SUPPLEMENTARY MATERIAL

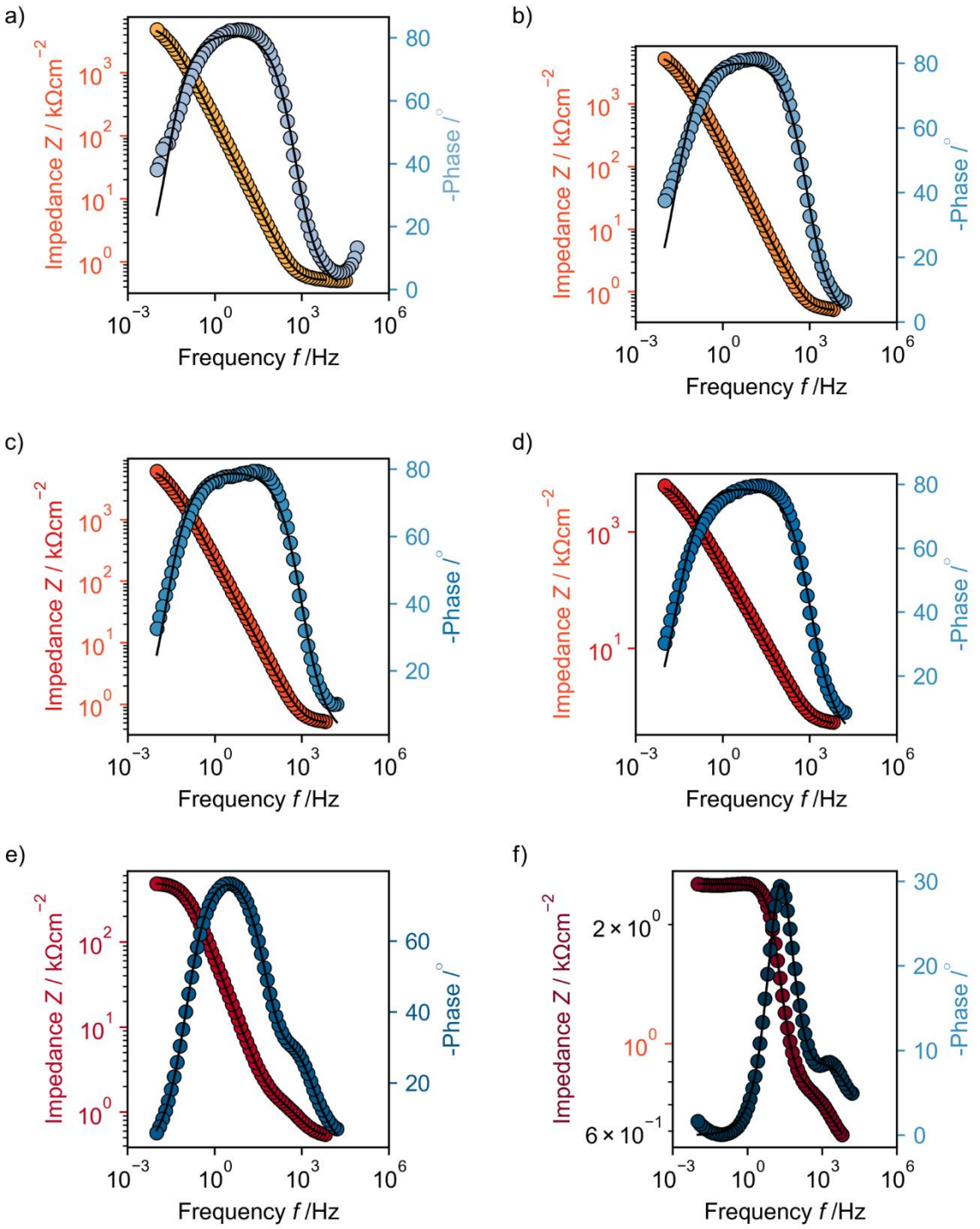

Figure 1: Bode plots of the iron electrode after polarization for 7200 s in borate buffer (+EDTA) at different polarization potentials; a) 0.2 V, b) 0.4 V, c) 0.6 V, d) 0.8 V, e) 1.0 V, f) 1.1 V

The EIS data (Figure 1) is fitted by Equivalent Electrical Circuits (EECs) to derive the film thickness by the fitting parameters. Two different EECs are used for the fiting, one for potentials between 0.0 V and 0.8 V and one for potentials of 1.0 V and 1.2 V (Figure 2).

The values of the EEC parameters are given in Table 1. R_{sol} represents the solution resistance, $R_{\mathrm{pol},i}$ are the polarization resistances attributed to the electrochemical reactions at the oxide film interfaces and/or reactions and charge transfer across the compact double layer. To model the capacitive behavior of the passive film and the compact double layer Constant Phase Elements (CPEs) are used instead of capacities. The impedance of a CPE can be written as $Z_{\mathrm{CPE}} = 1/((j\omega)^N Y)$. As can be seen, for $N = 0$ a CPE behaves like a real resistance, for $N = 1$ the impedance of the CPE is equal to the impedance of a capacity and for $N = -1$ the CPE behaves like an inductivity. By the usage of a CPE the impedance behavior of microscopic material properties that deviate from a smooth surface like defects, kinks or adsorbed species at the film surface can be represented[1].

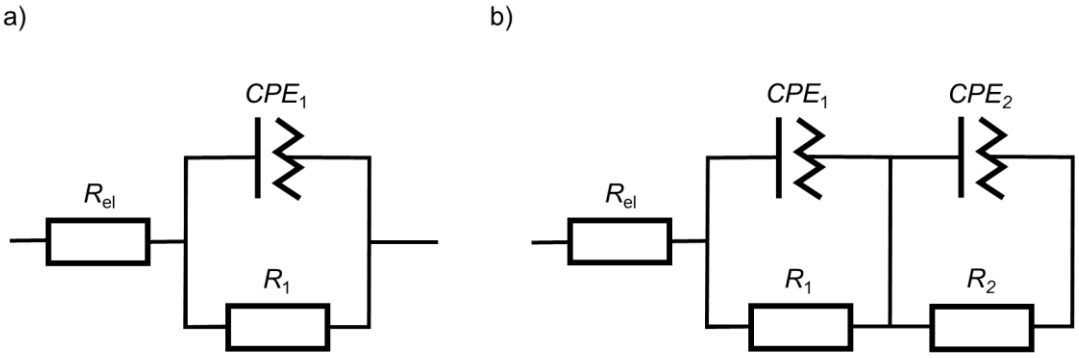

Figure 2: Equivalent Electrical Circuits to fit the EIS data; a) EEC used for potentials between 0.0 V and 0.8 V; b) EEC used for potential of 1.0 V and 1.1 V.

Table 1: EEC parameters

Potential V	$\mathbf{R_{sol}}$ $/\Omega\mathbf{cm^2}$	$\boldsymbol{R_{\mathrm{pol},1}} \times \mathbf{10^5}$ $/\Omega\mathbf{cm^2}$	$\boldsymbol{Y_1} \times \mathbf{10^{-5}}$ $/\mathbf{s^N\Omega^{-1}cm^{-2}}$	$\boldsymbol{N_1}$	$\boldsymbol{R_{\mathrm{pol},2}}$ $/\Omega\mathbf{cm^2}$	$\boldsymbol{Y_2} \times \mathbf{10^{-5}}$ $/\mathbf{s^N\Omega^{-1}cm^{-2}}$	$\boldsymbol{N_2}$
0.0	45.3	4.34	1.73	0.899			
0.2	45.5	4.78	1.23	0.909			
0.4	45.0	5.35	1.05	0.9			
0.6	44.3	6.02	0.99	0.885			
0.8	44.6	6.04	0.90	0.882			
1.0	43.1	0.447	3.30	0.907	67.64	2.74	0.79
1.1	44.7	0.002	10.6	0.956	26.58	10.7	0.64

From CPE parameters it is possible to derive a film thickness L by [2]:

$$L = \frac{(\varepsilon_0 \varepsilon)^N}{(gY\rho_{\mathrm{L}})^{1-N}}.$$

The necessary parameters for the calculation are: the permittivity of the vacuum ε_0, the dielectric constant of the film ε, the CPE parameters N and Y, $g = 1.2.88(1-N)^{2.375}$ and $\rho_{\mathrm{L}} = 450\ \Omega$ cm.

In case of the sample which was polarized at 1.1 V no film thickness was derived because a clear corrosion attack was visible which indicates that no passive film was present at the surface (nevertheless, porous oxidation products were formed at the electrodes surface).

The model parameters for the simulation of oxide film growth are given in Table 2, Table 3, Table 4 and Table 5:

Table 2: Parameter vacancies reactions and transport.

Parameter	**Description**	**Value**	**Unit**
z_{CV}	Charge number cation vacancies	-8/3	
z_{AV}	Charge number anion vacancies	2	
D_{CV}	Diffusion coefficient CV	1×10^{-15}	cm²/s
D_{AV}	Diffusion coefficient AV	1×10^{-15}	cm²/s
d_{dl}	Thickness defect layer	2×10^{-10}	m
$\varepsilon_{\mathrm{dl}}$	Relative permittivity defect layer	2	
ε_{F}	Relative permittivity film	14	
Ω	Molar volume oxide	14	cm³/mol
k^0	Relative reaction rate	4.5×10^{-8}	
k_1^0	Standard reaction rate CVC	$1 \times k^0$	m/s
k_2^0	Standard reaction rate AVP	$80 \times k^0$	mol/(m³s)
k_3^0	Standard reaction rate CVP	$0.1 \times k_0$	mol/(m³s)
k_4^0	Standard reaction rate AVP	$5 \times k_0$	m/s
k_5	Reaction rate FDR	$1.7 \times k_0$	mol/(m³s)
χ_2	Electrons generated during AVP	8/3	
α_1	Charge transfer coefficient reaction 1	0.3	
α_2	Charge transfer coefficient reaction 2	0.8	
α_3	Charge transfer coefficient reaction 3	0.3	
α_4	Charge transfer coefficient reaction 4	0.8	

Table 3: Parameter transpassive reaction (oxygen evolution, film dissolution).

Parameter	Description	Value	Unit
D_{O_2}	Diffusion coefficient oxygen	1×10^{-9}	m²/s
$k_{O_2}^0$	Standard rate constant oxygen	5×10^{-3}	m/s
α_{O_2}	Charge transfer coefficient oxygen	0.35	
$\varphi_{O_2}^0$	Equilibrium potential oxygen	1.35	V
k_{tp}^0	Standard rate const. transpassive diss.	0.9×10^{-8}	m/s
φ_{tp}^0	Equilibrium potential transpas. diss.	0.22	V
α_{tp}	Charge transfer coefficient	0.2	

Table 4: Parameter for modeling the active region and active/passive transition.

Parameter	Description	Value	Unit
μ_e^0	Electrochemical potential electrons	1.5	eV
e	Elementary charge	1.6022×10^{-19}	C
N_c	Density of states conduction band	1.6022×10^{5}	mol/m³
N_v	Density of states valence band	1.6022×10^{5}	mol/m³
E_c^0	Energy conduction band edge	3.2	eV
E_v^0	Energy valence band edge	1.0	eV
D_h	Diffusity holes	3.28×10^{-4}	m²/s
τ		4.98×10^{-13}	(s·mol)/m³
c_e	Concentration electrons (for calculating recombination)	9.53×10^{-28}	mol/m³
c_h^0	Equilibrium concentration holes	4.17×10^{-4}	mol/m³

Table 5: Parameter for the calculation of holes concentration.

Parameter	Description	Value	Unit
k^0_{FeOH}	Standard rate const. metal hydroxide	1×10^{-7}	mol/m²/s
$\varphi^0_{\mathrm{FeOH}}$	Equilibrium pot. metal hydroxide	-0.8	V
α_{FeOH}	Charge transfer coef. Metal hydroxide	0.5	
k^0_{FeOHox}	Standard rate const. FeOH oxidation	2×10^{-3}	/s
$\varphi^0_{\mathrm{FeOHox}}$	Equilibrium pot. FeOH oxidation	-0.82	V
α_{FeOox}	Charge transfer coef. FeOH oxidation	0.5	
k^0_{FeO}	Standard rate const. FeO formation	3×5	/s
φ^0_{FeO}	Equilibrium pot. FeO	-0.9	V
α_{FeO}	Charge transfer coef. FeO	0.5	

1. Cesiulis, H., Tsyntsaru, N., Ramanavicius, A. & Ragoisha, G. The study of thin films by electrochemical impedance spectroscopy. in *Nanostructures and thin films for multi-functional applications* 3–42 (Springer, 2016).
2. Hirschorn, B. *et al.* Constant-Phase-Element Behavior Caused by Resistivity Distributions in Films. *J Electrochem Soc* **157**, C458 (2010).