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1 **Refining anodic and cathodic dissolution mechanisms:**
2 **Combined AESEC-EIS applied to Al-Zn pure phase in alkaline solution**

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4

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13 **Abstract**

14 In this work, the use of atomic emission spectroelectrochemistry (AESEC) coupled to
15 electrochemical impedance spectroscopy (EIS) is presented as a method of revealing dissolution
16 mechanisms. To illustrate the method, the dissolution kinetics of Al cations from an Al-Zn pure
17 phase (Zn-68 wt.% Al) was investigated in an alkaline solution. In the cathodic potential domain,
18 a nearly direct formation of dissolved Al³⁺ was observed, while in the anodic potential domain
19 the Al dissolution occurred by migration across a ZnO/Zn(OH)₂ film. The localization of the
20 charge transfer mechanism depending on applied potential could be distinguished by comparing
21 the DC and AC faradaic yield using AESEC-EIS.
22

23 Introduction

24 Since its introduction to the corrosion field by Epelboin *et al.* [1], electrochemical
25 impedance spectroscopy (EIS) has proven itself an essential and ubiquitous technique in
26 corrosion research. For steady state corroding systems, the EIS spectrum may in some cases be
27 used to estimate the corrosion rate of the material without significant electrochemical
28 perturbation of the system [1], and the EIS spectrum itself is often considered as a fingerprint for
29 specific mechanisms revealing different kinetic processes over a wide range of time constants [2].
30 The difficulty of EIS alone is the inability to identify the specific faradaic reactions that occur
31 during charge transfer. This has given rise to the development of a variety of couplings such as
32 EIS – Raman spectroscopy [3]. The modulated Raman emission signal allows one to “tune in” to
33 surface chemical bonds that form and dissipate in resonance with the modulated electrochemical
34 potential. The theoretical development of such techniques has been addressed in the development
35 of a generalized EIS transfer function [4].

36 Atomic emission spectroelectrochemistry (AESEC) provides a direct measurement of
37 elemental dissolution rates [5]. One of the difficulties of this technique is that dissolution may be
38 directly related to a faradaic process, weakly related as in the case of anodic dissolution by way
39 of an oxide intermediate, or unrelated as when dissolution is due to a non-faradaic process. The
40 correlation of electrochemical current transients with dissolution transients is one means of
41 distinguishing between these possibilities as demonstrated by Jiang *et al.* [6, 7] for the dissolution
42 of Zn in the presence of conversion coatings. The coupling of EIS and AESEC allows for a more
43 sophisticated analysis of dissolution kinetics: the oscillating elemental dissolution rates may be
44 related to the oscillating current and the EIS data may be decomposed into elemental components
45 at least for the low frequencies. In this way, the EIS measurement may be obtained on an element

46 by element basis with the advantage that dynamic systems may be treated directly, by analyzing
47 data in the time domain. A detailed model for AESEC-EIS was developed by Shkirskiy and Ogle
48 [8], directly correlating the elemental dissolution rate and electrical current for pure Zn at open
49 circuit potential. Zn dissolution in 0.1 M NH_4Cl occurred without any significant intermediate
50 film formation as evidenced by the Zn dissolution rate being in-phase with the alternating current
51 (AC) component of the electrical current. In 0.5 M NaCl solution, no correlation between the AC
52 and the Zn dissolution rate was observed, indicating that oxide film formation and dissolution
53 were decoupled faradaic and non-faradaic processes, respectively. The goal of this article is to
54 extend the previous work to a multi-element system and to use the EIS spectra to distinguish
55 different mechanisms of dissolution by taking advantage of the time-resolved measurement of
56 each element of a multi-element system that AESEC technique provides.

57 The Al-Zn alloy system in alkaline solution was considered an ideal system for an early
58 demonstration of the method. The system is industrially significant: Al-Zn alloys are commonly
59 used as galvanic coatings on steel and occur as separate phases in Zn containing Al alloys, such
60 as the 6000 series, and are almost always exposed to alkaline solution in their lifetime either
61 during surface treatment by alkaline etching, or during corrosion when the cathodic reaction leads
62 to local pH changes. The mechanisms of anodic and cathodic dissolution of multi-phase Zn-5 wt.%
63 Al alloy coatings on steel were previously investigated [9, 10]. A complex interaction between
64 the Zn and Al was observed, however, interpretation of the mechanisms of these interactions was
65 hindered due to the multi-phase nature of the commercial coating material. Therefore, to simplify,
66 we isolated the chemistry of a single phase: the α -phase of Al-Zn (Zn-68 wt.% Al). The anodic
67 dissolution of Al and Zn were investigated as a function of potential in slightly alkaline (pH =

68 10.1) [11] and alkaline (pH = 12.8) [12] electrolytes. In the latter, the temperature dependence of
69 anodic dissolution was also investigated [13].

70 In summary of these results, three potential domains were identified where the dissolution
71 of the material occurred by very different mechanisms. Based on the individual Zn and Al
72 dissolution rate results and the electrochemical current, it was found that Al underwent a direct,
73 potential independent dissolution mechanism in the cathodic potential domain by reacting with
74 H_2O , and without the formation of a significant intermediate oxide film. Metallic Zn accumulated
75 on the surface in a mechanism of cathodic dealloying. In the anodic domain, Zn was transformed
76 into an oxide film and Al dissolution occurred by ionic transfer across the film. As the two
77 mechanisms are very different, it was felt that EIS coupled to AESEC might further confirm
78 these mechanisms and allow a higher degree of precision on the mechanistic details.

80 **Results and discussions**

81 *Overview of $Al_{5.2}Zn$ mechanisms as a function of potential*

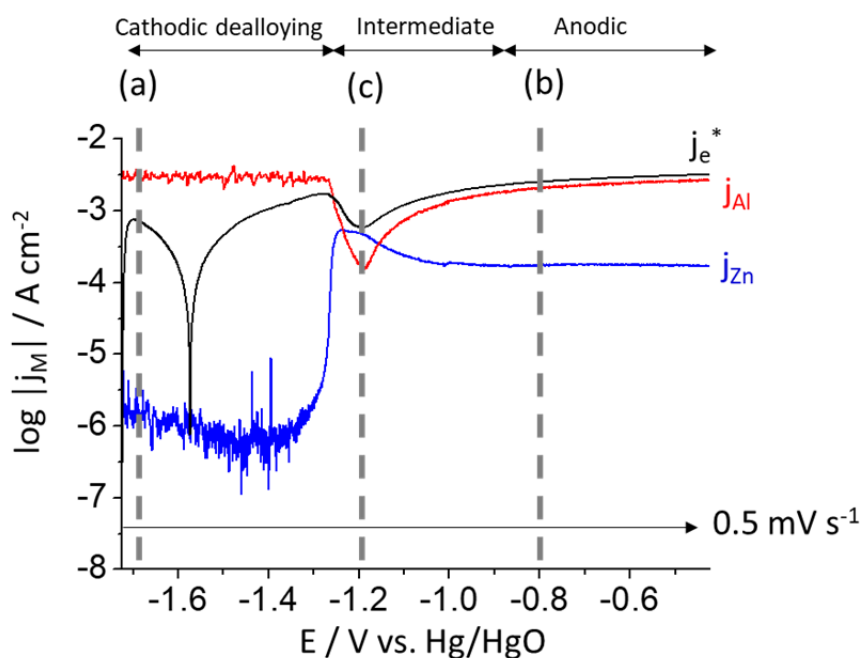
82 The sensitivity of the Al-Zn dissolution mechanism to potential is evident from the
83 AESEC-linear sweep voltammetry (AESEC-LSV) curve of $Al_{5.2}Zn$ (Zn-68 wt.% Al) phase in 0.1
84 M NaOH solution, shown in **Fig. 1**. Elemental dissolution rates (j_M) and the convoluted electrical
85 current density (j_e^*) as a function of potential are given with 0.5 mV s^{-1} scan rate. As previously
86 described, the polarization curve clearly shows three potential domains, to which can be ascribed
87 three unique mechanisms of dissolution. The *cathodic dealloying domain* occurs between -1.72 V
88 to -1.35 V vs. Hg/HgO. It is characterized by an intense Al dissolution rate, j_{Al} , and a Zn

89 dissolution rate, j_{Zn} , close to the detection limit. A direct reaction between Al and H_2O was
 90 inferred with significant hydrogen evolution reaction (HER) [14] and accumulation of metallic
 91 Zn.



93 Al dissolution rate was potential independent and in fact, did not reflect or correlate in anyway
 94 with the electrochemical current the magnitude of which was much lower and changed sign
 95 during this potential domain.

96



97

98 **Fig. 1.** Elemental AESEC-LSV curve of $Al_{5.2}Zn$ phase in 0.1 M NaOH, $pH=12.80$, Ar deaerated
 99 electrolyte at $T = 25^\circ C$. All potential values presented in this work are referenced to an Hg/HgO
 100 electrode in 0.1 M NaOH (-165 mV vs. SHE). Vertical dashed lines are selected potential values
 101 in the (a): cathodic dealloying, (b): anodic and (c): intermediate domains.

102 A totally different mechanism is apparent in the *anodic domain* (from -0.9 V to -0.4 V vs.
103 Hg/HgO), evidenced by the nearly congruent dissolution of Zn and Al, and the significantly
104 decreased amplitude of perturbations in the j_{Al} signal. The DC faradaic yield of elemental
105 dissolution may be determined as $\eta_{DC} = j_{\Sigma} / j_e^*$ when cathodic current contribution is negligible,
106 where $j_{\Sigma} = j_{Zn} + j_{Al}$. In this case, the dissolution rate follows the electrical current with nearly a
107 100% DC faradaic yield ($\eta_{DC} = 0.98$) of dissolution. The potential independence of Zn and Al
108 dissolution rates suggests an oxide film formation type of mechanism and indeed, Raman
109 spectroscopy and SEM analysis also demonstrated the formation of ZnO layer in this potential
110 domain [11, 12]

111 The elemental dissolution rates in the *intermediate domain* (from -1.35 V to -0.90 V vs.
112 Hg/HgO), is more complex and involves the accumulated metallic Zn enriched layer, Zn(0), that
113 was formed in the cathodic domain by the preferential Al dissolution. At the onset of Zn
114 dissolution, there is a notable decrease in the j_{Al} , that we previously termed a *negative correlation*
115 *effect* (NCE) in [12]. The j_{Zn} reached its maximum value in approximately the same potential
116 domain as j_{Al} obtained its minimum value.

117

118 **AESEC-EIS results**

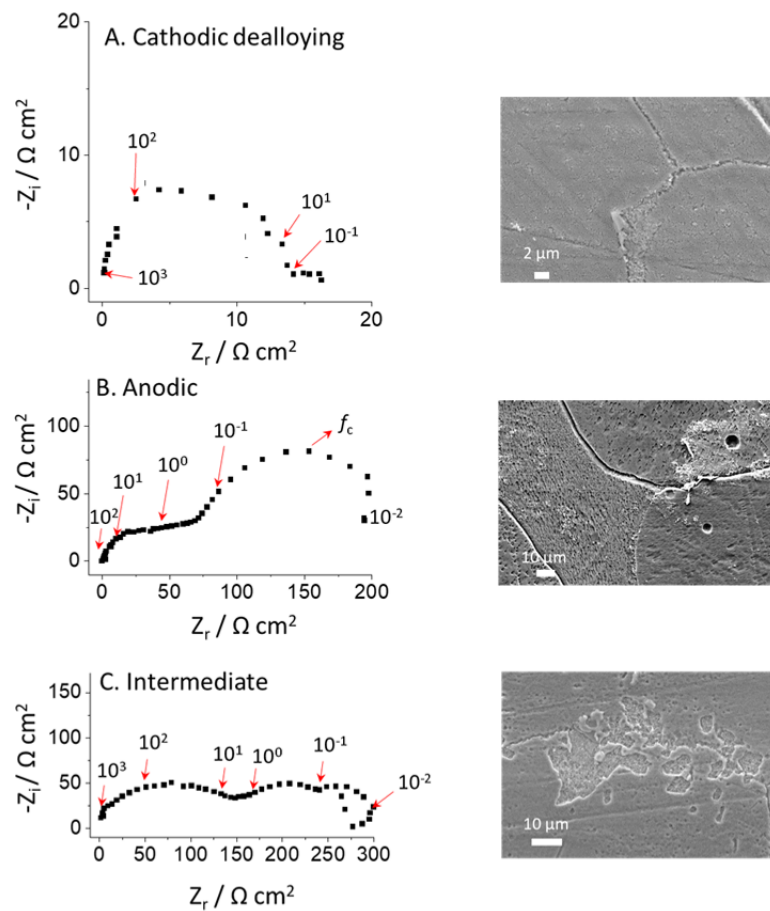
119 To corroborate and gain further insight into the proposed dissolution mechanisms,
120 potentiostatic EIS was performed simultaneously with AESEC in the three potential domains, at
121 potentials indicated as (a), (b), and (c) in **Fig. 1**. The Nyquist plots are presented in **Fig. 2** and the
122 corresponding AESEC-EIS dissolution profiles are given in **Figs. 3A – 3C**. The effective oxide

123 capacitance (C_δ) values determined by the complex capacitance curve [15], the constant phase
124 element (CPE) parameters (α and Q), and the corresponding effective oxide layer thicknesses (δ)
125 for each potential domain are summarized in **Table 1**.

126

127 *The Cathodic Dealloying Domain (-1.72 V to -1.35 V vs. Hg/HgO)*

128 EIS in the cathodic dealloying domain (**Fig. 2A**) revealed a single time constant
129 suggesting that H_2O reduction reaction was the dominating charge transfer reaction. The
130 dissolution profile obtained by AESEC (**Fig. 3A**) again demonstrates the potential independence
131 of Al dissolution, as the potential cycles at low frequency do not appear as oscillations in the
132 elemental dissolution rates. This is an important conclusion because it indicates that the EIS
133 spectra are revealing information on the interfacial electrochemical processes that may not
134 directly affect the dissolution rate.

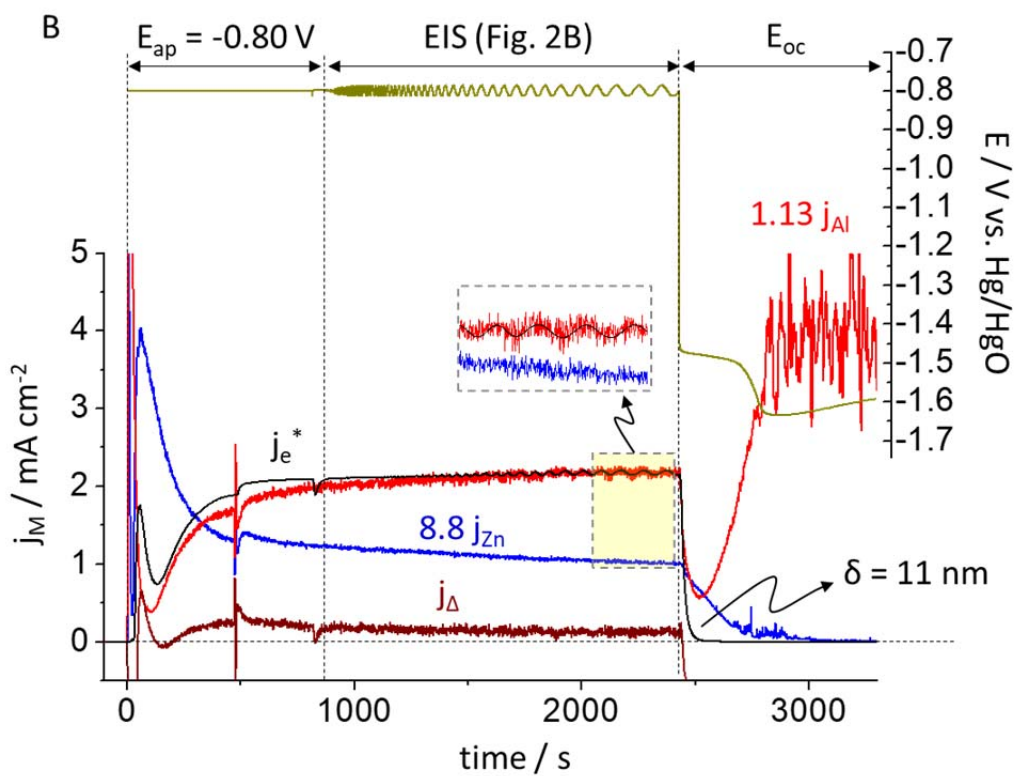
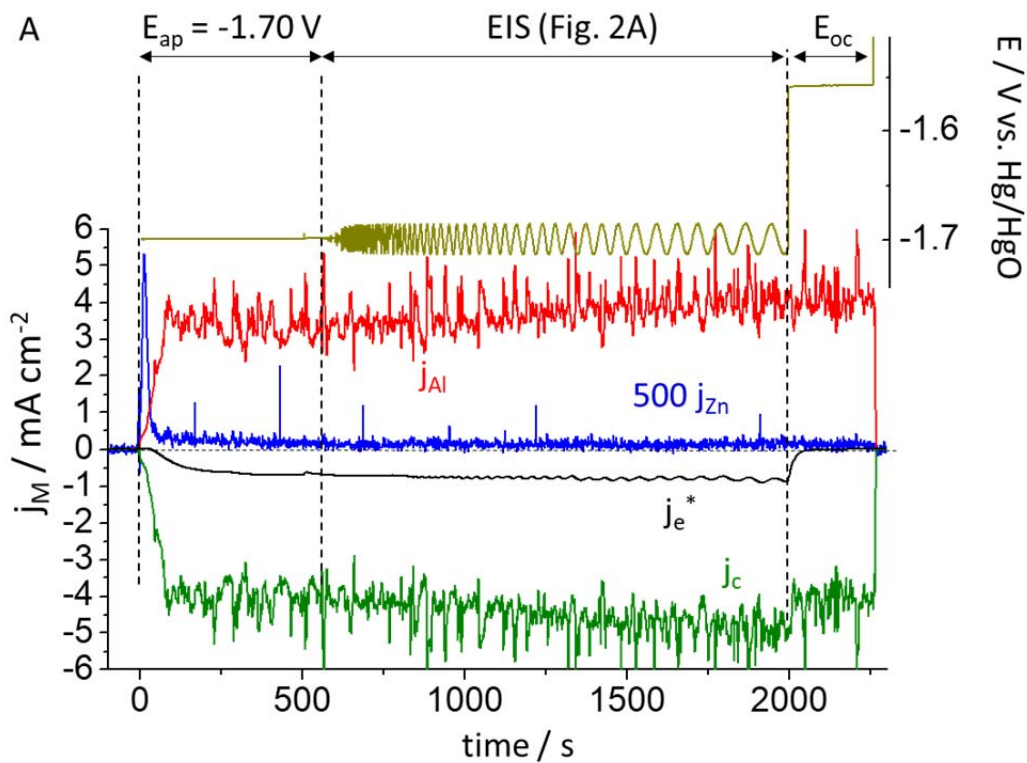


135

136 **Fig. 2.** Nyquist plots at each potential domain determined from **Fig. 1** and their corresponding
 137 SEM images; A: -1.70 V vs. Hg/HgO, B: -0.80 V vs. Hg/HgO and C: -1.20 V vs. Hg/HgO. Arrows
 138 are indicating frequency values (Hz).

139

140



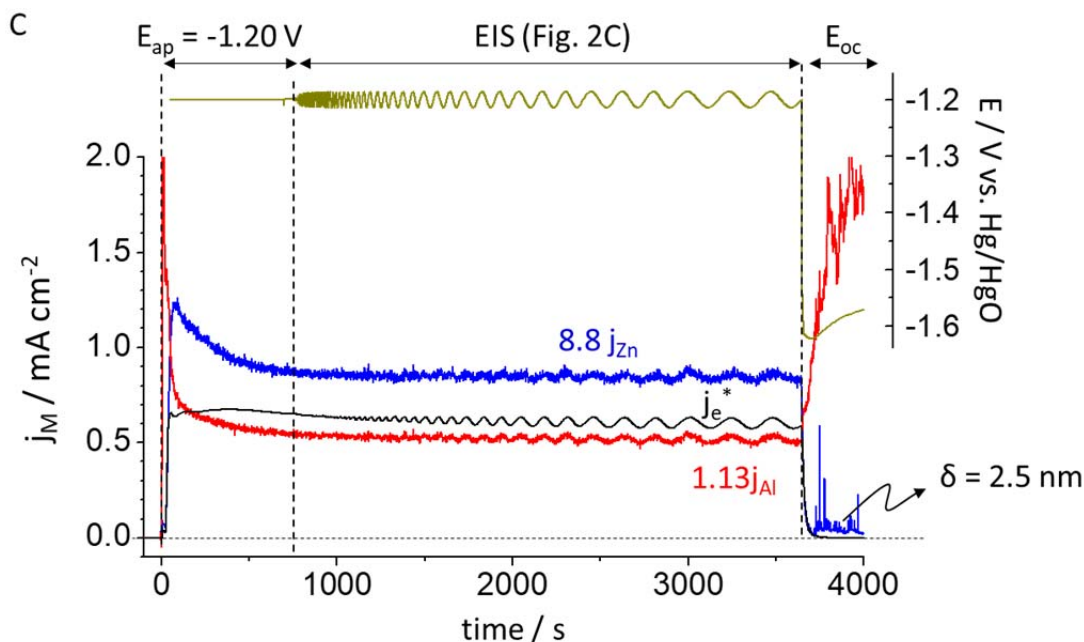
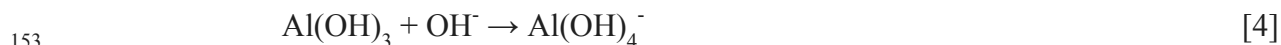
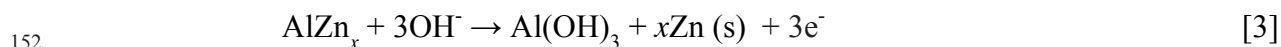


Fig. 3. AESEC-EIS curve of $Al_{5.2}Zn$ in 0.1 M NaOH, Ar deaerated electrolyte including potentiostatic hold (E_{ap}), EIS and open circuit measurement (E_{oc}). **A:** $E_{ap} = -1.70$ V vs. Hg/HgO, **B:** $E_{ap} = -0.80$ V vs. Hg/HgO and **C:** $E_{ap} = -1.20$ V vs. Hg/HgO. j_M ($M = Zn$ or Al) values are normalized based on the molar composition for **B** and **C**.

141

142 The analysis of the high frequency loop shows a CPE behavior where $\alpha = 0.73$ and $Q =$
 143 $(1.07 \pm 0.20) \times 10^{-3} \Omega^{-1} \text{ cm}^{-2} \text{ s}^{\alpha-1}$, estimated from a graphical analysis [16]. Assuming that this
 144 time constant is attributed to a 2D frequency distribution [17], Brug's relationships [18] allow an
 145 estimation of the equivalent capacitance from the CPE parameters, in this case the double layer
 146 capacitance, $C_{dl} = 191 \mu\text{F cm}^{-2}$. This value is about an order of magnitude larger than the
 147 expected value for a double layer capacitance and could represent the response of a very thin,
 148 perhaps a non-uniform oxide film. It is reasonable to suppose that $Al(OH)_3$ forms as a short lived

149 intermediate in Reaction 1 as previously discussed [12, 13]. Reaction 1 may be broken down into
150 more elementary steps as follows:



154 AESEC directly measures Reaction 4, which involves no electron transfer and in principle should
155 be potential independent. The EIS results indicate that water reduction was potential dependent
156 (**Fig. 2A**). This confirms the conclusions of [13]; the dissolution of Al oxide/hydroxide layer
157 (Reaction 4) was the rate determining step (RDS) in accordance with previous studies [19, 20, 21,
158 22]. At steady state, Reactions 3 – 4 must occur at identical rates. The properties of the film most
159 likely determine the reaction rate by controlling the access of H₂O to Al metal. The presence of
160 the film may not be directly detected by AESEC due to the intense dissolution rate and cathodic
161 current, however, the film is detected indirectly by EIS. The cathodic current resulting from the
162 HER may be determined simply as $j_{\Delta} = j_e^* - j_{\Sigma} = j_c$, shown in **Fig. 3A**.

163

164 *The anodic domain (-0.9 V to -0.4 V vs. Hg/HgO)*

165 In the anodic domain, the polarization curve (**Fig. 1**) demonstrates that Zn and Al
166 dissolution rates and the electrochemical current are stable and nearly independent of potential. In
167 the EIS spectrum (**Fig. 2B**), three-time constants are observed. The high frequency capacitive
168 loop may be attributed to the charge transfer resistance of Zn and / or Al oxidation in parallel
169 with the interfacial capacitance. In this system, independent anodic dissolutions from Zn and Al

170 simultaneously occur at different rate and thus the admittance is the sum of these contributions.
171 This may explain why the two entangled time constants are observed in the high frequency
172 domain. The low frequency loop shows a nearly 45° phase that suggests a diffusion process [23,
173 24]. The time constant observed at intermediate frequency (approximately $f = 1$ Hz) is poorly
174 resolved due to overlap with the high and low frequency contributions and will not be discussed.

175 The high frequency capacitive loop is flattened and this can be described by a CPE in
176 parallel with the charge transfer resistance. We assume that this CPE is due to the distribution of
177 properties in a thin oxide film [16], for instance, the distribution of resistivity according to a
178 power-law model [25, 26]. From the analysis of the complex capacitance calculated from the
179 impedance data [15], the high frequency limit of the of the capacitance was $C_\delta = 0.65 \pm 0.05 \mu\text{F}$
180 cm^{-2} . Such a low value is characteristic of the dielectric response of a thin oxide film. Assuming a
181 dielectric constant $\epsilon = 8.8 \pm 0.8$ for ZnO [27] the thickness of the thin oxide film, δ , formed at the
182 electrode interface is given by;

$$183 \quad \delta = \epsilon \epsilon_0 / C_\delta \quad [5]$$

184 where ϵ_0 is the vacuum permittivity ($8.85 \times 10^{-14} \text{ F cm}^{-1}$). This equation yields $\delta = 12 \pm 1 \text{ nm}$.
185 Such a value confirms the hypothesis that the interfacial capacitance is governed by the thin
186 oxide film contribution (*i.e.* the double layer capacitance which is in series with the capacitive
187 contribution of the oxide film, has in this case a negligible contribution).

188 The presence and characteristics of the oxide film may be further refined by consideration
189 of the low frequency capacitive loop. For the AESEC-EIS (**Fig. 3B**), very slight oscillations are
190 observed in the Zn and Al dissolution rate at low frequency (magnified curve is given in the

191 inset). The faradaic yield of dissolution for the total current, $\eta_{DC} = 0.96 \pm 0.03$ close to 1, in
192 agreement with [12]. The faradaic yield of the AC component, η_{AC} , is defined as:

$$193 \quad \eta_{AC} = \text{AC amplitude } (j_{\Sigma}) / \text{AC amplitude } (j_e^*) \quad [6]$$

194 From the data in **Fig. 3B**, $\eta_{AC} = 1.01 \pm 0.05$, reasonably identical to η_{DC} within experimental error.
195 Note that error bar of η_{AC} was obtained from different frequency domains. It appears to be
196 distributed essentially in the Al dissolution although slight peaks above background are observed
197 for Zn dissolution as well.

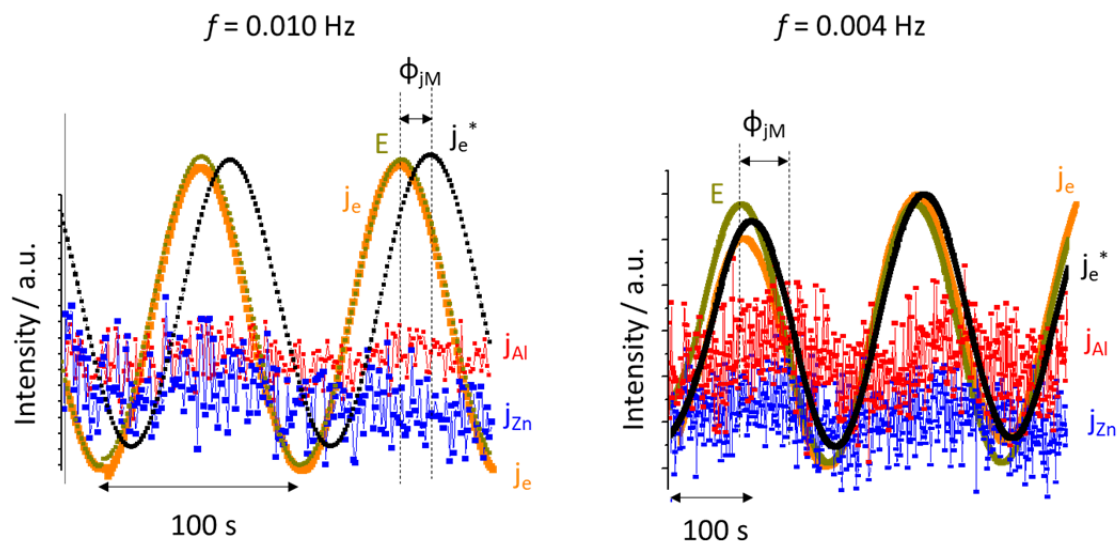
198 The second capacitive loop in **Fig. 2B** shows a typical diffusion-controlled charge transfer
199 mechanism through an oxide layer [24]. Interestingly, the characteristic frequency, $f_c = 0.032$ Hz
200 at the apex of the time constant of the diffusion process in the Nernst layer may be expressed as;

$$201 \quad f_c = 2.51 D / 2\pi \delta^2 \quad [7]$$

202 where δ is the thickness of the corrosion product, that can be in a first approximation evaluated to
203 be at least the thickness previously obtained from the CPE parameter ($\delta = 12$ nm). The diffusion
204 coefficient may be calculated from **Eq. 7**, $D = 1.15 \times 10^{-13} \text{ cm}^2 \text{ s}^{-1}$. Such a low value should be
205 due to the underestimated δ value because the calculation did not consider the porosity of the
206 oxide as well as the accumulation of corrosion products at the electrode surface. It may be
207 attributed to a diffusion of species inside of a micrometric diffusion layer of corrosion product. In
208 this case, the diffusion and migration caused by the large electric field inside the film should be
209 taken into account.

210

A. $E_{ap} = -0.80$ V vs. Hg/HgO



B. $E_{ap} = -1.20$ V vs. Hg/HgO

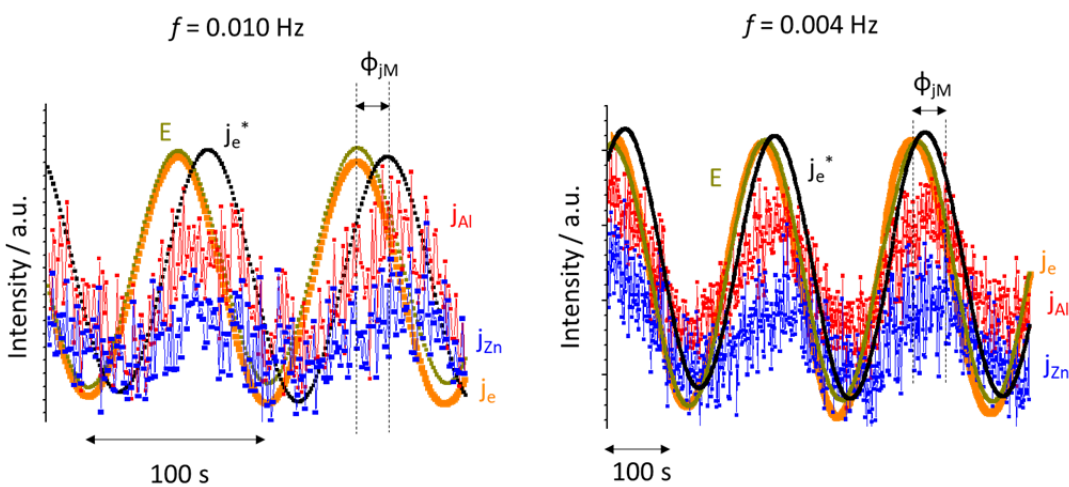


Fig. 4. The oscillation trends at low frequency domain for A: $E_{ap} = -0.80$ V vs. Hg/HgO and B: $E_{ap} = -1.20$ V vs. Hg/HgO from Figs. 3B and 3C, respectively.

211

212

213

Fig. 4 shows the oscillation trends of the j_e , j_e^* , j_M and applied potential (E) at a given frequency of AESEC-EIS result from **Fig. 3**. To facilitate the comparison, each profile is

214 presented in arbitrary units. The phase shift of j_M and j_e^* vs. E (ϕ_{j_M}) results from the residence
215 time distribution of the flow cell [5], which means that it is not frequency dependent but time
216 dependent. The actual phase shift between E and j_e (ϕ) was nearly zero in all cases as shown in

217 **Fig. 4.**

218 The impedance contribution from each elemental dissolution in real part, $Z_r(j_M)$, is given
219 in **Table 2**, calculated at each frequency domain as:

$$220 \quad Z_r(j_M) = (|dE| / |dj_M|) \cos(\phi) \quad [8]$$

221 For $E_{ap} = -0.80$ V vs. Hg/HgO (**Fig. 4A**), j_{Zn} oscillation is less evident than at $E_{ap} = -1.20$ V vs.
222 Hg/HgO (**Fig. 4B**), probably indicating a weak potential dependent Zn dissolution in the anodic
223 potential domain due to the Zn-based corrosion products formation. The high $Z_r(j_{Zn})$ values at
224 $E_{ap} = -0.80$ V vs. Hg/HgO could also be explained by the weak potential dependency of Zn
225 dissolution at this potential. For $E_{ap} = -1.20$ V vs. Hg/HgO, $Z_r(j_{Zn}) + Z_r(j_{Al}) \approx Z_r - R_e$, which may
226 indicate that j_{Zn} and j_{Al} contributed to the total impedance with a parallel relationship. Note that
227 Z_r is measured by potentiostat then subtracted by the electrolyte impedance, $Z_e = R_e$. It is
228 consistent with the previously proposed dissolution model of the $Al_{5.2}Zn$ phase in which Al
229 dissolution occurred through a porous Zn(0) layer in parallel with Zn dissolution [12]. It should
230 be mentioned that the dissolution is not a simple mechanism as it usually involves the adsorbed
231 intermediate species which may result in a delay between the j_e^* and j_M .

232 The correlation between the AC current and dissolution rates is highlighted by the
233 Lissajous analysis in **Figs. 5A** ($E_{ap} = -0.80$ V vs. Hg/HgO) and **5B** ($E_{ap} = -1.20$ V vs. Hg/HgO) at
234 $f = 0.004$ Hz. j_e^* curve is shown on the top, both for upper and lower potential scans. For j_M vs. E

235 curves in the middle, j_e^* assuming congruent dissolution of Al and Zn are also shown. For
236 example in **Fig. 5A**, Al dissolution was congruent as $j_{Al} \approx (j_e^* / 1.13)$ whereas Zn dissolution was
237 not as $j_{Zn} < (j_e^* / 8.8)$. The correlation of Zn dissolution rate with potential is less obvious than for
238 Al, but exists (also see **Fig. 4A**). In principle, at this potential, there is no significant cathodic
239 reaction, so we conclude that the AC current is primarily going to the formation and reduction of
240 ZnO or Zn(OH)₂. It was previously shown that the $\eta_{AC} \approx \eta_{DC} \approx 1$ at $E_{ap} = -0.80$ V vs. Hg/HgO,
241 supporting this assumption. The weak correlation is interesting since the overall faradaic yield of
242 dissolution based on the DC current density and elemental dissolution rates was nearly 100%
243 ($\eta_{DC} = 0.96 \pm 0.03$) at this potential. In this case, it could be concluded that the DC component
244 was due to the dissolution of the corrosion products [6, 7, 28].

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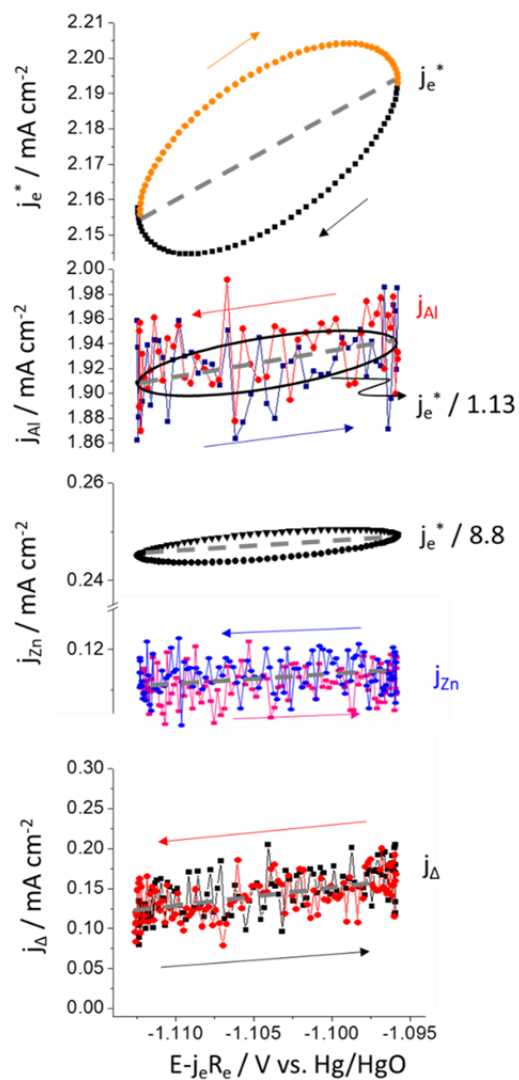
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A. $E_{ap} = -0.80$ V vs. Hg/HgO (0.004 Hz)



B. $E_{ap} = -1.20$ V vs. Hg/HgO (0.004 Hz)

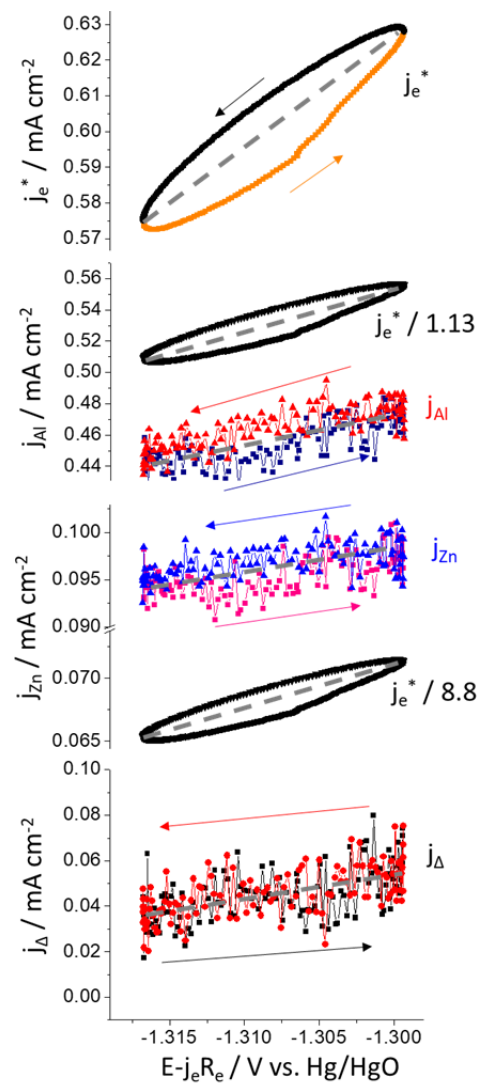
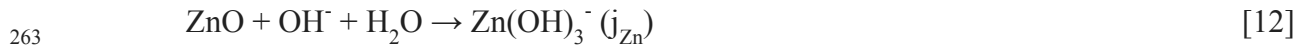
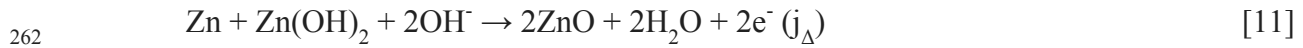


Fig. 5. Lissajous analysis at $f = 0.004$ Hz at **A:** $E_{ap} = -0.80$ V vs. Hg/HgO and **B:** $E_{ap} = -1.20$ V vs. HgO. The j_e^* , j_{Al} and j_{Zn} are shown as a function of IR drop compensated applied potential ($E - j_e R_e$). One cycle including upper and lower potential scans, indicated by arrows, is given.

257 The kinetic parameters for ZnO formation and reduction may be estimated from the j_{Δ} vs.
 258 E Lissajous plot, shown in the bottom of **Fig. 5**. The Zn dissolution in the anodic potential
 259 domain (**Fig. 5A**) may be the combination of a series of elementary reactions as:



264 The intermediate species such as ZnOH or ZnOH_{ads} [29, 30, 31] are not considered as the time
 265 scale of the AESEC experiment is too slow to measure these species. The formation rate of
 266 Zn(OH)₂ or ZnO (j_{Δ}) is potential dependent (Reactions 9 and 11) given that the Lissajous plot of
 267 j_{Δ} vs. E showed the linearity, neglecting the contribution of cathodic current at this potential. The
 268 anodic Tafel slope of j_M (b_{a,j_M}) may be calculated as;

$$269 \quad b_{a,j_M} = 2.303 \Delta E / \ln(j_M^+ / j_M^-) \quad [13]$$

270 where j_M^+ and j_M^- are j_M values measured at the highest and lowest potential, respectively. ΔE is
 271 the difference between the highest and lowest potential. $b_{a,j_{\Delta}} = 94 \text{ mV decade}^{-1}$ and $b_{a,j_{\text{Zn}}} = 2350$
 272 mV decade^{-1} are calculated by Eq. 13. It is clearly demonstrated that the formation of ZnO
 273 (Reaction 11) is faster than the dissolution (Reaction 12), resulting in the growth of the ZnO layer
 274 [12, 13].

275 The quantity of oxide formed during the AESEC-EIS experiment may be estimated by the
276 dissolution profile obtained after releasing the potential to open circuit at the end of the
277 experiment. The $E_{ap} = -0.80$ V vs. Hg/HgO AESEC-EIS profile of **Fig. 3B** illustrates this idea. At
278 the end of the experiment, the presence of oxide dissolution is indicated by a plateau in the E_{oc} vs.
279 time profile at approximately $E_{oc} = -1.50$ V vs. Hg/HgO. The removal of the oxide and the
280 exposure of the underlying metallic substrate is indicated by the sudden drop in potential to $< -$
281 1.6 V vs. Hg/HgO. The removal of the oxide film gives rise to a transient dissolution of Zn,
282 which decays steadily but at a rate significantly slower than the residence time distribution
283 associated with the flow cell. The latter is indicated by the drop of the convoluted
284 electrochemical current, j_e^* . Integration of the j_{Zn} yields a thickness of ZnO layer $\delta = 11$ nm was
285 obtained assuming a uniform ZnO layer formation over the geometrical surface area and a ZnO
286 density of 5.6 g cm^{-3} . This is in the same range as the thickness estimated from EIS of 12 ± 1 nm
287 (**Table 1**).

288

289 *The Intermediate Domain (-1.35 V to -0.9 V vs. Hg/HgO)*

290 In the intermediate domain, both j_{Zn} and j_{Al} showed clear in-phase oscillations, with the
291 low frequency AC current (**Fig. 3C**). The EIS response in **Fig. 2C** shows three capacitive time
292 constants and one inductive loop. An inductive loop has already been reported for both Zn and Al
293 dissolution. In the case of Zn, this loop is usually observed in the intermediate frequency range
294 [24, 32] whereas for Al, it can be only be seen in the low frequency domain in an alkaline
295 solution [33, 34]. We thus conclude that the inductive loop observed for $f < 10^{-2}$ Hz may be
296 attributed to the relaxation of the surface intermediates involved in the dissolution mechanism of

297 Al and Zn [35]. The third capacitive loop is similar to the one observed at $E_{ap} = -0.80$ V vs.
298 Hg/HgO and may be ascribed to diffusion processes inside a thin layer. The characteristic
299 frequency is also similar to the previous case in **Fig. 2B** confirming that convection-diffusion
300 controlled mechanism by the flux of the electrolyte in the AESEC experiment.

301 The second capacitive loop (10^{-1} Hz $< f < 10^0$ Hz) was also distributed and its analysis is
302 complicated by the fact that it is convoluted with other processes at both higher and lower
303 frequency. However, it may be ascribed to Zn dissolution [24]. The high frequency time constant
304 was analyzed as previously described. From the CPE behavior, the oxide film thickness was
305 estimated at $\delta = 2.4$ nm. The analysis of the high frequency loop for each potential showed that
306 the thin film formed on the alloy surface has a thickness that strongly depends on the applied
307 potential.

308 In **Fig. 3C**, a peak of Zn dissolution is observed after the potential release, albeit a much
309 smaller peak than at $E_{ap} = -0.80$ V vs. Hg/HgO (**Fig. 3B**). Nevertheless, this peak cannot be
310 unequivocally attributed to oxide dissolution as there is no clearly defined potential plateau
311 following the potential release. Assuming that this peak was due to oxide dissolution, an
312 estimated thickness of 2.5 nm is obtained with the same assumptions as before, in good
313 agreement with that obtained from the EIS analysis of 2.4 ± 0.3 nm (**Table 1**).

314 The low frequency Lissajous plots at $E_{ap} = -1.20$ V vs. Hg/HgO (**Fig. 5B**) show linear
315 behavior within experimental error indicating that the elemental dissolution current (j_M) for each
316 species is in-phase with the potential. In this case, the linearity of the Lissajous plots of j_{Zn} and j_{Δ}
317 is clearly demonstrated, indicating that both reactions are charge transfer limited. The cathodic
318 current would make a negligible contribution to j_e^* as E_{ap} was approximately +400 mV than the

319 zero current potential ($E_{j=0}$). The Zn oxidation reaction may be written by the combination of
320 Reactions 9 and 10 as;



322 and the formation of the ZnO (j_{Δ}) is via Reaction 11. $b_{a,j_{\Delta}} = 68 \text{ mV decade}^{-1}$ and $b_{a,j_{\text{Zn}}} = 864 \text{ mV}$
323 decade^{-1} were obtained by Eq. 13 from **Fig. 5B**. Given that the Tafel slope of j_{Zn} at $E_{\text{ap}} = -1.20 \text{ V}$
324 vs. Hg/HgO is lower than that at $E_{\text{ap}} = -0.80 \text{ V}$ vs. Hg/HgO, it could be concluded that the
325 dissolution of Zn is faster in former case resulting in a relatively thinner ZnO layer formation.

326 In this case, both Zn and Al dissolution were not faradaic in that $j_e^* / 1.13 \neq j_{\text{Al}}$ and $j_e^* / 8.8$
327 $\neq j_{\text{Zn}}$ (**Fig. 5B**). It showed a significant difference between $\eta_{\text{DC}} = 0.92 \pm 0.02$ and $\eta_{\text{AC}} = 0.65 \pm$
328 0.03 . It was proposed that the AC component is due to non-faradaic reactions at the metal/oxide
329 interface and the DC component to the faradaic dissolution of the film at the oxide/electrolyte
330 interface [6, 7, 28]. For the AC case in the intermediate domain, it can be concluded that
331 formation of the corrosion product would be the RDS, given that $\eta_{\text{DC}} \gg \eta_{\text{AC}}$, consistent with the
332 Tafel slope analysis. A simplified elemental dissolution at each interface in anodic potential
333 domain is illustrated in **Fig. 6**. The system extends our previous work with AESEC-EIS in that
334 the potential dependent and potential independent mechanisms are observed for two different
335 elements of a single system. In the previous work they were observed for Zn in different
336 electrolytes [8].

337 Interestingly, j_{Zn} was higher than its congruent dissolution level ($j_e^* / 8.8$) whereas j_{Al} was
338 lower than $j_e^* / 1.13$. The excess Zn dissolution could lead to a restrained Al dissolution,
339 referenced as the *NCE* [12].

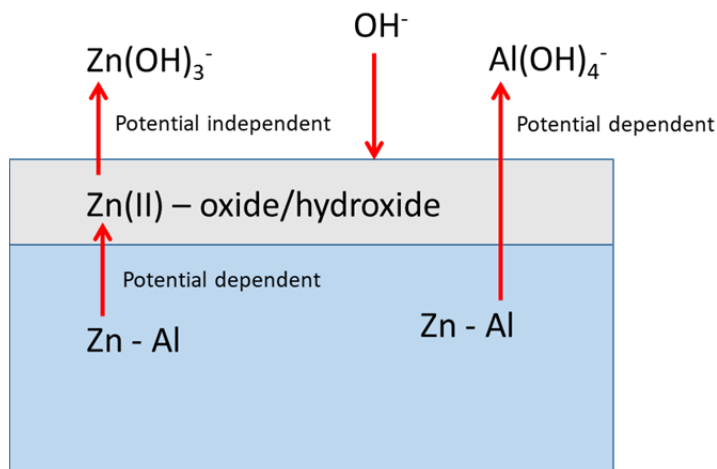


Fig. 6. Simplified schematic model of elemental dissolution at each interface of Al_xZn in 0.1 M NaOH solution in anodic potential domain.

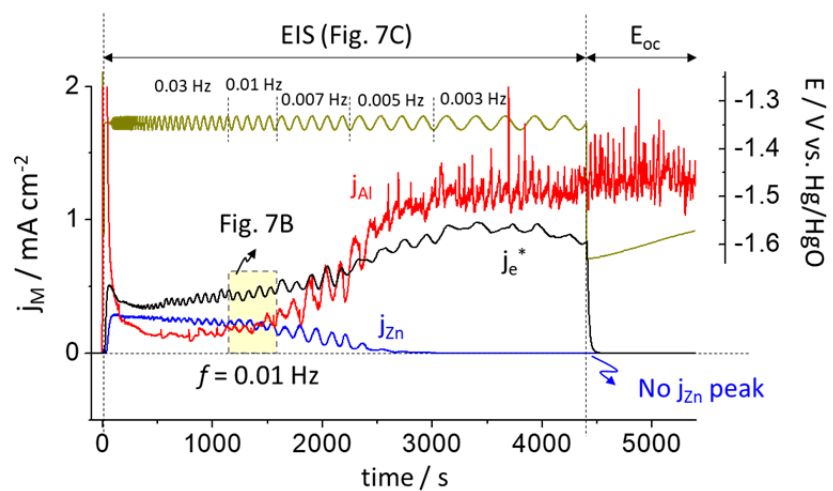
340

341 **$Al_{0.7}Zn$ (Zn-22 wt.% Al)**

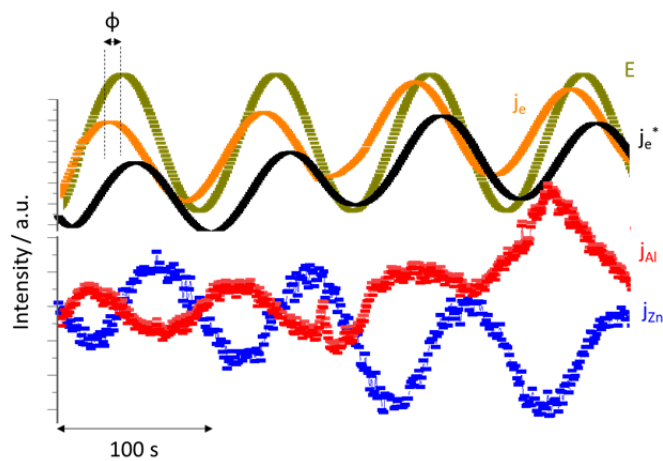
342 In this section, we will demonstrate the AESEC-EIS methodology with a system that is
 343 intrinsically unstable and shows a more usually observed dissolution case for the lower Al
 344 content Zn-Al system [36]. An AESEC-EIS curve (**Fig. 7A**), magnified oscillation trends at $f =$
 345 0.010 Hz (**Fig. 7B**) and a corresponding Nyquist plot (**Fig. 7C**) for the $Al_{0.7}Zn$ (Zn-22 wt.% Al)
 346 nominally pure phase at $E_{ap} = -1.36$ V vs. Hg/HgO (*i.e.* +150 mV from $E_{j=0}$) in the same
 347 electrolyte are given. It is clear from Fig. 7A that the elemental dissolution mechanism varies
 348 throughout the time period of the experiment. Initially, Zn dissolution was intense at
 349 approximately the same level as Al. However, for $t > 2700$ s ($f < 0.005$ Hz), j_{Zn} decreased to
 350 under the detection limit and Al dissolution changed from a charge transfer to a chemical
 351 dissolution mechanism. The latter is indicated by the disappearing oscillation of j_{Al} , and the
 352 significantly increased j_{Al} noise signal indicating HER [12, 14]. The non-charge transfer Al

353 dissolution mechanism is also revealed in the Nyquist plot (Fig. 7C) where an unambiguous
 354 diffusive impedance trend was observed ($\phi = 45^\circ$) in this frequency domain. ZnO/Zn(OH)₂
 355 formation and dissolution would occur for $f \geq 0.007$ Hz as Reactions 9 - 12:

A.



B.



C.

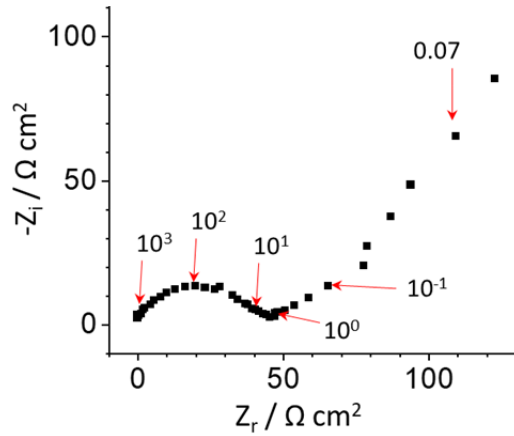


Fig. 7. A: AESEC-EIS curve of Zn-22 wt.% Al in 0.1 M NaOH, Ar deaerated electrolyte, at $E_{ap} = -1.36$ V vs. Hg/HgO, **B:** oscillation trends at $f = 0.010$ Hz, and **C:** corresponding Nyquist plot.

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j_{Zn} showed a clear oscillation from a relatively higher frequency domain ($f \approx 0.030$ Hz) where no j_{Al} oscillation was observed. j_{Al} oscillation disappeared with the dissolution of ZnO/Zn(OH)₂ for $t > 2700$ s, indicating that Al dissolution occurred through this Zn-based corrosion product layer (see also Fig. 6). The phase shift of E vs. j_e (ϕ) was not zero as summarized in **Table 3**, whereas $\phi \approx 0$ for Al_{5,2}Zn (Fig. 4). The measured total impedance was close to the sum of each elemental contribution calculated from Eq. 8, $Z_r - Z_e \approx Z_r(j_{Zn}) + Z_r(j_{Al})$, similar to the Al_{5,2}Zn in the same potential domain, which can be an indicative of the parallel relationship between Zn and Al dissolution. The phase shift between j_{Zn} and j_{Al} was 180° (**Fig. 7B**) whereas in-phase relation was monitored for Al_{5,2}Zn (**Fig. 4**). The out-of-phase of j_{Zn} and j_{Al} should have been explained by the fact that Al dissolution is related to the cathodic reaction at open circuit potential [28]. However, it is not probable in the present work because this phase shift was observed at a relatively positive potential where cathodic current contribution is

369 negligible. One possible explanation is that in this potential domain, the slope of the Al
370 dissolution rate - potential curve is negative [36] resulting in a negative low frequency-impedance
371 [37, 38].

372 For $f \leq 0.007$ Hz, j_{Zn} decreased to under the detection limit as all the previously formed
373 ZnO/Zn(OH)₂ dissolves. Previously for Al_{5,2}Zn phase, a clear Zn dissolution peak was observed
374 during the spontaneous dissolution after the AESEC-EIS experiments in **Figs. 3B and 3C**. It was
375 attributed to the residual ZnO/Zn(OH)₂ dissolution formed during the potentiostatic experiment.
376 In **Fig. 7**, no j_{Zn} peak was monitored in E_{oc} indicating that the oxide was completely dissolved
377 near $t = 2700$ s.

378

379 **Conclusion**

380 In this work, we have demonstrated the application of combined AESEC-EIS to identify
381 and quantify different anodic dissolution processes for a multi-element system, Al-Zn pure phase
382 in 0.1 M NaOH. The elemental dissolution mechanism at each potential domain was elucidated
383 by the AESEC-EIS technique.

384 AESEC gave immediate information on the elemental dissolution rates and transient
385 behavior while EIS gave information on the physical properties of intermediate oxide layers and
386 kinetic information for water reduction in the cathodic domain. A potential independent Al
387 dissolution without forming an oxide layer was observed by AESEC-EIS at a cathodic potential
388 domain ($E_{ap} = -1.70$ V vs. Hg/HgO).

389 By comparing the DC and AC faradaic yield, information on the localization of charge
390 transfer reactions could be obtained. In the anodic domain ($E_{ap} = -0.80$ V vs. Hg/HgO), $\eta_{DC} \approx \eta_{AC}$
391 indicating that the formation and dissolution of the corrosion products occur at the nearly same
392 rate, consistent with the previous observation [12, 13]. In the intermediate domain ($E_{ap} = -1.20$ V
393 vs. Hg/HgO), formation would be the RDS as $\eta_{DC} \gg \eta_{AC}$. In the former case, the oxidation of
394 metal occurred through a corrosion product layer. In the latter case, the oxidation would occur
395 directly from the metal/oxide complex. It was further demonstrated by the Tafel slope of j_{Zn} from
396 the elemental Lissajous analysis (**Fig. 5**). In this way, AESEC-EIS can be utilized to distinguish
397 the different elemental dissolution kinetics. Diffusion processes were identified although the
398 precise origin was not ascertained, *i. e.* across corrosion product films or within inter-granular
399 crevices and pits.

400 Elemental impedance contribution, $Z_r(j_M)$, demonstrated the potential dependent
401 elemental dissolution model of Al-Zn pure phase proposed in [12]. In the intermediate potential
402 domain, Al dissolution occur through the porous Zn(0) enriched layer in parallel with Zn
403 dissolution as $Z_r(j_{Zn}) + Z_r(j_{Al}) \approx$ total measured impedance ($Z_r - Z_e$).

404 For $Al_{5.2}Zn$, Al and Zn dissolution rates were in-phase regardless of the applied potential.
405 For $Al_{0.7}Zn$ and other low Al content alloys and phases [36], Al and Zn dissolution rates showed
406 a 180° phase shift. However, the origin of the phase shift is not ascertained to the satisfactory
407 level.

408

409 **Methods**

410 *Materials*

411 A nominally pure phases of Al-Zn (Zn-68 wt.% Al and Zn-22 wt.% Al), provided and
412 characterized by the *Department of Metals and Corrosion Engineering, University of Chemistry*
413 *and Technology*, Prague, were investigated in this work. Zn-68 wt.% Al phase is denoted as
414 $\text{Al}_{5.2}\text{Zn}$ and Zn-22 wt.% Al as $\text{Al}_{0.7}\text{Zn}$, based on their molar compositions to facilitate the
415 congruent dissolution analysis. The chemical composition of these materials were 67.6 wt.% Al
416 and 32.4 wt.% Zn (Zn-68 wt.% Al), and 21.4 wt.% Al and 78.6 wt.% Zn (Zn-22 wt.% Al),
417 respectively, measured by atomic absorption spectroscopy (AAS). All samples were ground with
418 Si-C paper up to P4000 under ethanol, dried with flowing N_2 gas then stored in a humidity
419 chamber of 50% relative humidity with saturated $\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ during 24 hours, providing a
420 reproducibly oxidized surface prior to the experiment [36, 39]. All the experiments were
421 performed in a 0.1 M NaOH (pH = 12.80) at $T = 25^\circ\text{C}$, prepared from analytical grade materials
422 using deionized water obtained by a MilliporeTM system (18.2 $\text{M}\Omega$ cm). The electrolytes were
423 deaerated by Ar gas for 30 min prior to the tests and maintained during the experiments.

424

425 *Atomic emission spectroelectrochemistry (AESEC)*

426 The AESEC technique has been described in detail elsewhere [5, 40]. The working
427 electrode was in contact with the flowing electrolyte in a specially designed flow cell [5, 41] with
428 conventional three-electrode system; a Hg/HgO in 0.1 M NaOH (-165 mV vs. SHE) as a
429 reference electrode and a Pt foil as a counter electrode. The elements released from the working
430 electrode were transported to an Ultima 2C Horiba Jobin-Yvon inductively coupled plasma
431 atomic emission spectrometer (ICP-AES). The concentrations of Zn and Al were determined

432 from the emission intensity at 213.86 nm (Zn with a Paschen-Runge polychromator) and at
433 167.08 nm (Al with a monochromator) wavelength, respectively, using standard ICP-AES
434 calibration techniques.

435 A Gamry Reference 600TM potentiostat was used to perform electrochemical impedance
436 spectroscopy (EIS) and linear sweep voltammetry (LSV). The electrochemical response (namely
437 the electrical current density, j_e , and the electrode potential, E) were recorded in real-time with
438 the elemental dissolution rates, using the analog data acquisition and the software interface
439 (QuantumTM, Horiba Jobin-Yvon) of the AESEC technique. The EIS was performed at different
440 potentials from 100 kHz to 0.004 Hz with 8 points per decade of frequency and applying a 10
441 mV_{rms} sinewave perturbation.

442

443 *Data analysis of the AESEC technique*

444 The atomic emission intensity at a characteristic wavelength (λ) of the element M, $I_{M, \lambda}$,
445 was recorded by the ICP-AES as a function of time downstream from an electrochemical flow
446 cell. The elemental concentration (C_M) is calculated as;

$$447 \quad C_M = (I_{M, \lambda} - I_{M, \lambda}^{\circ}) / \kappa_{\lambda} \quad [15]$$

448 where $I_{M, \lambda}^{\circ}$ is the background signal, and is κ_{λ} the sensitivity factor of M, obtained from a
449 standard ICP calibration method. The elemental dissolution rate (v_M) can be calculated from Eq.
450 15 with the flow rate of the electrolyte ($f = 2.8 \text{ mL min}^{-1}$) and the exposed surface area A (1.0
451 cm²) as:

$$452 \quad v_M = f C_M / A \quad [16]$$

453 The v_M was converted to an equivalent elemental current density (j_M) to facilitate comparison
454 with the electrical current density (j_e) measured by the potentiostat, in a relationship with;

$$455 \quad j_M = z F v_M \quad [17]$$

456 where F is the Faraday constant and z is the valance of the dissolving species (Al^{3+} , Zn^{2+}). It is
457 often useful to present j_e^* which represents the measured j_e after a numerical convolution with the
458 residence time distribution in the flow cell (a lognormal distribution), thereby allowing a direct
459 comparison between the instantaneous values of j_e^* and j_M [5]. Cathodic reactions and the
460 formation of insoluble or slightly soluble species are not directly detected by ICP-AES. If surface
461 charging is neglected, the faradaic component of these hidden processes may be determined by a
462 mass-charge balance as:

$$463 \quad j_{\Delta} = j_e^* - j_{Zn} - j_{Al} \quad [18]$$

464

465 *Surface characterization*

466 The sample surface after each potentiostatic AESEC-EIS experiment was characterized
467 by scanning electron microscopy (SEM) using a Zeiss LEO 1530TM microscope with field
468 emission gun source at 15 keV, and with 15 mm working distance. An equal mix of secondary
469 electron and back-scattered electron detector was used.

470

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473 Prague, Czech Republic for supplying Zn-22 wt.% Al and Zn-68 wt.% Al samples.

474
475 **Author Contributions**
476 J. H. carried out the AESEC-EIS experiments and coordinated analysis between two techniques.
477 V. V. was responsible for the EIS data interpretation. K. O. conceptualized the AESEC-EIS
478 analysis. All authors contributed to write the paper and revision.

479
480 **Data availability**
481 The authors declare that the data supporting the findings of this study are available within the
482 paper. The supplementary data will be available upon reasonable request.

483
484 **Competing interests**
485 The authors declare no competing interests.

486
487
488 **Figure captions**
489 **Fig. 1.** Elemental AESEC-LSV curve of Al_{5,2}Zn phase in 0.1 M NaOH, pH=12.80, Ar deaerated
490 electrolyte at T = 25°C. All potential values presented in this work are referenced to an Hg/HgO
491 electrode in 0.1 M NaOH (-165 mV vs. SHE). Vertical dashed lines are selected potential values
492 in the (a): cathodic dealloying, (b): anodic and (c): intermediate domains.

493 **Fig. 2.** Nyquist plots at each potential domain determined from Fig. 1 and their corresponding
494 SEM images; A: -1.70 V vs. Hg/HgO, B: -0.80 V vs. Hg/HgO and C: -1.20 V vs. Hg/HgO.
495 Arrows are indicating frequency values (Hz).

496 **Fig. 3.** AESEC-EIS curve of $Al_{5.2}Zn$ in 0.1 M NaOH, Ar deaerated electrolyte including
497 potentiostatic hold (E_{ap}), EIS and open circuit measurement (E_{oc}). **A:** $E_{ap} = -1.70$ V vs. Hg/HgO,
498 **B:** $E_{ap} = -0.80$ V vs. Hg/HgO and **C:** $E_{ap} = -1.20$ V vs. Hg/HgO. j_M (M = Zn or Al) values are
499 normalized based on the molar composition for **B** and **C**.

500 **Fig. 4.** The oscillation trends at low frequency domain for A: $E_{ap} = -0.80$ V vs. Hg/HgO and B:
501 $E_{ap} = -1.20$ V vs. Hg/HgO from Figs. 3B and 3C, respectively.

502 **Fig. 5.** Lissajous analysis at $f = 0.004$ Hz at A: $E_{ap} = -0.80$ V vs. Hg/HgO and B: $E_{ap} = -1.20$ V vs.
503 HgO. The j_e^* , j_{Al} and j_{Zn} are shown as a function of IR drop compensated applied potential (E -
504 $j_e R_e$). One cycle including upper and lower potential scans, indicated by arrows, is given.

505 **Fig. 6.** Simplified schematic model of elemental dissolution at each interface of Al_xZn in 0.1 M
506 NaOH solution in anodic potential domain.

507 **Fig. 7. A:** AESEC-EIS curve of Zn-22 wt.% Al in 0.1 M NaOH, Ar deaerated electrolyte, at $E_{ap} =$
508 -1.36 V vs. Hg/HgO, **B:** Oscillation trends at $f = 0.010$ Hz, and **C:** Corresponding Nyquist plot.

509
510 **Table 1.** The effective capacitance values obtained from Brug's relation [18] **(a)**, complex
511 capacitance curve [15] **(b)** and **(c)**. CPE parameters (α and Q) are provided. The corresponding

512 effective oxide layer thickness (δ) calculated by Eq. 5 and obtained from the AESEC mass-
 513 balance are given.

	E_{ap} / V vs. Hg/HgO	C / $\mu\text{F cm}^{-2}$	α	Q / $\Omega^{-1} \text{cm}^{-2} \text{s}^{\alpha-1}$	Effective thickness (δ) / nm	
					EIS	AESEC
(a)	-1.70 V	$C_{dl} = 191$	0.73	$(1.07 \pm 0.20) \times 10^{-3}$	-	
(b)	-0.80 V	$C_{\delta} = 0.65$	0.78	$(12.6 \pm 0.2) \times 10^{-4}$	12 ± 1	11
(c)	-1.20 V	$C_{\delta} = 3.3$	0.77	$(4.5 \pm 1.3) \times 10^{-5}$	2.4 ± 0.3	2.5

514
 515 **Table 2.** The real part impedance measured by the potentiostat ($Z_r - Z_e$), contribution of Zn
 516 dissolution ($Z_r(j_{Zn})$) and Al dissolution ($Z_r(j_{Al})$).

f / Hz	$Z_r - Z_e$ / Ωcm^2	$Z_r(j_{Zn})$ / Ωcm^2	$Z_r(j_{Al})$ / Ωcm^2
$E_{ap} = -0.80 \text{ V vs. Hg/HgO (anodic domain)}$			
0.010	194	878	19
0.004	192	872	61
$E_{ap} = -1.20 \text{ V vs. Hg/HgO (intermediate domain)}$			
0.013	305	270	48
0.010	297	274	37
0.008	287	275	37
0.006	279	234	29
0.004	275	266	34

517
 - 32 -

Table 3. The real part of impedance, and ϕ obtained from Fig. 7.

f / Hz	$(Z_r - Z_e) / \Omega \text{ cm}^2$	$Z_r(j_{Zn}) / \Omega \text{ cm}^2$	$Z_r(j_{Al}) / \Omega \text{ cm}^2$	ϕ (E vs. j_e)
0.013	101	61	67	-29°
0.010	103	67	75	-32°
0.007	110	66	28	-63°

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