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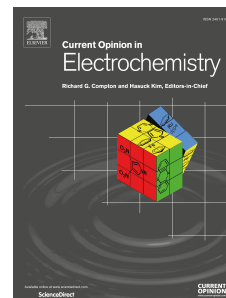
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Current state of electrochemical techniques and corrosion rate analysis for next-generation materials

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1 **Current state of electrochemical techniques and corrosion rate analysis for next-generation**
2 **materials**

3

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8 **Keywords:** Corrosion rate; electrochemical techniques; new generation alloys

9

10 **Abstract**

11 Current theoretical models and electrochemical techniques used to investigate corrosion mechanisms,
12 including corrosion rates, have been tailored for conventional alloy systems. However, the application of
13 conventional theories and techniques toward next-generation alloys such as multi-principal element alloys
14 and additively manufactured alloys needs to be revisited due to the increased chemical complexity and
15 refined microstructures of these alloys, which may yield different electrochemical properties from the
16 conventional alloys. This review aims to discuss to which extent the current models and techniques used in
17 corrosion science can be applied to these new alloy systems, and outline some of the challenges that need
18 to be overcome to accurately describe their electrochemical reactivity.

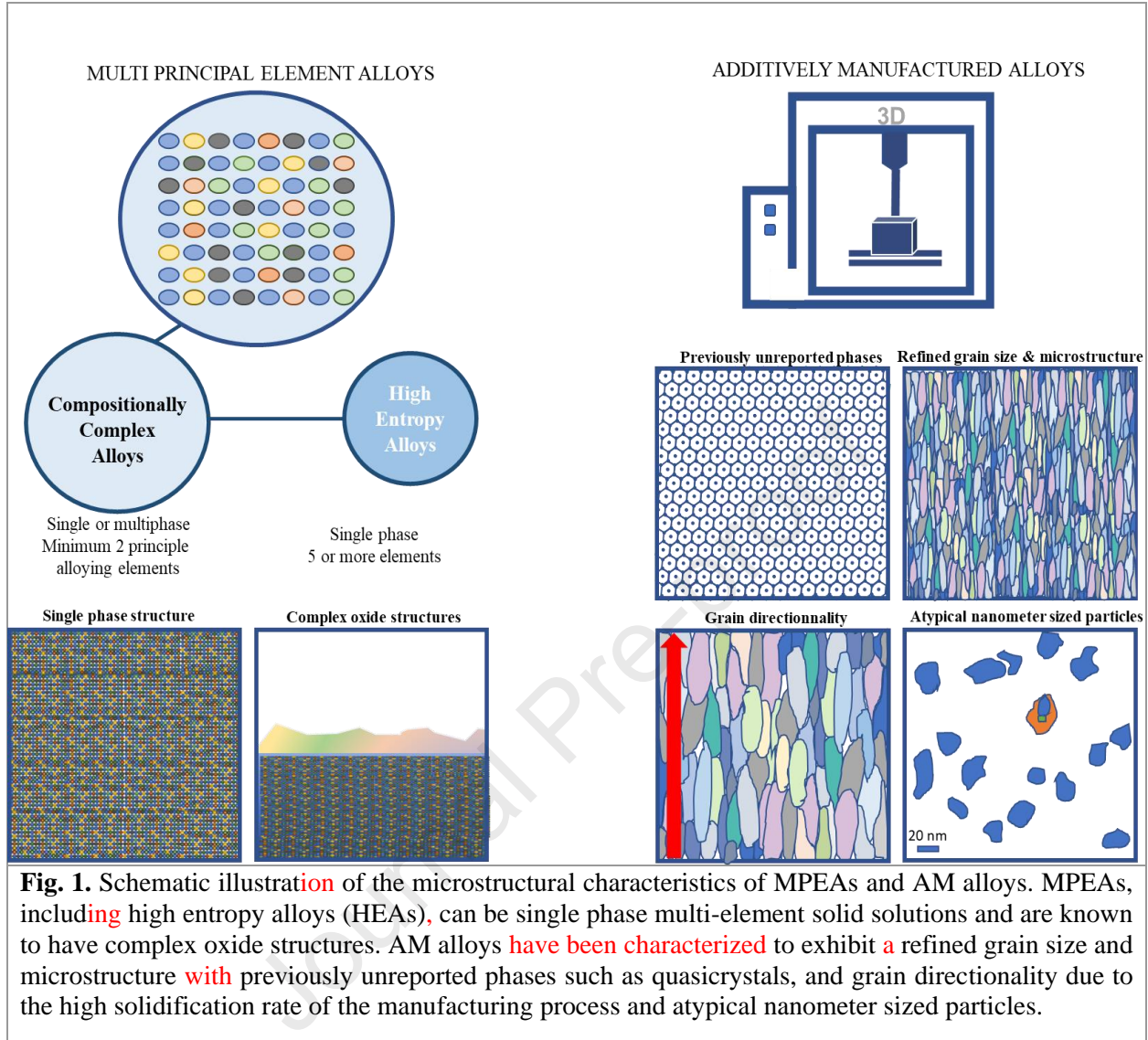
19 Introduction

20 Since the Bronze Age, humanity has constantly developed new technological strategies and
21 fabrication processes to produce alloys. The conventional alloy making procedure is based on adding minor
22 alloying elements to one principal element to obtain the desired mechanical properties. In the early 2000s,
23 the materials science community witnessed an important shift in the alloy making process with the
24 emergence of two new alloy generations; namely multi-principal element alloys (MPEAs) [^{1, 2, 3}] and
25 additively manufactured (AM) alloys described in **Fig. 1**. [^{4, 5}].

26 In the light of recent technical advances, MPEAs are considered as promising materials that could
27 be used in highly corrosive environments due to their superior aqueous corrosion resistance to conventional
28 alloys such as stainless steel [⁶], as well as enhanced thermal resistance and irradiation-induced corrosion
29 [⁷]. Conversely, AM alloys opened the door to complex net shape components production. However, the
30 origins of their enhanced passivity, and the relationship between their unique microstructures (**Fig. 1**) and
31 corrosion properties remain under investigation.

32 Theoretical models have been developed over the years to understand the dissolution/passivation
33 mechanisms of metals and alloys. These are often subsequently validated by experiments such as weight
34 loss measurements and electrochemical techniques. However, the concepts associated with passivity or
35 corrosion rate analysis were established based on “conventional” alloy systems (*e.g.*, Al alloys, steels).
36 Therefore, an important question is to which extent corrosion scientists may use such electrochemical tools
37 (*i.e.*, theories and experimental techniques) mostly built on the conventional alloys to the new emerging
38 class of alloys. Determination of a reliable corrosion rate of these alloys will be critical to control and
39 predict the sustainability of future engineered structures using these materials.

40 Herein, a brief review of the electrochemical theories and techniques used to determine the
41 corrosion rate of the conventional alloy systems is presented. The relevance of applying these current
42 electrochemical tools used on MPEAs and AM alloys by the corrosion science community is also discussed.
43 The objective of this review is to convey the current knowledge on the conventional alloys to newly
44 introduced complex materials.



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48 **From passivity to corrosion rates on MPEAs and AM alloys: approximations and limitations**

49 The electrochemical properties of the MPEAs and AM alloys are currently a subject of great interest
50 to researchers due to their enhanced mechanical properties and corrosion resistance. This section firstly
51 reviews the conventional theoretical models including passivation and corrosion rate determination, then
52 discusses their application to the MPEAs and AM alloys. The range of spatial resolution of each alloy
53 system and the reliability of the conventional theories which have been used to investigate these alloys are
54 summarized in **Table 1**.

55

56 *Conventional metal oxidation and passivity models*

57 The passivity is often related to the formation of a protective film following the oxidation of a
58 metal or an alloy. The passive film, generally assimilated to an oxide layer, is characterized by its
59 composition, thickness, ionic and electronic properties which may regulate the overall corrosion of a
60 system. Oxide growth models have been proposed and applied to understand the passivation kinetics of the
61 metals and conventional alloys such as the Cabrera-Mott model [8], the Fehlner-Mott model [9], the place
62 exchange model [10], the generalized growth model [11], and the point defect model (PDM) [12, 13].

63 Kinetic models of passive film growth of MPEAs and AM alloys have been reported in the literature
64 based on theories built upon the conventional alloy systems. The question is whether the passive films of
65 the MPEAs and AM alloy systems exhibit unique properties or differ from the conventional systems. For
66 example, it has not been well understood whether these alloys show a critical threshold composition of the
67 principal passivating element as it is for the conventional alloys [2]. Another example is the PDM, originally
68 developed to describe the corrosion mechanism of austenitic alloys. The PDM was recently used to explain
69 the transpassive dissolution mechanism of an AlTiVCr MPEA *via* conventional Mott-Schottky analysis
70 using EIS, coupled with element-resolved characterization techniques [14]. However, a general issue of
71 applying the PDM to the multi-principal element alloy systems is that the PDM does not account for the
72 non-constant electric field across the passive film, possible cation migration, and substrate composition. In
73 addition, the PDM does not consider yet preferential segregation of alloying elements which may result to
74 the formation of multi-oxide structures as shown in recent studies of MPEAs [15, 16, 17]. Although a fourth
75 generation PDM is under development to account for these limitations and consider the preferential
76 segregation of alloying elements into the barrier or outer layer, the remaining question is how to validate
77 the PDM to be applicable to the newly developed compositionally complex alloys.

78

79 *Validity of corrosion rate determination: currently used techniques*

80 Corrosion rate monitoring in aqueous environments is generally carried out by potentiodynamic
81 polarization experiments. Tafel extrapolation derived from the Butler-Volmer relation is subsequently used
82 to experimentally determine the corrosion current (rate) and potential of a system. The “conventional”
83 corrosion rate has been measured using an experimentally determined polarization resistance (R_p) by Stern-
84 Geary equation assuming the system follows Tafel kinetics [18]. However, a number of other assumptions
85 have to be made to apply this equation to even a simple metal or alloy system, such as a stationarity during
86 the polarization, a uniform corrosion on the substrate (*i.e.*, no localized corrosion), and no changes in
87 electrode potential due to additional reactions [19, 20, 21, 22, 23]. The application of these assumptions to a
88 non-uniform corrosion process (*e.g.*, intergranular or pitting corrosion) is more challenging for MPEAs and
89 AM alloys due to their complex chemistry and microstructure.

90 An example illustrating the difficulty of determining a corrosion rate solely from Tafel
91 extrapolation is given in **Fig. 2** in the case of an as-printed AM alloy AA2024 (AM2024) and a conventional
92 AA2024-T3, exposed to a 0.01 M NaCl solution under anodic polarization [24]. Note that the AM2024 has
93 a similar elemental composition to AA2024-T3. The corrosion rate (i_{corr}) determined from conventional
94 Tafel extrapolation (**Fig. 2(a)**) showed similar values for both alloys as provided in **Fig. 2(b)**. The AM2024
95 alloy exhibited a slightly higher anodic current density than AA2024-T3 shown in **Fig. 2(a)**. The elemental-
96 resolved atomic emission spectroelectrochemistry (AESEC) gives complementary information to the
97 conventional polarization curves as shown in **Fig. 2(c)** and **2(d)**. For both alloys, the total electrical current
98 density measured from the potentiostat (i_e , **Fig. 2(a)**) was one order of magnitude higher than the equivalent
99 total current density ($i_{\text{tot}} = i_{\text{Mg}} + i_{\text{Fe}} + i_{\text{Cu}} + i_{\text{Al}}$, as illustrated in **Figs. 2(c)** and **2(d)**) measured by AESEC. This
100 result indicates the formation of a thicker passive film during anodic polarization on the AM2024 surface
101 (**Fig. 2(d)**) than AA2024-T3 (**Fig. 2(c)**) indicated by the larger $i_{\text{film}} (= i_e - i_{\text{tot}})$ for the AM2024 (mass-charge
102 balance). This larger unaccounted charge (i_{film}) was attributed to the refined microstructure of the AM2024,
103 limiting the onset and propagation of localized corrosion. Similar findings have been reported for other
104 MPEA systems highlighting how the conventional potentiodynamic polarization results can be even more
105 misleading, especially for MPEAs where the role of each alloying element in the anodic and cathodic
106 reaction cannot be easily distinguished [25, 26, 27, 28, 29]. The AESEC technique, under this scenario, can be
107 useful to monitor the element-resolved dissolution kinetics including the elemental corrosion rate.
108 However, the current technical setup is limited to macroscale electrochemical analysis and does not provide
109 information on nanometer level local events [30, 31].

110 The recent literature reveals the growing need to use tools considering the nanostructural
111 complexity of these new alloys. The examples displayed herein highlight the inevitable upcoming

112 obsolescence of founding models and techniques used to characterize the corrosion susceptibility if no
 113 forthcoming update is realized. Under this scenario, the collection of a valid experimental data-set would
 114 be a first step to depict the origins of localized corrosion on these alloys, which ultimately means
 115 downscaling local techniques to the nanometer level.

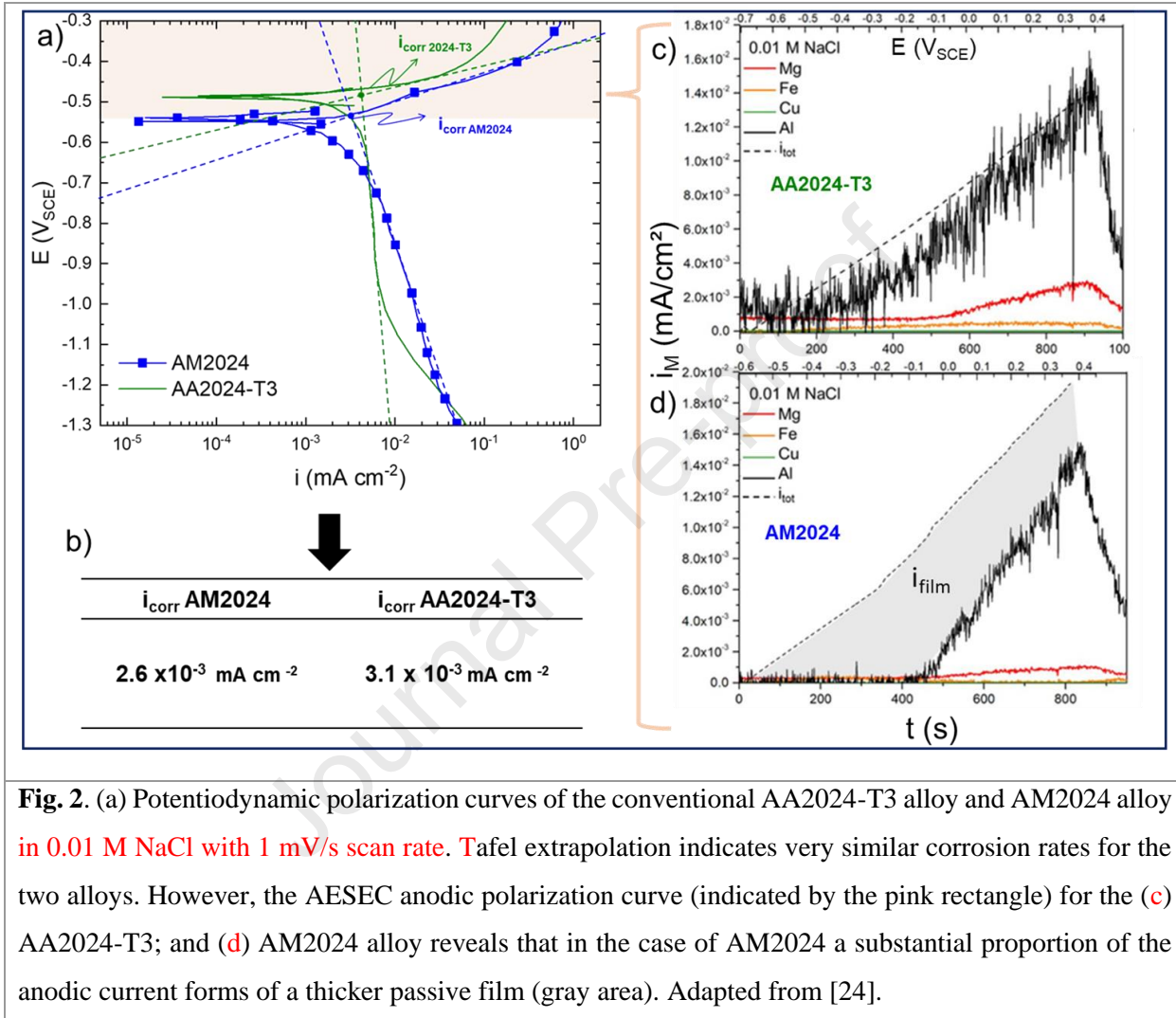


Fig. 2. (a) Potentiodynamic polarization curves of the conventional AA2024-T3 alloy and AM2024 alloy in 0.01 M NaCl with 1 mV/s scan rate. Tafel extrapolation indicates very similar corrosion rates for the two alloys. However, the AESEC anodic polarization curve (indicated by the pink rectangle) for the (c) AA2024-T3; and (d) AM2024 alloy reveals that in the case of AM2024 a substantial proportion of the anodic current forms of a thicker passive film (gray area). Adapted from [24].

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124 **Table 1.** Summary of the microstructural specificities of each alloy system and their potential impact on
 125 mechanisms interpretation.

Conventional alloys	MPEAs	AM alloys
<ul style="list-style-type: none"> Well-reported micro- to nano-scales particles and precipitates. Micro-scale localized corrosion processes can be identified by current local techniques. Tafel extrapolation for corrosion rate determination can be applicable if occurring uniformly on the matrix. Passive film compositions are usually associated with one metal (matrix). 	<ul style="list-style-type: none"> Tafel extrapolation and interpretation is difficult. Anodic current density can be associated with several elements from the matrix [25 - 29]. Complex passive films (more than one metal present) with the presence of unoxidized species [14 - 17]. Passive film formation mechanism different from conventional alloys, including stainless steels. 	<ul style="list-style-type: none"> Formation of previously unreported non-equilibrium phases for new and well-known alloy systems due to high solidification rate [4, 5]. Refined microstructures with nanometer sized particles and precipitates [4, 5, 24]. Difficult to identify localized corrosion processes with the current local electrochemical techniques due to the limit of spatial resolution, and refined microstructure. Tafel extrapolation does not consider the proportion of current density associated with passive film formation [24].

126

127 **Local electrochemical techniques for MPEA and AM alloys: to the origins of passivity and** 128 **localized corrosion**

129 If a system undergoes localized corrosion, the measured corrosion rate can significantly exceed that
 130 of uniform corrosion [32]. A passive film formed on an alloy surface can contribute to decreasing the
 131 uniform corrosion rate, however, it can also accelerate the localized corrosion rate by pitting or crevice
 132 corrosion associated with the local passive film breakdown. To this end, local electrochemical techniques
 133 have been developed in the last few decades to address localized surface reactivity usually masked in
 134 macroscale electrochemical measurements. The difference between global corrosion rate measurement and
 135 the actual localized rate would be more significant for the AM alloys and some of the MPEAs where the
 136 refined microstructural features have been reported. It is therefore essential to use high spatial resolution
 137 local techniques for these alloys, in particular to identify corrosion initiation sites. In this section, recent
 138 studies using conventional and newly introduced local techniques to investigate the electrochemical
 139 properties of a system including MPEAs and AM alloys are discussed. A better understanding of the local
 140 reactivity of the surface could be obtained by combining conventional electrochemical and imaging
 141 techniques with novel high-resolution techniques.

142 *Local electrochemistry for MPEA and AM alloys: current limitations*

143 Despite the technical advances, only limited studies on the MPEAs or AM alloys using local
144 electrochemical techniques have been reported to date. Recently, the scanning vibrating electrochemical
145 technique (SVET) technique has been used to investigate a micro-galvanic corrosion between the two
146 eutectic phases of an AlCoCrFeNi MPEA with a 500 nm level step size scans [33]. The SVET technique
147 generally visualizes a real-time the local cathodic and anodic reactions by the potential difference in a
148 solution between a vibrating conductive probe and the sample of interest [34, 35, 36]. Theoretically, it can
149 identify the location of half-reactions and quantify their associated corrosion rates. However, a few
150 technical limitations, such as trade-off sample size [37] and surface topography, could affect the potential
151 measurement leading to an error in quantitative analysis. In addition, real-time corrosion rate determination
152 using this technique for the MPEAs and AM alloys will be significantly influenced by the experimental
153 protocol. For example, high vibrational amplitude may provide an artifact signal due to the accelerated O₂
154 reduction reaction which is often the rate-determining diffusion-controlled step, giving an incorrect overall
155 corrosion rate [38, 39]. The SVET should be carried out more systematically to the MPEAs and AM alloys
156 considering these limitations to investigate the local corrosion processes.

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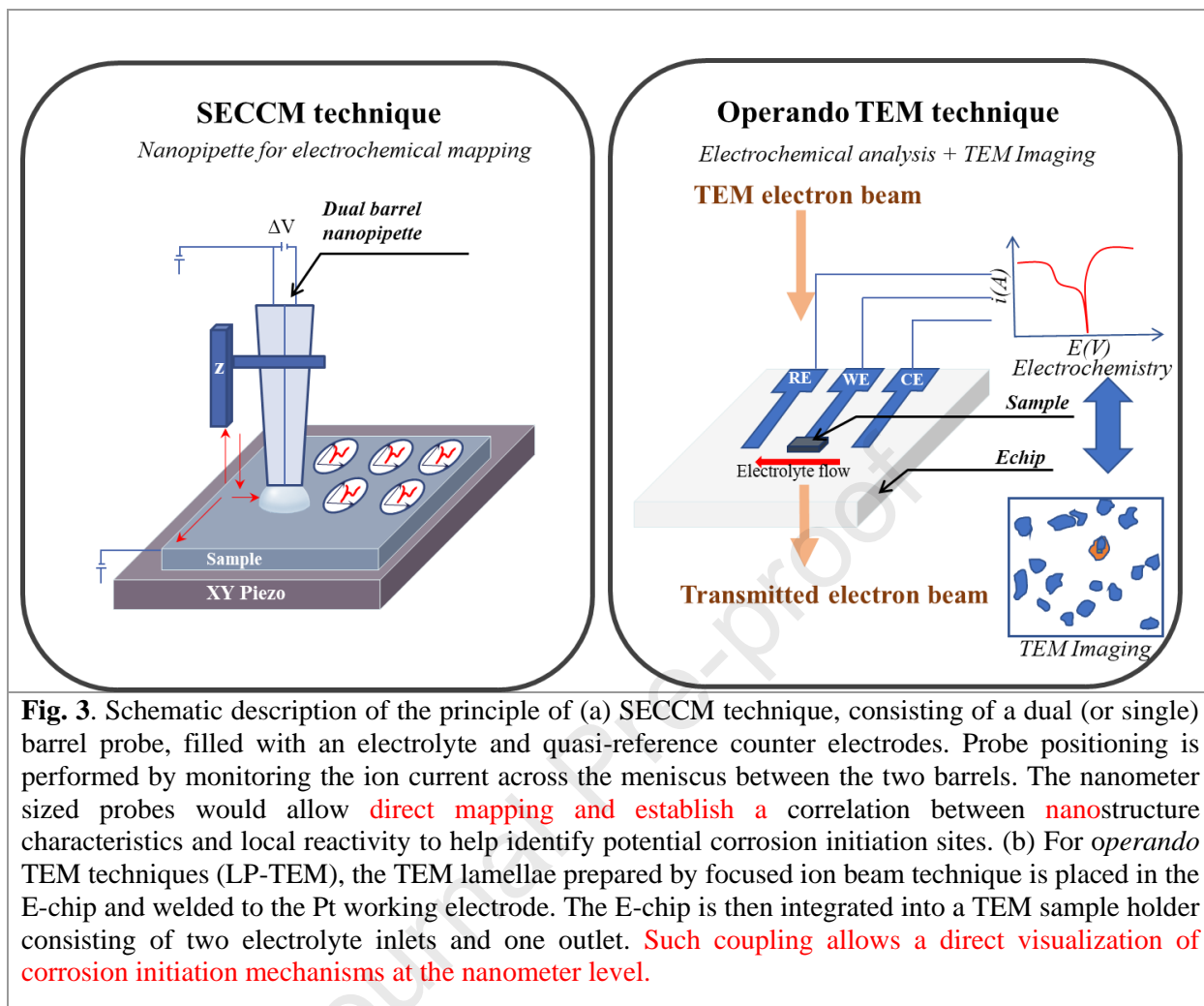
158 *Downscaling electrochemical techniques for next-generation materials: towards the nanoscale?*

159 Although nanoscale electrochemical measurement can be performed today using scanning
160 electrochemical microscopy (SECM), SECM measurement usually requires the use of a redox mediator
161 that could alter the overall corrosion mechanism. Recently, a nanoscale electrochemical setup equipped
162 with nano-pipette imaging probe known as scanning electrochemical cell microscopy (SECCM) has been
163 used to monitor local electrochemical events [40, 41]. This concept resembles the electrochemical droplet
164 cell used to visualize anodic and cathodic reactions, in which a nanometer sized mobile meniscus (down to
165 ~ 30 nm [42, 43]) is positioned on the alloy surface (**Fig. 3**). The SECCM technique was applied to
166 investigate the reactivity of each crystallographic orientation on a polycrystalline alloy defining a structural
167 factor that governs the corrosion mechanism [44]. However, the SECCM technique applied to corrosion
168 studies is still limited to low carbon steel (using a 2 μm probe) and simple systems such as polycrystalline
169 Zn to date [40, 41, 45, 46, 47]. In addition, several technical challenges remain. For example, it has been shown
170 that the exposed surface is often non-reproducible and evolves with reaction time, *e.g.*, by O₂ ingress into
171 the droplet if the O₂ reduction reaction is the dominant cathodic reaction, leading to a significant surface
172 alteration during measurement [48]. The stability of the probe can be affected by the formation of corrosion
173 products or the formation of gas bubbles (*e.g.*, H₂ reduction reaction) during the measurement. Moreover,

174 the tip-substrate distance (currently controlled by conductivity measurement) which can be influenced by
175 the surface reactivity (and by extension, the surface composition), must be reproducible at each
176 measurement.

177 Nonetheless, the nano-pipette probe could open the door to nanoscale electrochemical impedance
178 spectroscopy measurements. Local electrochemical impedance spectroscopy (LEIS) has been utilized to
179 probe the surface reactivity giving a mechanistic information on a specific phase or location of the sample
180 surface [49, 50, 51, 52]. LEIS has demonstrated to be a powerful technique to investigate local corrosion events,
181 however, the current experimental setup has a limited spatial resolution (down to 10 μm to date). Besides
182 the remaining technical challenges, the SECCM technique could be a pathway to nanoscale corrosion
183 studies and provide new insights into the corrosion mechanism of the next-generation alloys if the
184 abovementioned experimental constraints are addressed in the future.

185 Through the miniaturization of electrochemical liquid cells designs, the development of
186 electrochemical chips (E-chips) *operando* transmission electron microscopy (TEM) has recently emerged
187 [53, 54] to monitor real-time chemical/electrochemical reactions at the metal/oxide/electrolyte interface [55]
188 *Operando* TEM shows nanometric morphological and compositional evolution during electrochemical
189 measurements as illustrated in **Fig. 3** [56]. The liquid phase TEM (LP-TEM) consists of a 300 μm -thick E-
190 chip containing a 5 μm width working, reference, and counter electrodes in a specially designed TEM
191 sample holder [57]. Recent work investigated the dissolution of micro- and nanoscale MnS inclusions from
192 stainless steel lamellae during a real-time potentiodynamic polarization experiment. *In situ* monitoring of
193 surface evolution using TEM may give light to determine the local corrosion process (*e.g.*, the effect of
194 nanostructure) of multi-oxide films or identify the reactivity of previously unreported phases recently found
195 in the AM alloys [58, 59]. However, the development of an optimized liquid cell is still at its premises and
196 requires further investigation. The quantitative measurement of the reaction rate using this technique is still
197 limitedly accessible and has not been applied to the new-generation alloys.



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201 **Perspectives and closing remarks**

202 Recent advances in alloy metallurgy require prompt action if we want to accurately estimate the
203 lifetime of structural materials currently used and to be used in our society. Experimental discrepancies in
204 the measurement of corrosion rate, for example, reveal the need to develop more elaborate theoretical
205 models and appropriate experimental verification techniques.

206 First, the development of high spatial resolution nanoscale characterization and local *in situ*
207 electrochemical techniques is necessary for a better mechanistic understanding of the corrosion mechanisms
208 of next-generation materials which are possibly more complex than conventional alloy systems. Promising
209 new imaging techniques coupled with electrochemistry using nano-pipettes have recently been introduced
210 to monitor the local reactivity of a system although they are still limited to the conventional alloys. The
211 novel local measurement techniques would allow a direct correlation between local corrosion sites and the
212 nanostructure, particularly in the case of unreported or non-equilibrium phases which are difficult to isolate
213 from the matrix. Second, *operando* TEM technique will allow a direct visualization of corrosion and
214 passivation mechanisms at the nanometer level. However, it is more experimentally challenging and has
215 not yet been applied to MPEAs or AM alloys.

216 Finally, the emergence of computational materials science and machine learning for
217 thermodynamic simulations combined to an adequate experimental dataset, for the design of corrosion
218 resistant alloys can be a path to future work. The adjustment of existing theoretical models with
219 experimental justification is essential to rationalize their passivation and corrosion mechanisms and to
220 accurately predict the lifetime of next-generation alloys.

221 **Conflict of interest statement**

222 Nothing declared.

223

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229 **References**

230 * of special interest

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* This paper classifies notions of the multi-principal element alloys with compositionally complex alloys (CCAs) and high-entropy alloys (HEAs). The up-to-date corrosion resistance researches on the MPEAs were reviewed and the perspectives of the future research are suggested.

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Declaration of interest statement

Nothing declared.

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