cr(OH)₃ layer suggests that this is coupled to the OER, which occurs in this potential range. The difference in potential dependence for the Mo⁶⁺ oxide formation is shown in Figure 4e, which shows that the Mo⁶⁺ formation occurs first at pH 7 and then at pH 2, which indicates that this is coupled to a pH-dependent process such as the OER.

So far, it has been shown that at potentials ≈700–900 mV, the current density is higher at pH 7 due to the OER, which also causes a dramatic change of the surface chemistry evidenced by the growth of a Mo⁶⁺/Cr(OH)₃ layer. However, from the Mott–Schottky plots in Figure 2c, it is seen that the oxide film is a p-type semiconductor typical of Cr₂O₃. In contrast, Mo⁶⁺ oxide should show an n-type semiconducting behavior.^[6] This suggests that the Mo⁶⁺/Cr(OH)₃ layer is not part of the solid passive film but a precipitated layer of corrosion products formed on top of the thin oxide layer.

Figure 5 shows the quantification of the metal dissolution as well as the chemical state of the dissolved products. At potentials above which the dramatic surface chemistry change occurred, pronounced metal dissolution is observed in the electrolyte by in situ XRF measurements, as shown in the top panel of Figure 5a. The data analysis is described in the Supporting Information.

Detectable dissolution of Ni is seen at 900 mV, while Cr and Mo dissolution is observed at potentials of 1000 mV and above. This demonstrates that passive film breakdown occurs at 900 mV and above for pH 7 and pH 2. The dissolution rate increases at higher anodic potentials, and Ni shows the highest dissolution rates because it is the base metal in the alloy. The chemical state of the dissolved species was investigated with in situ XANES as shown in Figure 5b, where the experimental data from the electrolyte is shown as a thick black line and measured references for comparison are shown in thin colored lines. The experimental spectra of the Ni K edge correspond to Ni(OH)₂ as seen by comparison to the reference spectra, consistent with data for hydrated Ni²⁺ ions in an aqueous solution.^[62] NiO can be ruled out due to the absence of the peak at ≈8450 eV. Cr is dissolved as Cr(OH)₃, consistent with data for hydrated Cr³⁺ ions in an aqueous solution.^[62] Cr⁶⁺ species in the solution can be ruled out due to the absence of the characteristic pre-edge peak of Cr⁶⁺. Mo dissolves as MoO₃, as confirmed by the characteristic pre-edge peak of Mo⁶⁺ compounds and ions. This is also consistent with previously reported XANES data of dissolved MoO₃ and with data of dissolved Na₂MoO₄ in acidic solutions.^[63] The XANES data overlayed with the references are shown in the Figure S20 (Supporting Information). The potential for the onset of dissolution is close to the transpassive potential for Cr³⁺ containing passive films,^[64–66] where stable Cr³⁺ oxide species can be further oxidized to Cr⁶⁺ species that are soluble. However, the observed onset of dissolution occurs at much lower potentials than the experimentally observed breakdown on highly alloyed steels^[67] and other Ni alloys with lower Mo content, as

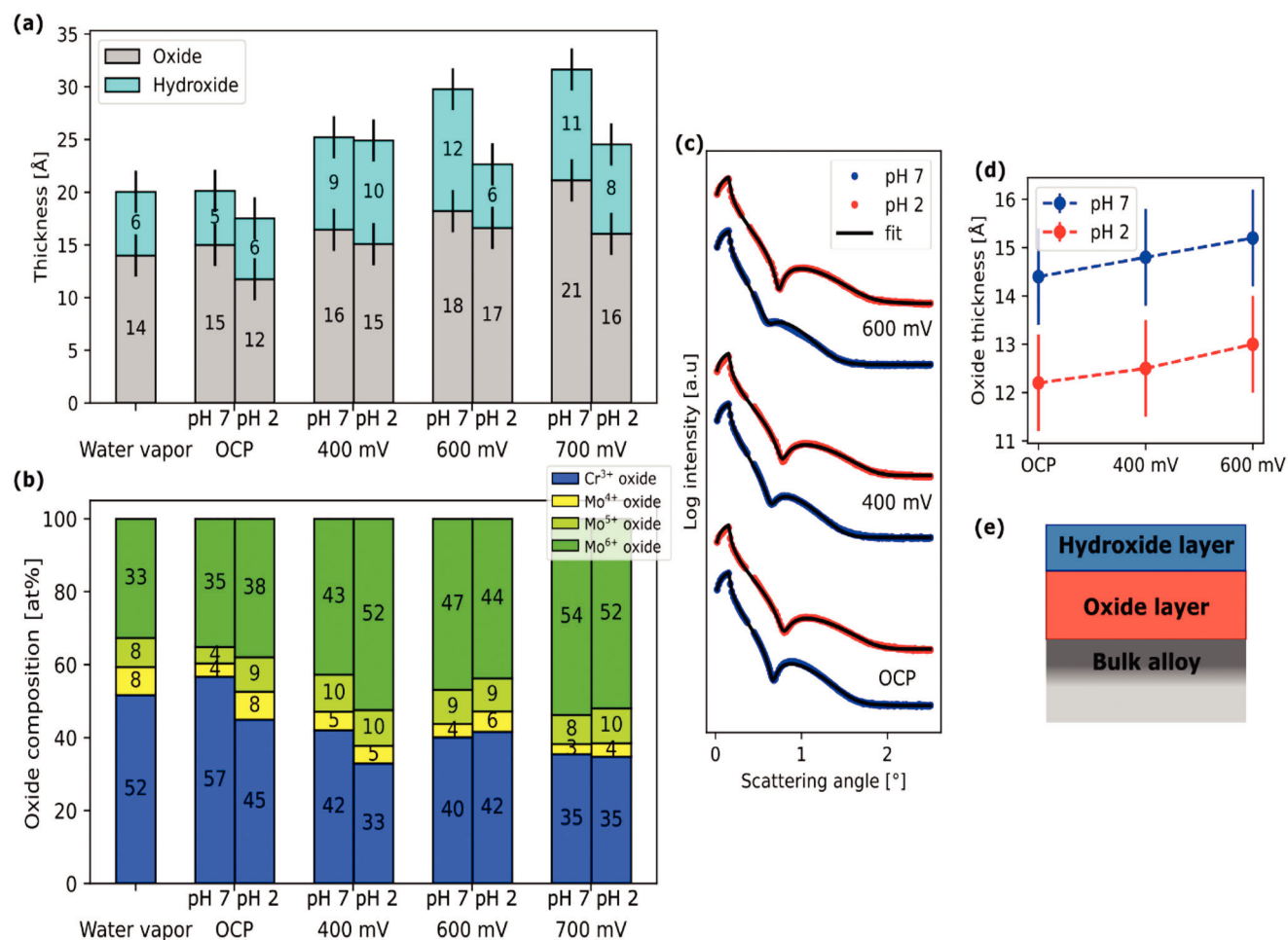


Figure 3. Passive film growth. a) Oxide and hydroxide thickness in 0.1 M NaCl at pH 7 and pH 2, calculated from the AP-XPS data. b) Oxide composition extracted from the AP-XPS data with an uncertainty of $\approx 2\%$. c) Fitted in situ XRR data obtained at OCP and under polarization at 400 and 600 mV vs Ag/AgCl in 1 M NaCl at pH 7 and pH 2. d) Oxide thickness extracted from the XRR data. e) Schematic model of the surface region. The fitting procedure and data analysis are described in the Supporting Information.

shown in Figure S2 (Supporting Information). Since no change in the oxidation state was observed, as indicated by the absence of Cr⁶⁺ in the XANES spectra, the classical transpassive breakdown mechanism for Cr-containing alloys can be ruled out. This suggests that another mechanism contributes to the observed low-potential metal dissolution coupled to the OER, as will be discussed in more detail below.

Further proof that the OER contributes significantly to the electrochemical current can be found when comparing the dissolution current density to the total measured current density, presented in the bottom panel of Figure 5a. The discrepancy between the total current and dissolution current is due to the current associated with OER, and the OER current density was calculated as the difference between the total measured current and the dissolution current extracted from the in situ XRF data (described in more detail in the Supporting Information).

The OER current is higher than the dissolution current at the potentials investigated here for the Ni–Cr–Mo alloy. In the Figure S2 (Supporting Information), data for a Fe-containing Ni alloy with lower Mo content is shown, which exhibits much lower

OER current densities and onset of dissolution at higher potentials to further illustrate and highlight the effect and presence of OER for the studied Ni–Cr–Mo alloy. Another key finding is that at higher potentials above 1000 mV, the dissolution behavior in the two pH values starts to converge in the same way as was observed in the polarization curves and EIS data in Figure 2, which is explained by the local acidification of the solution near the electrode surface during OER as will be further discussed below.

Figure 6 shows the post characterization of the sample surface after the experiment. When taking the samples out from the electrolyte solution once the experiments had been terminated, scales of dried and cracked corrosion products were observed on the surface, as can be seen in the SEM images in Figure 6a,b. The drying and cracking of the corrosion product film are likely a consequence of exposure to UHV. The elemental composition (only considering the metallic components and ignoring oxygen) reveals that the scales are rich in Mo and Cr and depleted in Ni relative to the bulk substrate composition, as seen in Figure 6c. This aligns with the AP-XPS results, which also showed a large

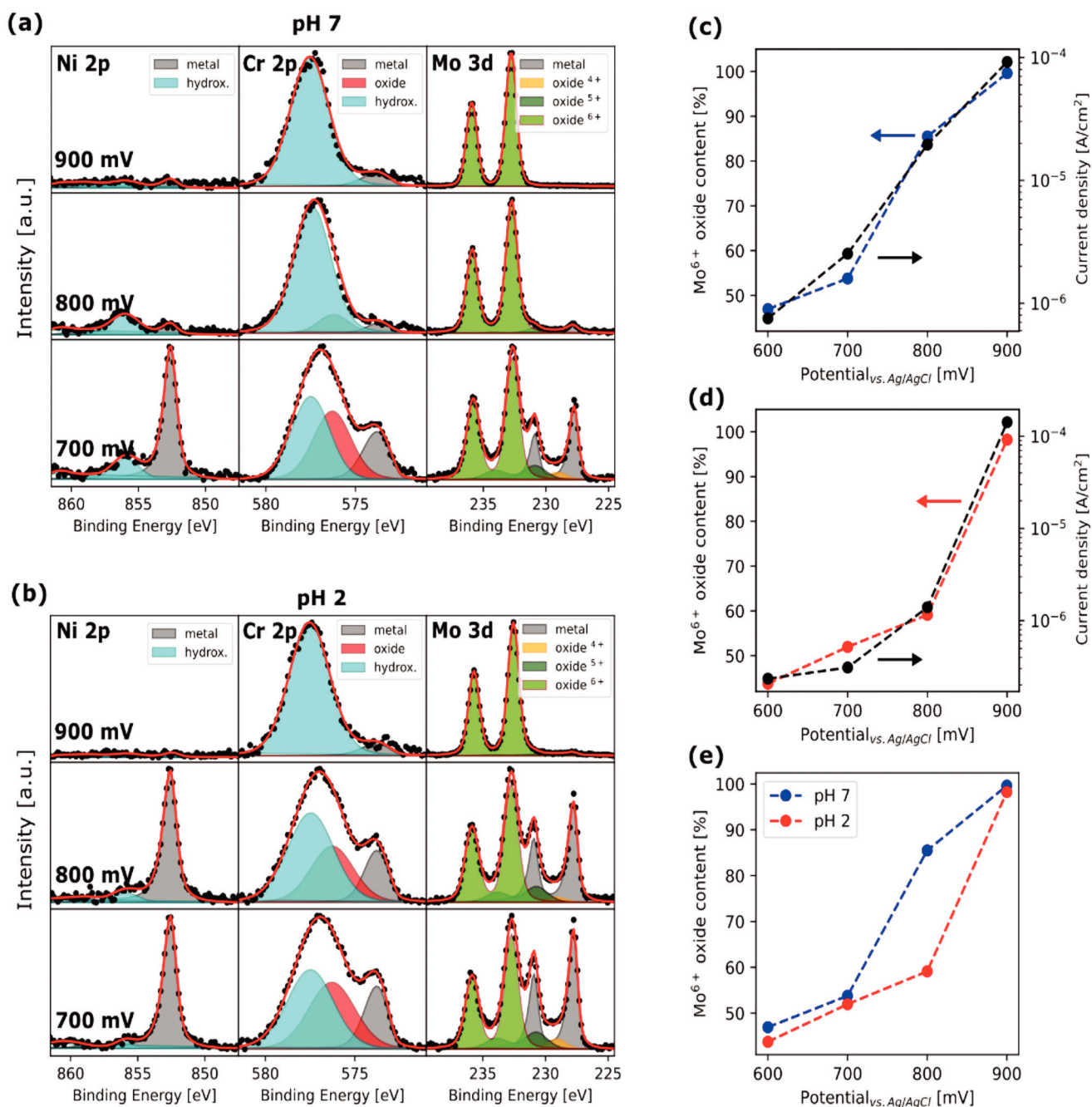


Figure 4. Passive film breakdown. a) In situ AP-XPS spectra of Ni 2p_{3/2}, Cr 2p_{3/2}, and Mo 3d measured at pH 7 for the potential range 700–900 mV. b) In situ AP-XPS spectra of Ni 2p_{3/2}, Cr 2p_{3/2}, and Mo 3d measured at pH 2 for the potential range 700–900 mV. c) Mo⁶⁺ oxide content and current density after 10 min vs potential at pH 7. d) Mo⁶⁺ oxide content and current density after 10 min vs potential at pH 2. Arrows indicate the axis corresponding to the data. e) Comparison of Mo⁶⁺ oxide content at pH 7 and pH 2 vs potential.

contribution from Mo⁶⁺ oxide and Cr(OH)₃ at potentials above 800 mV. The chemical state of the species in the scales was determined using grazing-incidence XANES (GI-XANES), and the results are presented in Figure 6e. Only the metallic component is seen at high incidence angles, but the chemistry of the scales can be observed at low incidence angles due to the increased surface sensitivity, as shown in the Figure S21 (Supporting Information). The chemical states of the scales were determined

qualitatively by comparing the experimental GI-XANES spectra to the reference spectra of compounds. The scales consisted of Ni(OH)₂, Cr(OH)₃, and a mix of MoO₃ and molybdate ions, as shown in the Figure S22 (Supporting Information). The chemical states determined with GI-XANES align with the AP-XPS and EDS results. The fact that GI-XANES detected Ni(OH)₂ but not AP-XPS can be due to the large difference in penetration depth where AP-XPS is

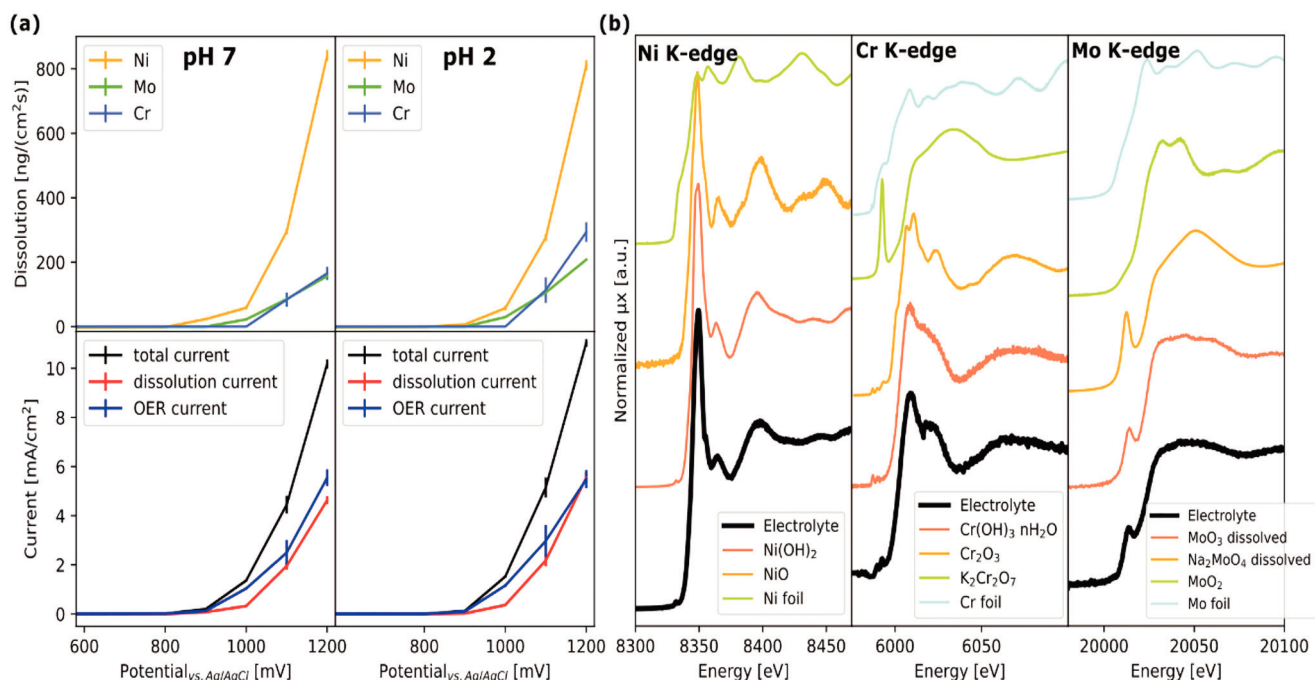


Figure 5. Metal dissolution. a) (Top) Metal dissolution rate calculated from in situ XRF data. (Bottom) Dissolution current density and OER current density, compared to the total current density. b) Chemical state determination of the dissolved species using in situ XANES (only for pH 7). Spectra of references are also shown for qualitative comparison.

orders of magnitude more surface sensitive. The corrosion process also changes the sub-surface metal lattice underneath the oxide film, as seen in Figure 6d. From the GI-XRD data, the lattice parameter was calculated, which increases at potentials ≈ 900 mV, where the pronounced dissolution starts. It is noted that the lattice parameter values start converging for pH 7 and 2

at higher potentials. The change in the lattice parameter during the dissolution is explained by the preferential dissolution of Ni, as seen in Figure 5. This results in an enrichment of Mo and Cr in the lattice, and since Mo has a much greater atomic radius, this results in an increase in the lattice parameter, according to Vegard's law.^[68]

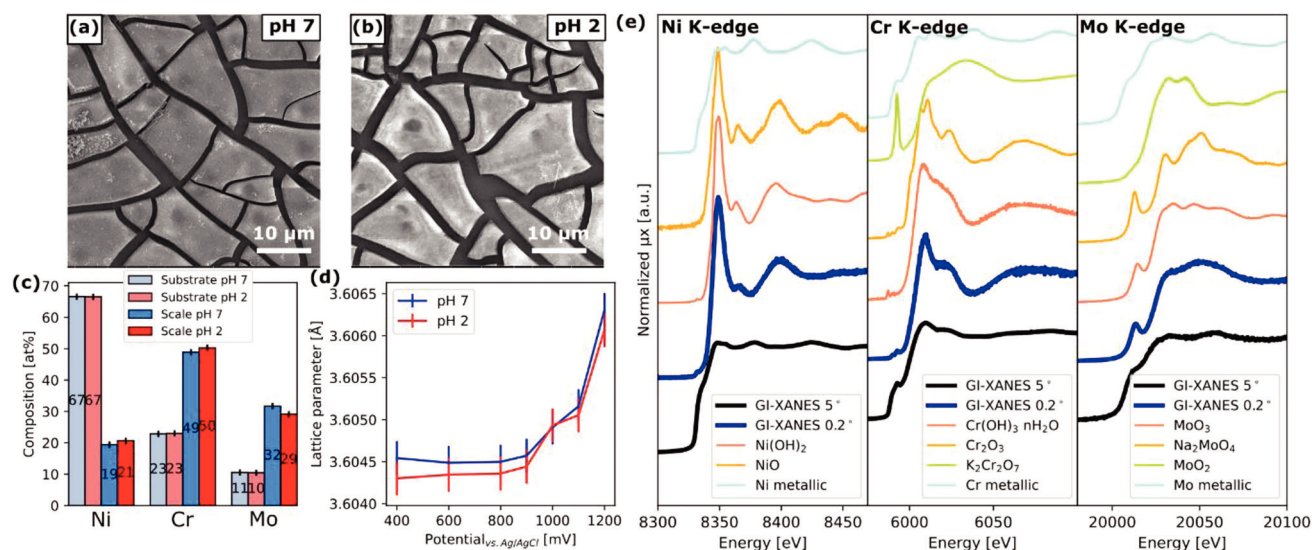


Figure 6. Corrosion products. a) SEM image of sample surface after polarization up to 1200 mV vs Ag/AgCl in pH 7. b) SEM image of sample surface after polarization up to 1200 mV vs Ag/AgCl in pH 2. c) EDS analysis of the substrate and scales seen in (a) and (b); the measurement positions are shown in the Supporting Information. d) Lattice parameter of sub-surface alloy extracted from GI-XRD. e) GI-XANES from the corroded sample measured ex situ at large and small incidence angles to be surface or bulk sensitive. Spectra of references are also shown for qualitative comparison.

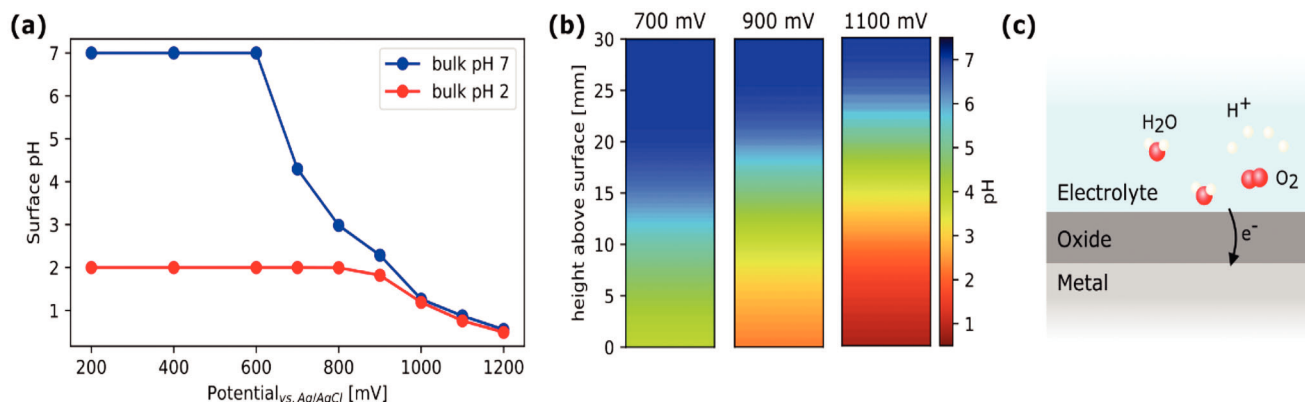
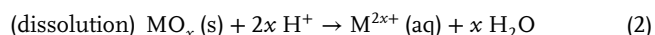
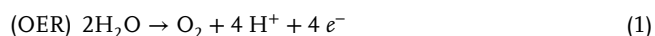


Figure 7. Simulation of local pH. a) Local pH near the electrode surface as a function of potential extracted from COMSOL simulations. b) Simulated pH profiles as a function of height and potential for a bulk electrolyte of pH 7. c) Schematic of OER at the electrode–electrolyte interface giving rise to the production of H⁺ that causes a decrease of the local pH.

3. Discussion

The comprehensive data presented above demonstrate that the Ni–Cr–Mo alloy is active toward the OER and that the onset of OER correlates with a dramatic change in surface chemistry associated with the formation of Mo⁶⁺ oxide, breakdown of passivity, metal dissolution, and the build-up of corrosion products. Since Cr³⁺ was the only oxidation state of dissolved Cr ions, as seen from the XANES data in Figure 5, metal dissolution does not occur by the so-called transpassive mechanism where Cr³⁺ is oxidized to Cr⁶⁺, which is soluble,^[6,64,69] hence leading to a breakdown of the passive oxide film and severe metal dissolution. A significant difference in material behavior in the two bulk electrolyte pH values is only observed at the onset of OER. Subsequently, the behavior in bulk electrolyte pH values of 7 and 2 converge at higher potentials. The unusual behavior can be explained by considering the side products of the OER reaction, which are protons, as shown in Reaction (1).



Proton (H⁺) concentration determines the pH value and affects the stability of oxides in a solution through a chemical dissolution mechanism shown in reaction 2. At large current densities generated by the OER, H⁺ will accumulate locally in the electrolyte close to the surface, resulting in a lower pH and, thus, a more corrosive solution. The charge of the generated H⁺ near the surface must be balanced by counterions, in this case, Cl⁻ ions present in the solution. This results in the acidification and enrichment of Cl ions near the metal surface during OER. In other words, it is the catalytic activity of the material that locally changes the solution chemistry by generating H⁺ that is charge balanced by Cl⁻, which causes the behavior in the two different bulk pH values to converge at high potentials due to the converging low local pH.

Figure 7 shows simulations of the H⁺ concentration above the electrode surface and the pH decrease at the onset of OER. As the potential increases and the OER current density becomes suf-

ficiently high, the pH further drops near the electrode surface and the local pH becomes independent of the bulk electrolyte pH, which explains the convergence between the results obtained with the bulk pH value of 7 and 2 at high potentials (the surface pH when considering full mixing of the H⁺ concentration in the cell volume is shown in Figure S25c (Supporting Information), but there is no significant difference as compared to the situation without mixing). The fact that the near-surface pH drops below one can partly explain the pronounced metal (Ni, Cr, and Mo) dissolution that occurs below the transpassive potential for highly alloyed stainless steel (containing Cr).^[67] It is known that the rate of metal dissolution increase at low pH, which can lead to the breakdown of passivity.^[69] However, the change in the pH near the surface cannot explain the drastic change in surface chemistry seen from the AP-XPS data in Figure 4, where a large increase in the Mo⁶⁺ intensity was observed at the onset of OER. The near-surface pH simulations show that the pH is ≈3 (for a bulk pH value of 7) at 800 mV, where a drastic increase in Mo⁶⁺ was observed. At the same potential in bulk pH 2, the system was still stable, which indicates that the drastic change in surface chemistry revealed by the detection of a thick layer of Mo⁶⁺ oxide cannot be explained by the local pH effects. This suggests that the OER reaction mechanism influences the oxide layer's stability and degradation.

It is well established in the literature that an inverse relationship exists between the stability of metal oxide catalysts and their activity toward OER, suggesting that the reaction mechanism of OER is coupled with metal dissolution.^[41,43,70,71] Theoretical predictions also suggest a universal correlation between OER activity and dissolution.^[40] IrO₂ and RuO₂, well-studied model systems for OER, have been found to degrade through the dissolution of a metal oxide complex of a higher oxidation state, namely IrO₄²⁻, IrO₃, or RuO₄²⁻.^[72–77] During OER, the surface atoms of Ir or Ru oxide that take part in the reaction are further oxidized from the 4+ oxidation state to a 6+ oxidation state complex in the OER catalytic cycle. This higher oxidation state complex can then be dissolved through a coordination inversion process.^[76] This can explain the drastic change in surface chemistry observed for the Ni–Cr–Mo alloy at the onset of OER where Mo⁴⁺ oxide, which is catalytically active^[36] and present in the oxide film as shown

in Figure 3, takes part in the OER mechanism similar to that of IrO_2 and RuO_2 and is dissolved and redeposited as MoO_3 on the surface as observed in the AP-XPS data shown in Figure 4. This explanation is also in line with the chemical state of the dissolved Mo species, which was found to be MoO_3 , as shown in Figure 5, as well as the detected chemical state in the layer of corrosion products in Figure 6, where MoO_3 was detected. The fact that Mo exists partly as MoO_2 in the passive oxide film, as revealed by the AP-XPS data, but only in the Mo^{6+} oxidation state in both the solution and on the surface after the onset of OER, strongly suggests that further oxidation of Mo^{4+} to Mo^{6+} occurs during the catalytic cycle of OER and that Mo^{6+} can be dissolved similar to the coordination inversion mechanism proposed for RuO_2 . At the onset of OER, before severe acidification near the surface has occurred, this proposed degradation mechanism is mainly responsible for the loss of passivity and the observed re-deposition of Mo^{6+} as a corrosion product on the surface.

Another mechanism of degradation during OER is from the participation of lattice oxygen in the reaction shown through isotopic labeling studies.^[41,42,44,78] Some reports claim that oxygen vacancies are left at the oxide surface when lattice oxygen is involved in the OER, which means breaking metal–oxygen bonds.^[38] These vacancies can be filled by oxygen atoms from water, essentially healing the oxide, or react with other anions present, such as Cl, further weakening the oxide structure. Suppose the rate of vacancy generation during OER is higher than that of replenishing the vacancies by oxygen from the water. In that case, it will eventually lead to the dissolution of the cation without a change in its oxidation state,^[38] leaving behind a cation vacancy. This aligns with the observed chemical states of the dissolved Ni and Cr metal ions, as shown in Figure 5, which have the same oxidation state as the Ni and Cr cations in the oxide film determined with AP-XPS. Furthermore, the generation of cation vacancies through dissolution during OER could lead to passivity breakdown, as described by the PDM, where passivity breakdown occurs due to the condensation of cation vacancies at the metal–oxide interface.^[6] If lattice oxygen participation during OER results in cation dissolution and the generation of cation vacancies which diffuse to the metal–oxide interface, this could drive the breakdown of the passive oxide film.

All mechanisms of OER induced passivity breakdown mentioned above are related to the dissolution of cations from the oxide surface. If this rate is slow, as in the passive state, it can be balanced by continuously reforming the thin surface oxide. However, if the dissolution rate of the oxide surface is faster than the reformation of the oxide, real passivity breakdown occurs.^[6–9] OER always takes place on the oxide surface and leads to cation dissolution through degradation of the oxide surface; this is in turn how OER leads to severe dissolution of the metal substrate.

As seen from the Mott–Schottky analysis in Figure 2c, the negative slope at higher potentials suggests that the passive film is still present after polarization to 900 mV where OER is taking place. The negative slope indicates p-type semiconducting properties characteristic of Cr^{3+} oxide, not MoO_3 . This suggests that the Mo^{6+} species observed with AP-XPS on the surface after the onset of OER are redeposited corrosion products, as discussed above, and are not part of the solid oxide film. The observed layer of corrosion products at the end of the experiment is simply the continuation of the redeposition of species dissolved during OER

conditions. The presence of MoO_3 , $\text{Cr}(\text{OH})_3$, $\text{Ni}(\text{OH})_2$, and water suggests an amorphous hydrous hydrogen-bonded network in the precipitated corrosion product film. A picture of the sample can be found in the Figure S26 (Supporting Information). Precipitation of Mo^{6+} rich compounds on the surface during corrosion has been discussed as a potential passivation property of Mo ,^[20,30,79] which explains why even small additions of Mo can substantially increase the corrosion resistance of stainless steel and Ni-based alloys.^[26,80] The dissolved molybdate ions can also counterbalance the positive charge of the protons generated during local corrosion, which otherwise would attract Cl ions and further make the local solution more aggressive. This could explain why we observe no local corrosion of the Ni–Cr–Mo alloy even at such high potentials.

However, at these high potentials, Mo also plays another role in this material system as it is active toward OER. The observed OER-coupled passivity breakdown of the Ni–Cr–Mo alloy in this study is very different from the passivity breakdown of duplex stainless steel^[67] or even other Ni-based alloys with a low Mo content, as discussed in the supplementary information in Figure S2 (Supporting Information). For those alloys with low Mo content, passivity breakdown, i.e., enhanced metal dissolution, is observed at higher anodic potentials, and the observed current increase is mainly due to metal dissolution and not OER. However, for Ni alloys with high Mo content, the OER plays an important role in the metal dissolution and thus passivity breakdown. The effect of OER, therefore, cannot be ignored in the study of passivity breakdown if the material is catalytically active toward OER since it is not only a by-standing side reaction but closely coupled to the dissolution of the material. Industrial electrochemical tests using current density as a criteria for judging corrosion rate are not applicable for this class of Ni–Cr–Mo alloys, showing an apparent catalytic activity toward OER. A more direct measure of the true material degradation is needed to judge the behavior of these alloys properly, and the OER reaction and the subsequent degradation should be considered in the interpretation of electrochemical measurement results.

The solid–liquid interface is not easy to access, and few surface science techniques are suitable for this purpose. Here we combine several state-of-the-art in situ techniques that give unique and comprehensive insights into the chemistry and structure of the surface region immersed in an electrolyte and the chemistry of dissolved species during the passive film growth, corrosion initiation, and progression. This powerful combination of techniques provides a detailed understanding of the passivity breakdown of the Ni-alloys and opens the possibility of shining new light on complex processes in the field of corrosion as well as other fields of electrochemistry, such as batteries, fuel cells, and electrocatalysis.

4. Conclusion

The solid–liquid interface is notoriously difficult to study in situ. Combining synchrotron-based techniques and electrochemical methods, we demonstrate that the Ni–Cr–Mo alloy is active toward OER, where a current increase and associated bubble formation were observed at relatively low overpotentials compared to other highly corrosion resistant alloys. The studied Ni–Cr–Mo alloy exhibits a stable passive film in the NaCl solution until the

onset of OER. At the onset of OER, the passive film starts to degrade, which is associated with the OER-induced mechanism where catalytically active Mo^{4+} oxide sites in the oxide film are further oxidized into Mo^{6+} complexes that are dissolved and partly redeposited on the surface during the catalytic OER cycle. This results in the breakdown of passivity and the dissolution of Ni and Cr ions without a change in their oxidation state compared to that in the oxide film. This observed mechanism is different from the traditional transpassive corrosion mechanism of Cr-containing alloys where Cr^{3+} is oxidized to soluble Cr^{6+} at sufficiently anodic potentials. Our comprehensive experimental results provide a detailed understanding of the passivity breakdown of Ni–Cr–Mo alloys, which is associated with the onset of OER. The OER results in the acidification of the solution near the surface, which further facilitates the dissolution of the protective oxide. The concentration of protons near the surface also has to be counterbalanced by Cl ions or dissolved molybdate ions. This interplay between OER and material degradation makes simple electrochemical assessment and accelerated industrial tests of Ni alloys problematic, and the role of OER must be taken into account when considering the degradation of catalytically active alloys.

5. Experimental Section

The material used in the present study was an industrial-grade Ni–Cr–Mo alloy (Ni alloy 59, UNS no: N06059) containing 62.3 at% Ni, 26.3 at% Cr, and 9.7 at% Mo (minor alloying elements are shown in the Table S1, Supporting Information) provided by Alleima (former Sandvik Materials Technology). The typical microstructure of the material is shown in the Figure S1 (Supporting Information). After polishing, the samples were stored in air for several weeks, allowing the native oxide layer to form. Before the experiments, the samples were cleaned by sonication in acetone for 5 min, later ethanol for 5 min, and then rinsed in ethanol and dried using N_2 gas before being mounted in the electrochemical cell.

In situ, GI-XRD, XRF, and XRR measurements were performed at the Swedish Materials Science beamline P21.2 at DESY, Hamburg, Germany. An X-ray energy of 38 keV and a beam size of 50×500 ($V \times H$) μm^2 were used. The sample was mounted in a dedicated in situ electrochemical flow cell (described below) on the surface diffractometer (see photos in Figure S7, Supporting Information). The sample surface was aligned parallel to the X-ray beam, with the surface normal in the vertical direction. GI-XRD was measured with an incidence angle of 0.3° and recorded with a VAREX flat panel detector. The detector distance and position were calibrated using a CeO_2 sample. The GI-XRD data were integrated using pyFAI,^[81] and Le Bail refinements were performed using the GSAS-II software^[82] to extract the lattice parameter of the surface region at each polarization step. XRR was measured using a Cyberstar X2000 scintillator on a motorized stage which was scanned at angles of 0.02 to 3° . The measured XRR data was modeled using GenX.^[83] XRF was measured using an Amptek FAST SDD ultra high-performance silicon drift detector. The XRF detector was mounted perpendicular to the incoming X-ray beam and positioned 10 cm away from the beam. An acquisition time of 60 s was used to detect the fluorescence from the dissolved metal ions in the electrolyte. The energy scale was calibrated using fluorescence of Cu, Rb, Mo, and Ag excited by a radioactive Am source. The XRF intensities were calibrated using a series of reference solutions of known concentrations (0.1 M, 0.01 M, and 0.001 M) of Ni, Cr, and Mo salts. Surface optical reflectance was used to monitor the formation of bubbles in the cell to confirm the presence of OER.^[84–87] The synchrotron measurements were performed in a sequential manner at stepwise increased potential while the current was recorded and electrochemical impedance spectroscopy was measured. The electrolyte was not flow-

ing during the in situ measurements while the potential was applied. Instead, the cell was used in batch mode. Between each potential step, the cell was flushed with fresh electrolyte solution. The treatment of the GI-XRD, XRR, and XRF data and the whole measurement procedure are further described in the Supporting Information.

The in situ XANES measurements of the chemical state of the dissolved metal ions and the ex situ XANES measurements of the chemical state of the corrosion products left on the surface were performed at the advanced XAFS beamline P64 at DESY, Hamburg, Germany.^[88] The in situ determination of the chemical state of the dissolved metal ions in the solution was performed using the electrochemical cell described below. The Ni, Cr, and Mo K edges were measured in fluorescence mode using a passivated implanted planar silicon (PIPS) detector after polarization at 1200 mV versus AgCl for 30 min. The ex situ determination of the chemical states of the corrosion products was performed in a grazing incidence geometry using the PIPS detector in fluorescence mode while varying the incidence angle between 0.2 and 5° while recording the Ni, Cr, and Mo K edges separately. Self-absorption corrections were necessary to perform on the GI-XANES as well as for the in situ Ni K edge data measured in the electrolyte, as described in more detail in the Supporting Information. The solid references of compounds were made as pellets of powders with cellulose as a binder and the metallic components were measured from a Ni alloy foil of similar composition ($\text{Ni}_{62}\text{Cr}_{22}\text{Mo}_9\text{Fe}_5$ and $\text{Ni}_{62}\text{Mo}_{28}\text{Fe}_5\text{Cr}_5$). The solution references were made as 2 wt% dissolved in 1 M NaCl to mimic the solution used for the in situ measurements. All references were measured in transmission mode using ion chambers, while the XANES from the dissolved species in the electrolyte and the scales were measured in fluorescence mode. For the Cr and Ni K edge, 100% N_2 gas was used in the ion chambers. For the Mo K edge, 10% Kr and 90% N_2 were used in the ion chambers. All XANES spectra were background subtracted and normalized using the ATHENA XAS data processing software.^[89] The data treatment and further experimental details are provided in the Supporting Information.

For the in situ measurements at both P21.2 and P64, a custom-made electrochemical flow cell dedicated to in situ synchrotron studies was used (shown in the Figure S8, Supporting Information).^[67,84,85,90] A Pt rod was used as the counter electrode, a mini leakless Ag/AgCl reference electrode from eDAQ (calibrated against a large Ag/AgCl reference electrode from GAMRY) was used, and the sample acted as the working electrode. The cell, tubing, and counter electrode were cleaned by flowing 25% nitric acid for 30 min and flushed with Milli-Q water. The samples for the P21.2 and P64 experiments were polished by SPL (Surface Preparation Laboratory in the Netherlands) to a mirror finish. For the in situ experiments, a 1 L solution of 1 M NaCl prepared using Milli-Q water was used, and for the pH 2 solution HCl was used to adjust the pH. The electrolyte solution was degassed using N_2 before and during the experiments. An Autolab PG-STAT204 potentiostat was used for the electrochemical experiments.

The in situ AP-XPS measurements were performed at the HIPPIE beamline at MAX IV, Lund, Sweden, using their electrochemical end-station.^[91] The experimental details are described in refs. [92,93]. The sample, reference electrode (Ag/AgCl eDAQ leakless mini electrode), and counter electrode (Pt foil) were mounted in a special holder allowing electrical connection and the possibility to ground the sample, which acts as the working electrode (Figure S3, Supporting Information). The sample and electrodes, mounted on a manipulator, could then be submerged and retracted into a glass beaker placed on a water-cooled copper plate at the bottom of the vacuum chamber. The experiment was performed with a background pressure of 17 mbar in the entire chamber, equal to the electrolyte's vapor pressure. To avoid rapid evaporation of the electrolyte due to continuous pumping of the chamber during the experiment, the copper plate supporting the electrolyte beaker was cooled to 10°C . AP-XPS was measured in normal emission, and an excitation energy of 1600 eV was used to measure the Ni 2p, Cr 2p, and O 1s core levels, and an excitation energy of 1400 eV was used to measure the Mo 3d core level. A slit of $30 \mu\text{m}$ and a pass energy of 200 eV were used for all core levels measured at ambient pressure. Measuring all core levels took ≈ 25 min. The beam size was $25 \times 60 \mu\text{m}^2$ ($V \times H$). The sample was translated between the measurements at each potential step to avoid beam-induced damage or

effects on the sample surface. Peak fitting and quantitative analysis were performed using Python and the LMFIT package.^[94] An asymmetric Voigt line shape^[95] was used to fit the metal components of the Ni 2p, Cr 2p, and Mo 3d core levels, which all display asymmetry toward higher binding energy. All other peaks were fitted using Voigt line profiles. All spectra were background-subtracted using a Shirley background.^[96] The AP-XPS spectra of Ni 2p were background subtracted with a linear model plus a Shirley background to compensate for the nonflat background before and after the peak (The survey shown in the Figure S6 (Supporting Information) illustrates the large nonflat background caused by inelastic scattering in the water vapor environment between the sample and the analyzer). The chemical shifts of the metal oxide components were calibrated relative to the well-known binding energy of the metal components. The fitted AP-XPS spectra, peak fitting parameters, and details of the quantitative analysis are given in the Supporting Information.

In-house electrochemical measurements were performed with a GAMRY eurocell cleaned with 20% nitric acid, an Ag/AgCl reference electrode from GAMRY mounted in a lugging capillary, and a coiled Pt wire as a counter electrode. The samples were polished to 600 grit before each measurement and allowed to reach a stable OCP value for 30 min. The electrolyte volume was 200 mL of 1 M NaCl, which was prepared using Milli-Q water, and for the pH 2 solution HCl was used to adjust the pH. The electrolyte solution was degassed using N₂ before and during the experiments. An Autolab PGSTAT204 potentiostat was used for the electrochemical experiments. Polarization curves were measured from −400 to 1100 mV with a scan rate of 0.5 mV s^{−1} and 100 mV s^{−1}. Mott–Schottky analysis was performed after polarization at 900 mV (formation potential) for 30 min. The potential was then reduced in steps of 50 mV from 900 to −300 mV, the impedance was measured using 10 and 100 Hz, and the capacitance was calculated using an R_s value of 10 Ω. A 10 mV amplitude was used for the EIS and Mott–Schottky measurements. The linear part of the negative slope of the Mott–Schottky plot was fitted. From the slope, the cation vacancy density was calculated using the equation^[97] shown below.

$$\frac{dC^{-2}}{dE} = - \left(\frac{2}{q\epsilon\epsilon_0 N_A} \right) \quad (3)$$

where C is the capacitance, q is the charge of the electron, ε₀ is the vacuum permittivity, ε is the dielectric constant of the oxide, and E is the applied potential. A value of 15.8 was used for the dielectric constant of the oxide layer, taken from refs. [98,99].

Simulations of the local pH near the electrode surface during OER were performed using COMSOL Multiphysics with the transport of dilute species module.^[100] A time-dependent solution (with a time frame of 30 min) was used. A rectangular model with sides of 30 mm was used to mimic the volume of the in situ electrochemical cell. No flow was used to reproduce the static conditions used in the study, as described in the Supporting Information. The initial concentration of the dilute species (H⁺) was defined by the bulk pH of either 2 or 7. The flux of species from the bottom surface of the cell volume representing the sample surface was defined based on the electrochemical current at each potential step. Further details are given in the Supporting Information.

Ex situ electron microscopy and EDS were performed at the DESY Nano lab^[101] using a high-resolution field emission SEM (Nova Nano SEM 450, FEI Thermofisher) equipped with an X-Max 150 EDS silicon drift detector (Oxford) for elemental analysis. For imaging, an acceleration voltage of 5 keV was used. An acceleration voltage of 10 keV was used for the EDS analysis.

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

Acknowledgements

Financial support was acknowledged from the Swedish Research Council (2018-03434 and 2020-06154) and the Swedish Foundation for Strategic Research under contract ID19-0032. The authors acknowledge DESY (Hamburg, Germany), a member of the Helmholtz Association HGF, for the provision of experimental facilities. Parts of this research were carried out at PETRA III, and at the DESY Nanolab, and the authors would like to thank Malte Blankenburg and Sven Gutschmidt for assistance in using the Swedish Material Science beamline P21.2. The authors would also like to thank Akhil Tayal, Wolfgang Calibe, and Claudia Schwan for assistance in using the Advanced XAFS beamline P64 and Milena Lippmann for assistance with the chemistry laboratories at DESY. Beamtime at DESY was allocated for the proposal II-20190755 EC and I-20211350 EC. The authors acknowledge MAX IV Laboratory for time on the Beamline HIPPIE under Proposal 20210831. Research conducted at MAX IV, a Swedish national user facility, is supported by the Swedish Research Council under contract 2018-07152, the Swedish Governmental Agency for Innovation Systems under contract 2018-04969, and Formas under contract 2019-02496. Konstantin Simonov is grateful for the financial support to Swedish Research Council under project 2018-06378.

Conflict of Interest

The authors declare no conflict of interest.

Data Availability Statement

The data that support the findings of this study are available from the corresponding author upon reasonable request.

Keywords

corrosion mechanisms, nickel alloys, Ni–Cr–Mo, oxygen evolution reaction, passivity breakdown, transpassive dissolution

Received: May 16, 2023
Revised: June 29, 2023
Published online: August 3, 2023

- [1] P. Marcus, *Corrosion mechanisms in theory and practice*, CRC Press, Boca Raton, FL, USA 2011.
- [2] G. Koch, in *Trends in Oil and Gas Corrosion Research and Technologies*, (Ed: A.M. El-Sherik), Woodhead Publishing, Boston, MA, USA, 2017, pp. 3–30.
- [3] B. Hou, X. Li, X. Ma, C. Du, D. Zhang, M. Zheng, W. Xu, D. Lu, F. Ma, *npj Mater. Degrad.* **2017**, 1, 4.
- [4] R. Bender, D. Féron, D. Mills, S. Ritter, R. Bäßler, D. Bettge, I. De Graeve, A. Dugstad, S. Grassini, T. Hack, M. Halama, E.-H. Han, T. Harder, G. Hinds, J. Kittel, R. Krieg, C. Leygraf, L. Martinelli, A. Mol, D. Neff, J.-O. Nilsson, I. Odneval, S. Paterson, S. Paul, T. Prošek, M. Raupach, R. I. Revilla, F. Ropital, H. Schweigart, E. Szala, et al., *Mater. Corros.* **2022**, 73, 1730.
- [5] X. Zhong, M. Hu, S. Deetman, B. Steubing, H. X. Lin, G. A. Hernandez, C. Harpprecht, C. Zhang, A. Tukker, P. Behrens, *Nat. Commun.* **2021**, 12, 6126.
- [6] D. D. Macdonald, *Pure Appl. Chem.* **1999**, 71, 951.
- [7] D. D. Macdonald, *J. Electrochem. Soc.* **1992**, 139, 3434.
- [8] L. F. Lin, C. Y. Chao, D. D. Macdonald, *J. Electrochem. Soc.* **1981**, 128, 1194.

- [9] P. Schmuki, *J. Solid State Electrochem.* **2002**, 6, 145.
- [10] C.-O. A. Olsson, D. Landolt, *Electrochim. Acta* **2003**, 48, 1093.
- [11] T. Massoud, V. Maurice, L. H. Klein, P. Marcus, *J. Electrochem. Soc.* **2013**, 160, C232.
- [12] B. Zhang, J. Wang, B. Wu, X. W. Guo, Y. J. Wang, D. Chen, Y. C. Zhang, K. Du, E. E. Oguzie, X. L. Ma, *Nat. Commun.* **2018**, 9, 2559.
- [13] P. Marcus, *Electrochim. Acta* **1998**, 43, 109.
- [14] P. Marcus, V. Maurice, H.-H. Strehblow, *Corros. Sci.* **2008**, 50, 2698.
- [15] V. Maurice, P. Marcus, *Electrochim. Acta* **2012**, 84, 129.
- [16] P. Marcus, V. Maurice, *Philos. Trans. R. Soc., A* **2017**, 375, 20160414.
- [17] V. Maurice, P. Marcus, *Prog. Mater. Sci.* **2018**, 95, 132.
- [18] W. Z. Friend, M. Cohen, *J. Electrochem. Soc.* **1980**, 127, 421C.
- [19] J. R. Hayes, J. J. Gray, A. W. Szmodis, C. A. Orme, *Corrosion* **2006**, 62, 491.
- [20] A. C. Lloyd, J. J. Noël, S. McIntyre, D. W. Shoesmith, *Electrochim. Acta* **2004**, 49, 3015.
- [21] W. H. Blades, M. R. Barone, P. Reinke, *npj Mater. Degrad.* **2021**, 5, 17.
- [22] J. R. Hayes, J. J. Gray, A. W. Szmodis, C. A. Orme, *Corrosion* **2006**, 62, 491.
- [23] Z. Wang, C. Carrière, A. Seyeux, S. Zanna, D. Mercier, P. Marcus, *J. Electrochem. Soc.* **2021**, 168, 041503.
- [24] P. Marcus, *Corros. Sci.* **1994**, 36, 2155.
- [25] N. S. Zadorozne, C. M. Giordano, M. A. Rodríguez, R. M. Carranza, R. B. Rebak, *Electrochim. Acta* **2012**, 76, 94.
- [26] K. Lutton Cwalina, C. R. Demarest, A. Y. Gerard, J. R. Scully, *Curr. Opin. Solid State Mater. Sci.* **2019**, 23, 129.
- [27] X. Li, J. D. Henderson, F. P. Filice, D. Zagidulin, M. C. Biesinger, F. Sun, B. Qian, D. W. Shoesmith, J. J. Noël, K. Ogle, *Corros. Sci.* **2020**, 176, 109015.
- [28] C. Volders, V. A. Angelici, I. Waluyo, A. Hunt, L. Árnadóttir, P. Reinke, *npj Mater. Degrad.* **2022**, 6, 52.
- [29] J. D. Henderson, X. Li, F. P. Filice, D. Zagidulin, M. C. Biesinger, B. Kobe, D. W. Shoesmith, K. Ogle, J. J. Noël, *J. Electrochem. Soc.* **2021**, 168, 021509.
- [30] K. Gusieva, K. L. Cwalina, W. H. Blades, G. Ramalingam, J. H. Perepezko, P. Reinke, J. R. Scully, *J. Phys. Chem. C* **2018**, 122, 19499.
- [31] N. Ebrahimi, M. C. Biesinger, D. W. Shoesmith, J. J. Noël, *Surf. Interface Anal.* **2017**, 49, 1359.
- [32] E. Bettini, C. Leygraf, J. Pan, *Int. J. Electrochem. Sci.* **2013**, 8, 11791.
- [33] C.-W. Chen, C.-Y. Chiang, *Int. J. Hydrogen Energy* **2017**, 42, 29773.
- [34] P. F. Liu, S. Yang, L. R. Zheng, B. Zhang, H. G. Yang, *Chem. Sci.* **2017**, 8, 3484.
- [35] H. Liao, X. Zhang, S. Niu, P. Tan, K. Chen, Y. Liu, G. Wang, M. Liu, J. Pan, *Appl. Catal., B* **2022**, 307, 121150.
- [36] I. C. Man, H.-Y. Su, F. Calle-Vallejo, H. A. Hansen, J. I. Martínez, N. G. Inoglu, J. Kitchin, T. F. Jaramillo, J. K. Nørskov, J. Rossmeisl, *ChemCatChem* **2011**, 3, 1159.
- [37] S. Geiger, O. Kasian, M. Ledendecker, E. Pizzutillo, A. M. Mingers, W. T. Fu, O. Diaz-Morales, Z. Li, T. Oellers, L. Fruchter, A. Ludwig, K. J. J. Mayrhofer, M. T. M. Koper, S. Cherevko, *Nat. Catal.* **2018**, 1, 508.
- [38] K. Schweinar, B. Gault, I. Mouton, O. Kasian, *J. Phys. Chem. Lett.* **2020**, 11, 5008.
- [39] A. H. Tajuddin, M. Wakisaka, T. Ohto, Y. Yu, H. Fukushima, H. Tanimoto, X. Li, Y. Misu, S. Jeong, J.-I. Fujita, H. Tada, T. Fujita, M. Takeguchi, K. Takano, K. Matsuoka, Y. Sato, Y. Ito, *Adv. Mater.* **2023**, 35, 2207466.
- [40] T. Binninger, R. Mohamed, K. Waltar, E. Fabbri, P. Levecque, R. Kötz, T. J. Schmidt, *Sci. Rep.* **2015**, 5, 12167.
- [41] A. Lončar, D. Escalera-López, S. Cherevko, N. Hodnik, *Angew. Chem., Int. Ed.* **2022**, 61, 202114437.
- [42] O. Kasian, S. Geiger, T. Li, J. P. Grote, K. Schweinar, S. Zhang, C. Scheu, D. Raabe, S. Cherevko, B. Gault, K. J. J. Mayrhofer, *Energy Environ. Sci.* **2019**, 12, 3548.
- [43] S. Cherevko, A. R. Zeradjanin, A. A. Topalov, N. Kulyk, I. Katsounaros, K. J. J. Mayrhofer, *ChemCatChem* **2014**, 6, 2219.
- [44] O. Diaz-Morales, F. Calle-Vallejo, C. De Munck, M. T. M. Koper, *Chem. Sci.* **2013**, 4, 2334.
- [45] F.-u.-M. Li, L. Huang, S. Zaman, W. Guo, H. Liu, X. Guo, B. Yu Xia, *Adv. Mater.* **2022**, 34, 2200840.
- [46] Z. Wang, C. Carrière, A. Seyeux, S. Zanna, D. Mercier, P. Marcus, *Appl. Surf. Sci.* **2022**, 576, 151836.
- [47] A. Larsson, G. D'acunto, M. Vorobyova, G. Abbondanza, U. Lienert, Z. Hegedüs, A. Preobrajenski, L. R. Merte, J. Eidhagen, A. Delblanc, J. Pan, E. Lundgren, *J. Alloys Compd.* **2022**, 895, 162657.
- [48] J. Eidhagen, A. Larsson, A. Preobrajenski, A. Delblanc, E. Lundgren, J. Pan, *J. Electrochem. Soc.* **2023**, 170, 021506.
- [49] A. Machet, A. Galtayries, S. Zanna, L. Klein, V. Maurice, P. Jolivet, M. Foucault, P. Combrade, P. Scott, P. Marcus, *Electrochim. Acta* **2004**, 49, 3957.
- [50] A. Mazenc, A. Galtayries, A. Seyeux, P. Marcus, S. Leclercq, *Surf. Interface Anal.* **2013**, 45, 583.
- [51] A. Seyeux, Z. Wang, S. Zanna, C. Carrière, D. Mercier, P. Marcus, *Electrochim. Acta* **2022**, 426, 140797.
- [52] X.-X. Yu, A. Gulec, Q. Sherman, K. L. Cwalina, J. R. Scully, J. H. Perepezko, P. W. Voorhees, L. D. Marks, *Phys. Rev. Lett.* **2018**, 121, 145701.
- [53] Q. Zhang, Y. Hu, H. Wu, X. Zhao, M. Wang, S. Wang, R. Feng, Q. Chen, F. Song, M. Chen, P. Liu, *ACS Nano* **2023**, 17, 1485.
- [54] K. L. Cwalina, H. M. Ha, N. Ott, P. Reinke, N. Biribilis, J. R. Scully, *J. Electrochem. Soc.* **2019**, 166, C3241.
- [55] K. Lutton, J. Han, H. M. Ha, D. Sur, E. Romanovskaia, J. R. Scully, *J. Electrochem. Soc.* **2023**, 170, 021507.
- [56] J. D. Henderson, X. Li, D. W. Shoesmith, J. J. Noël, K. Ogle, *Corros. Sci.* **2019**, 147, 32.
- [57] X. Li, K. Ogle, *J. Electrochem. Soc.* **2019**, 166, C3179.
- [58] J. G. Vos, Z. Liu, F. D. Speck, N. Perini, W. Fu, S. Cherevko, M. T. M. Koper, *ACS Catal.* **2019**, 9, 8561.
- [59] D.-e.-S. Kong, S.-H. Chen, C. Wang, W. Yang, *Corros. Sci.* **2003**, 45, 747.
- [60] B. Ter-Ovanesian, B. Normand, *J. Solid State Electrochem.* **2016**, 20, 9.
- [61] G. Song, *Corros. Sci.* **2005**, 47, 1953.
- [62] P. J. Merklings, A. Muñoz-Páez, E. Sánchez Marcos, *J. Am. Chem. Soc.* **2002**, 124, 10911.
- [63] K. Yokoi, N. Matsubayashi, T. Miyahara, I. Watanabe, S. Ikeda, *Polyhedron* **1993**, 12, 911.
- [64] A. Fattah-Alhosseini, A. Saatchi, M. A. Golozar, K. Raeissi, *Electrochim. Acta* **2009**, 54, 3645.
- [65] I. Betova, M. Bojinov, T. Laitinen, K. Mäkelä, P. Pohjanne, T. Saario, *Corros. Sci.* **2002**, 44, 2675.
- [66] I. Olefjord, B. Brox, U. Jelvestam, *J. Electrochem. Soc.* **1985**, 132, 2854.
- [67] M. Långberg, C. Örnek, J. Evertsson, G. S. Harlow, W. Linpé, L. Rullik, F. Carlà, R. Felici, E. Bettini, U. Kivisäkk, E. Lundgren, J. Pan, *npj Mater. Degrad.* **2019**, 3, 22.
- [68] L. Vegard, *Z. Phys.* **1921**, 5, 17.
- [69] D. D. Macdonald, *Electrochim. Acta* **2011**, 56, 1761.
- [70] S. Cherevko, S. Geiger, O. Kasian, N. Kulyk, J.-P. Grote, A. Savan, B. R. Shrestha, S. Merzlikin, B. Breitbach, A. Ludwig, K. J. J. Mayrhofer, *Catal. Today* **2016**, 262, 170.
- [71] N. Danilovic, R. Subbaraman, K.-C. Chang, S. H. Chang, Y. J. Kang, J. Snyder, A. P. Paulikas, D. Strmcnik, Y.-T. Kim, D. Myers, V. R. Stamenkovic, N. M. Markovic, *J. Phys. Chem. Lett.* **2014**, 5, 2474.

- [72] R. Kötz, S. Stucki, D. Scherson, D. M. Kolb, J. *Electroanal. Chem. Interfacial Electrochem.* **1984**, 172, 211.
- [73] R. Kötz, H. Neff, S. Stucki, J. *Electrochem. Soc.* **1984**, 131, 72.
- [74] O. Kasian, J.-P. Grote, S. Geiger, S. Cherevko, K. J. J. Mayrhofer, *Angew. Chem., Int. Ed.* **2018**, 57, 2488.
- [75] A. S. Raman, A. Vojvodic, J. *Phys. Chem. C* **2022**, 126, 922.
- [76] F. Hess, H. Over, *ACS Catal.* **2023**, 13, 3433.
- [77] F. Hess, S. Rohrlack, M. Knapp, H. Over, J. *Phys. Chem. C* **2022**, 126, 946.
- [78] S. Fierro, T. Nagel, H. Baltruschat, C. Comninellis, *Electrochem. Commun.* **2007**, 9, 1969.
- [79] M. Sakashita, N. Sato, *Corros. Sci.* **1977**, 17, 473.
- [80] G. O. Ilevbare, G. T. Burstein, *Corros. Sci.* **2001**, 43, 485.
- [81] J. Kieffer, V. Valls, N. Blanc, C. Hennig, J. *Synchrotron Radiat.* **2020**, 27, 558.
- [82] B. H. Toby, R. B. Von Dreele, J. *Appl. Crystallogr.* **2013**, 46, 544.
- [83] M. Björck, G. Andersson, J. *Appl. Crystallogr.* **2007**, 40, 1174.
- [84] W. Linpé, G. S. Harlow, A. Larsson, G. Abbondanza, L. Rämisch, S. Pfaff, J. Zetterberg, J. Evertsson, E. Lundgren, *Rev. Sci. Instrum.* **2020**, 91, 044101.
- [85] S. Pfaff, A. Larsson, D. Orlov, G. S. Harlow, G. Abbondanza, W. Linpé, L. Rämisch, S. M. Gericke, J. Zetterberg, E. Lundgren, *ACS Appl. Mater. Interfaces* **2021**, 13, 19530.
- [86] S. Pfaff, L. Rämisch, S. M. Gericke, A. Larsson, E. Lundgren, J. Zetterberg, *ACS Catal.* **2022**, 12, 6589.
- [87] W. Linpé, L. Rämisch, G. Abbondanza, A. Larsson, S. Pfaff, L. Jacobse, J. Zetterberg, L. Merte, A. Stierle, Z. Hegedues, U. Lienert, E. Lundgren, G. S. Harlow, J. *Electrochem. Soc.* **2021**, 168, 096511.
- [88] W. A. Caliebe, V. Murzin, A. Kalinko, M. Görlitz, *AIP Conf. Proc.* **2019**, 2054, 060031.
- [89] B. Ravel, M. Newville, J. *Synchrotron Radiat.* **2005**, 12, 537.
- [90] T. Weber, V. Vonk, D. Escalera-López, G. Abbondanza, A. Larsson, V. Koller, M. J. S. Abb, Z. Hegedüs, T. Bäcker, U. Lienert, G. S. Harlow, A. Stierle, S. Cherevko, E. Lundgren, H. Over, *ACS Catal.* **2021**, 11, 12651.
- [91] S. Zhu, M. Scardamaglia, J. Kundsén, R. Sankari, H. Tarawneh, R. Temperton, L. Pickworth, F. Cavalca, C. Wang, H. Tissot, J. Weissenrieder, B. Hagman, J. Gustafson, S. Kaya, F. Lindgren, I. Källquist, J. Maibach, M. Hahlin, V. Boix, T. Gallo, F. Rehman, G. D'acunto, J. Schnadt, A. Shavorskiy, J. *Synchrotron Radiat.* **2021**, 28, 624.
- [92] A. Larsson, K. Simonov, J. Eidhagen, A. Grespi, X. Yue, H. Tang, A. Delblanc, M. Scardamaglia, A. Shavorskiy, J. Pan, E. Lundgren, *Appl. Surf. Sci.* **2023**, 611, 155714.
- [93] X. Yue, A. Larsson, H. Tang, A. Grespi, M. Scardamaglia, A. Shavorskiy, A. Krishnan, E. Lundgren, J. Pan, *Corros. Sci.* **2023**, 214, 111018.
- [94] M. Newville, T. Stensitzki, D. B. Allen, M. Rawlik, A. Ingargiola, A. Nelson, LMFIT: Non-Linear Least-Square Minimization and Curve-Fitting for Python, **2014**.
- [95] M. Schmid, H.-P. Steinrück, J. M. Gottfried, *Surf. Interface Anal.* **2014**, 46, 505.
- [96] D. A. Shirley, *Phys. Rev. B* **1972**, 5, 4709.
- [97] S. R. Morrison, S. Morrison, *Electrochemistry at Semiconductor and Oxidized Metal Electrodes*, Vol. 126, Springer, New York **1980**.
- [98] M. Da Cunha Belo, N. E. Hakiki, M. G. S. Ferreira, *Electrochim. Acta* **1999**, 44, 2473.
- [99] N. B. Hakiki, S. Boudin, B. Rondot, M. Da Cunha Belo, *Corros. Sci.* **1995**, 37, 1809.
- [100] M. C. O. Monteiro, A. Mirabal, L. Jacobse, K. Doblhoff-Dier, S. C. Barton, M. T. M. Koper, *JACS Au* **2021**, 1, 1915.
- [101] A. Stierle, T. F. Keller, H. Noei, V. Vonk, R. Roehlsberger, J. *Large-Scale Res. Facil.* **2016**, 2, A76.