Universität Bremen

CHEMISCHE VERFAHRENS-TECHNIK

Modeling Electrochemical Oxide Film Growth

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Abstract

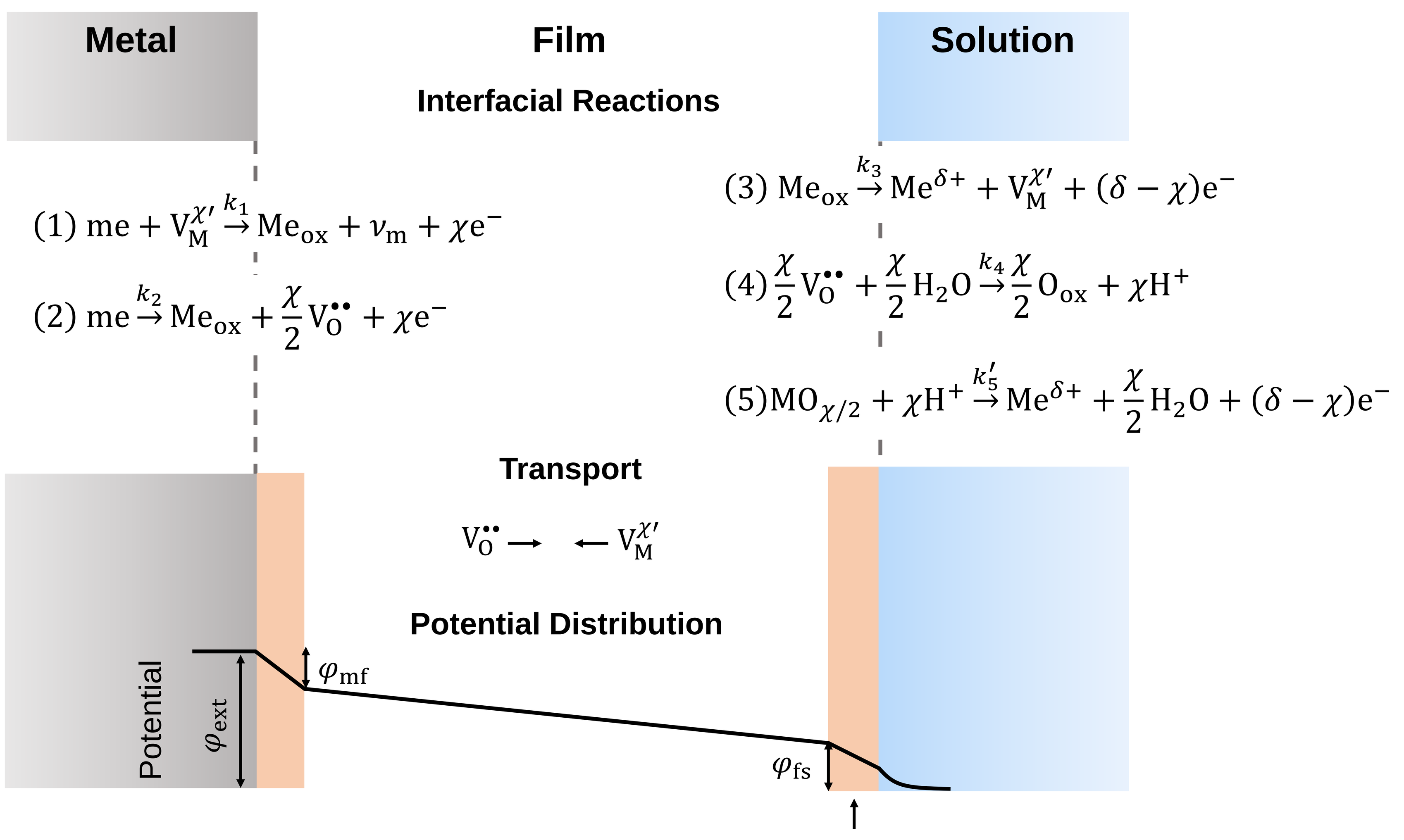
Metal oxides play an important role in our civilization. From titanium oxide as whitening nanoparticles, over iridium oxide electrodes for water electrolysis, MOSFETs in electrical components to passive films that protect against corrosion, metal oxides surround us in our daily live. Despite their importance and omnipresent there are still unresolved open questions regarding their properties and behavior.

In corrosion science, the growth of protective oxide films on metals and alloys (passive films), their properties and breakdown are of great interest. We present a comprehensive model, based on the PDM, the Refined-PDM (R-PDM) to simulate oxide film growth from the initial steps, over stable oxide film growth to transpassive dissolution.

Model Description

An external potential is applied to the metal. Interfacial reactions, driven by interfacial potentials $\varphi_{mf}, \varphi_{fs}$ lead to film growth and injection of crystal defects to the film.

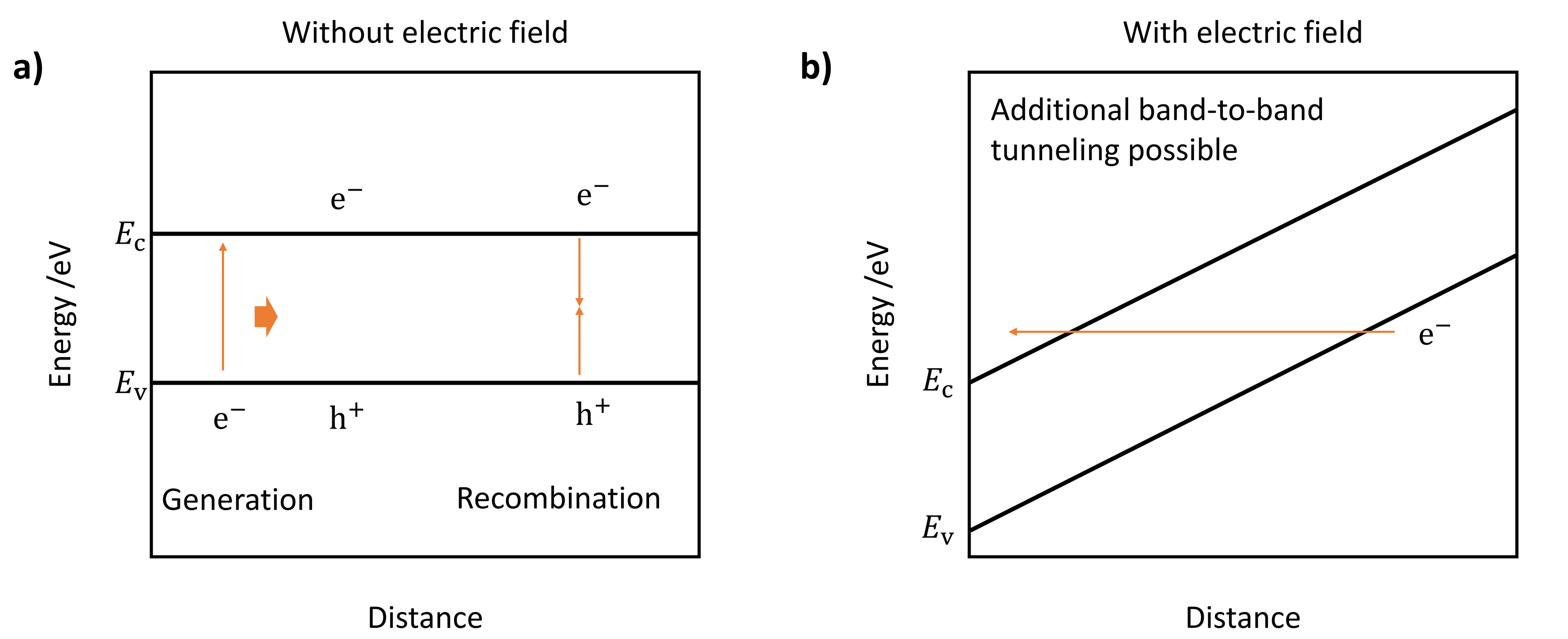
Transport of crystal defects ($V_O^{\bullet\bullet}$, $V_M^{\chi'}$) is given by migration and diffusion (Nernst-Planck).



Kröger-Vink Notation

$V_O^{\bullet\bullet}$: Oxygen vacancy
$V_M^{\chi'}$: Metal vacancy χ times negatively charged
Me_{ox}: Metal in the oxide
me: Metal atom in the metal
O_{ox}: Oxygen in the oxide
$M^{\delta+}$: Metal ion in soultion

Impact of Electrons and Holes

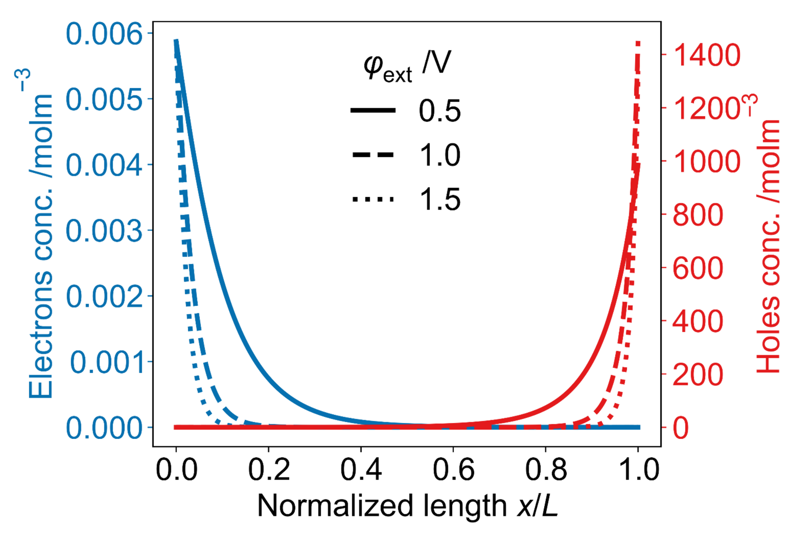


Electrons in the conduction band and holes in the valence band can be generated by **a)** thermal generation, **b)** band-to-band tunneling in the presence of strong electric fields

An accumulation of holes at the film/solution interface can accelerate oxidation reactions. In the transpassive region oxygen evolution and transpassive breakdown (in absence of haldie ions) of the film due to:

$$MeO_{\frac{\chi}{2}} + \chi H^+ + (\delta - \chi)h^+ \rightarrow Me^{\delta+} + \frac{\chi}{2} H_2O$$

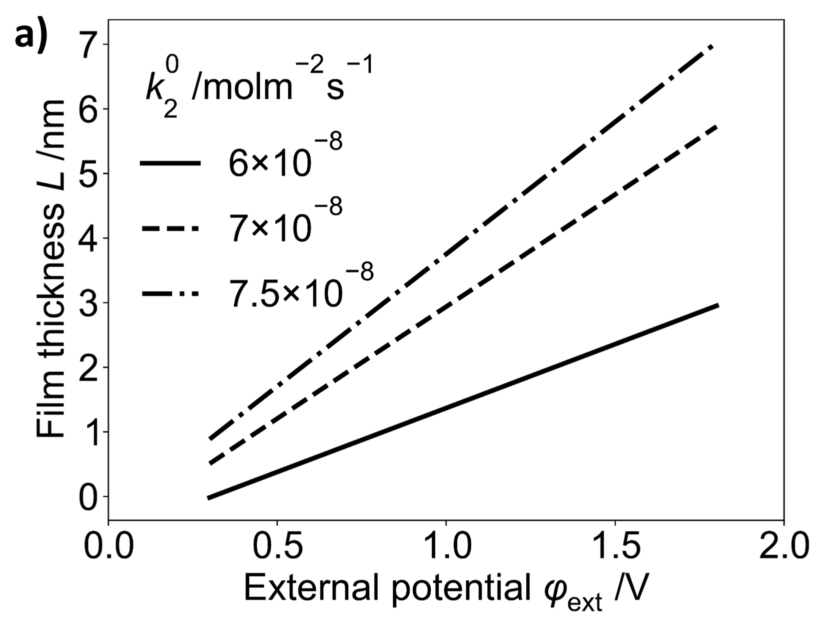
is the consequence.



Electrons and holes concentration at the interfaces without electrochemical reaction

Insight into the Oxide

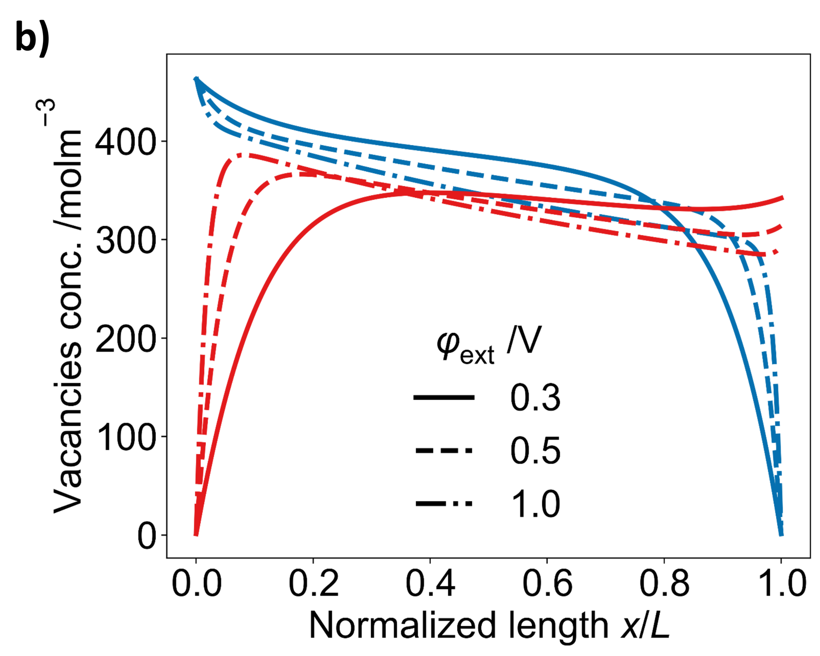
Modeling of steady state oxide film under potential control on an artificial metal

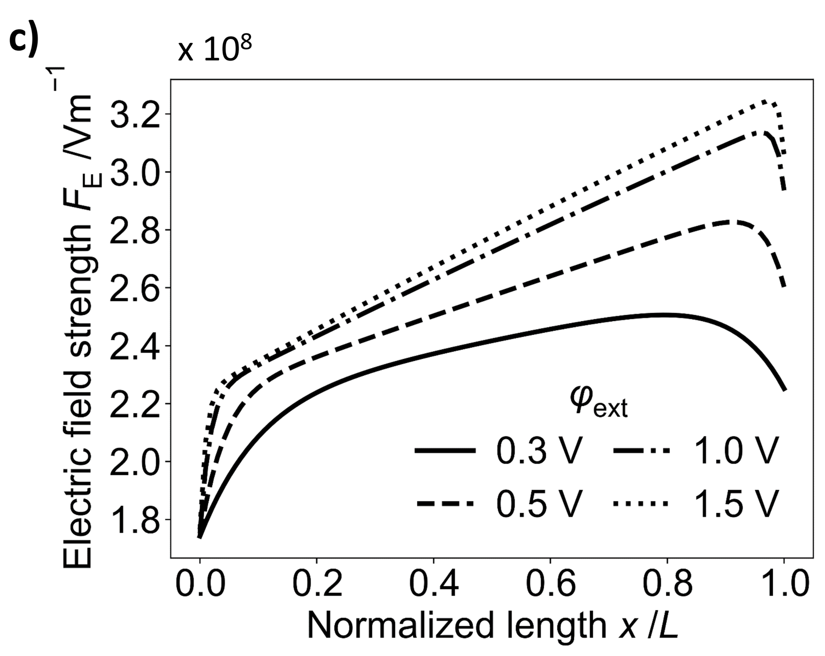


a) Film thickness depending on reaction constant for film formation,

b) Vacancies concentration

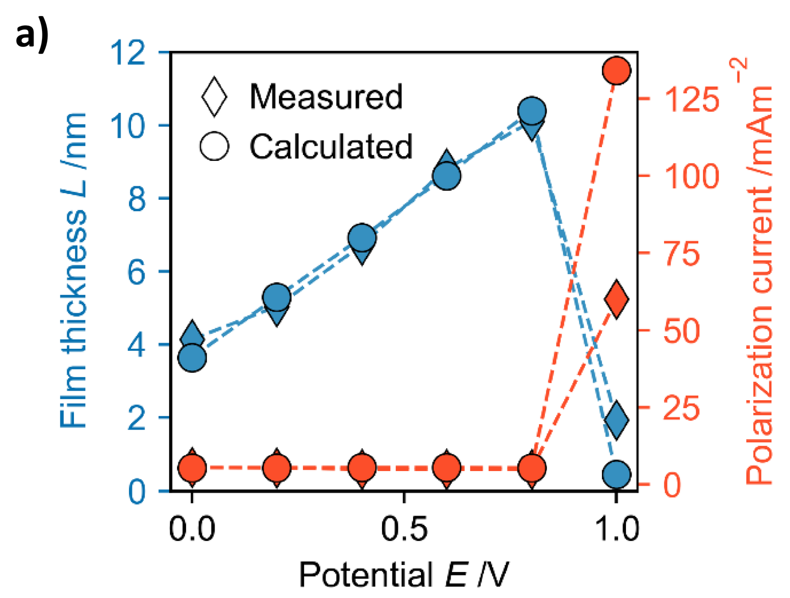
c) Electric field strength insde the film – all depending on the external potential calculated for an artificial metal and metal oxide

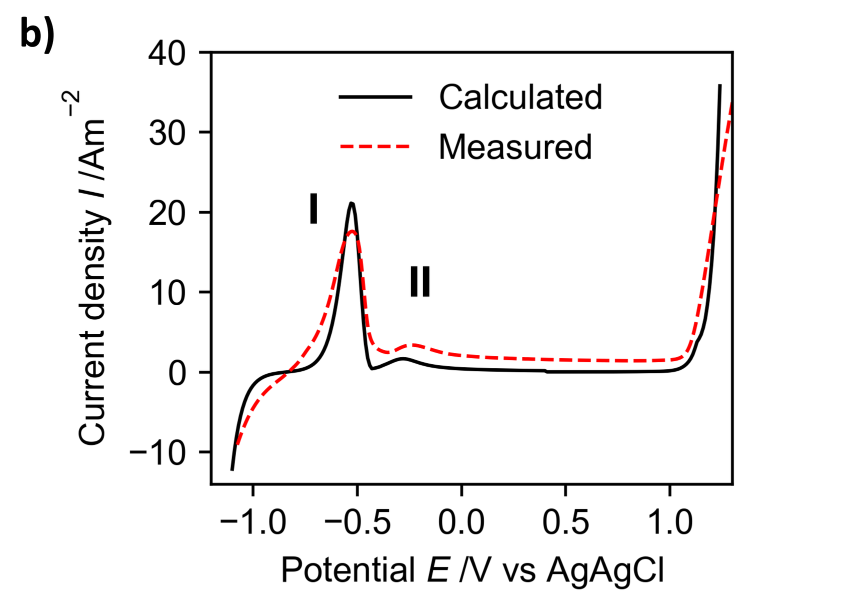


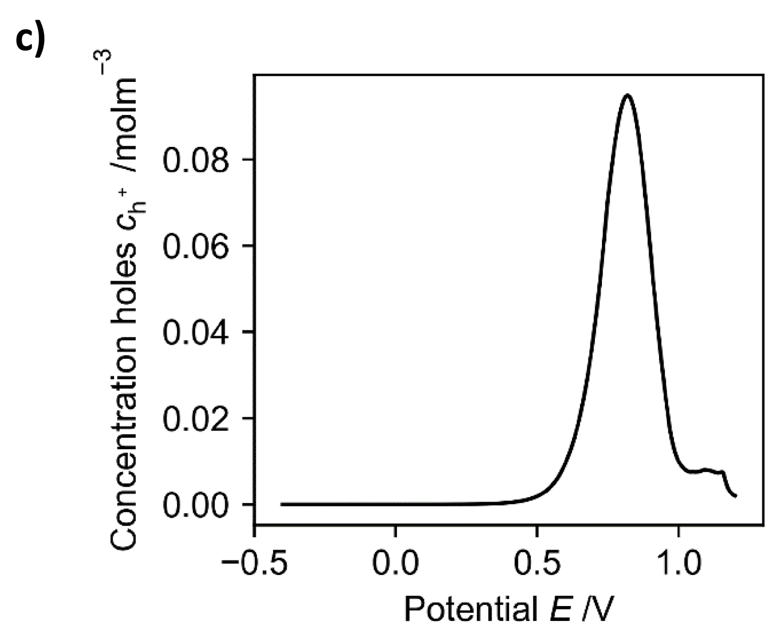


Experiment and Simulation

Anodic polarization of iron in 0.1 M borate buffer (pH 8.4) containing 0.01 M EDTA







a) Measured and calculated film thickness (blue) and polarization current (red) during potentiostatic film growth.

b) Potentiodynamic polarization.
Peak **I**: active corrosion, adsorbtion of metal hydroxides and initial oxide film formation
Peak **II**: $Fe(II) \rightarrow Fe(III) + e^-$
E > 1.0 V oxygen evolution & film breakdown.

c) Holes concentration at the film/solution boundary. Concentration increases due to the applied potential. Consumtion of holes at higher potentials due to transpassive oxidation and oxygen evolution

Summary

Oxide film growth under potential control is modeled by interfacial reactions, transport of crystal defects and electrons and holes through the oxide film. Modeling of the oxide enables understanding of the impact of different model parameters on the growth, stability and defect concentration, electric field etc.

A transpassive breakdown mechanism is proposed based on the holes concentration at the film/solution interface. A high agreement of the model with experiments was achieved

Outlook

- Transpassive breakdown by halide Ions
  - Injection of halide ions into the film $V_O^{\bullet\bullet} + Cl^- \times n\,H_2O \rightarrow Cl_{ox}^{\bullet} + n\,H_2O$ leads to accelerated metal vacancies production (charge balance) and film thinning.
- Multi-element Model
- 2D Model
- Heterogeneous elements distribution

References
[1] Bösing et al. "Modeling of electrochemical oxide film growth–impact of band-to-band tunneling." Electrochimica Acta 406 (2022): 139848
[2] Bösing et al. "Modeling of electrochemical oxide film growth - a PDM refinement." Electrochimica Acta 406 (2022): 139847
[3] Bösing et al. "Effect of heat treatment of martensitic stainless steel on passive layer growth kinetics studied by electrochemical impedance spectroscopy in conjunction with the point defect model." Corrosion and materials degradation 1.1 (2020): 77-91.